STEEPEST-ENTROPY-ASCENT AND MAXIMAL-ENTROPY-PRODUCTION DYNAMICAL MODELS OF IRREVERSIBLE RELAXATION TO STABLE EQUILIBRIUM FROM ANY NON-EQUILIBRIUM STATE. UNIFIED TREATMENT FOR SIX NON-EQUILIBRIUM FRAMEWORKS

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ABSTRACT

By suitable reformulations, we review the mathematical frameworks of six different approaches to the description of non-equilibrium dynamics with the purpose to set up a unified formulation of the Maximum Entropy Production (MEP) principle valid in all these contexts. In this way, we extend to such frameworks the concept of Steepest Entropy Ascent dynamics introduced by the present author in previous work on quantum thermodynamics. Actually, the present formulation constitutes a generalization also in the quantum thermodynamics framework. The analysis emphasizes that in the SEA-inspired implementation of the MEP principle, 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. We conclude that in most of the existing theories of non-equilibrium the time evolution of the 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. The resulting unified family of SAE/MEP dynamical models are all intrinsically consistent with the second law of thermodynamics. The nonnegativity of the entropy production is a general and readily proved feature of SEA dynamics. In several of the different approaches to non-equilibrium description we consider here, the SEA concept has not been investigated before. 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 non-equilibrium states. The six mathematical frameworks are: A) Classical Statistical Mechanics; B) Small-Scale and Rarefied Gases Dynamics (i.e., kinetic models for the Boltzmann equation); C) Statistical or Information Theoretic Models of Relaxation; D) Rational Extended Thermodynamics, Macroscopic Non-Equilibrium Thermodynamics, and Chemical Kinetics; E) Mesoscopic Irreversible Thermodynamics; F) Quantum Statistical Mechanics, Quantum Thermodynamics, Mesoscopic Non-Equilibrium Quantum Thermodynamics, and Intrinsic Quantum Thermodynamics.

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 non-equilibrium.

In this paper, we show how to construct Steepest Entropy Ascent (SEA) and Maximum Entropy Production (MEP) models of non-equilibrium dynamics by adopting a unified mathematical formulation that allows us to do it at once in several different well-known frameworks of non-equilibrium 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 then 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 unified treatment of the MEP principle (for a recent review see [1]) in the various frameworks, but also extends to all frameworks an observation that we have been developing in the quantum thermodynamics

framework for the last three decades [2; 3; 4; 5]. In doing so, we introduce an important generalization also in the quantum thermodynamics 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 it with a metric with respect to which to compute the distance traveled in state space 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 Non-Equilibrium Thermodynamics [6; 7] shows that standard results such as the Fokker-Planck equation and Onsager theory emerge as straightforward results of SEA/MEP dynamics with respect to a metric characterized by a generalized metric tensor that is directly related to the inverse of the generalized conductivity 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 appear 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/MEP.

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

An investigation of the interrelations between the SEA and MEP concepts and Ziegler's [8] and Edelen's [9] formulations for the study of highly non-equilibrium dynamics in the nonlinear domain is under way and will be communicated elsewhere.

The unified formulation of the local SAE/MEP variational problem is as follows and it is not restricted to near equilibrium: *the time evolution and transport equations 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*. The measure of distance traveled in state space requires the choice of a metric defined over the state space. The standard near-equilibrium results obtain when the local metric tensor is proportional to the inverse of the local matrix of generalized conductivities.

In the next six sections we introduce slightly nonstandard notations in several non-equilibrium contexts with the purpose to formulating, in the seventh section, a unified construction and implementation of the SAE/MEP concept.

FRAMEWORK A: CLASSICAL STATISTICAL MECHANICS

Let Ω be the classical position-momentum q–p phase space, and $\mathscr{L}$ the set of real, square-integrable functions $A, B, \ldots$ on Ω, equipped with the inner product $(\cdot|\cdot)$ defined by

$$(A|B) = \mathrm{Tr}(AB) = \int_{\Omega} AB \, d\Omega \qquad (1)$$

where $\mathrm{Tr}(\cdot)$ in this framework denotes $\int_{\Omega} \cdot \, d\Omega$, with $d\Omega = d\mathbf{q} \, d\mathbf{p}$.

In Classical Statistical Mechanics, the index of statistics from a generally heterogeneous ensemble of identical systems (with associated phase space Ω) distributed over a range of possible classical mechanical states is represented by a nonnegative (Gibbs) density-of-phase distribution function $f_G = f_G(\mathbf{q}, \mathbf{p}, t)$ in $\mathscr{L}$.

Borrowing from the formalism we originally developed for the quantum framework [2; 3] (later introduced also in [4; 10]), in order to easily impose the constraint of preservation of the nonnegativity of f_G during its time evolution, we adopt as state representative not f_G itself but its square root, that we assume is a function in $\mathscr{L}$ that denote by $\gamma = \gamma(\mathbf{q}, \mathbf{p}, t)$. Normalization is not imposed at this stage but later as one of the constraints. Therefore, we clearly have

$$f_G = \gamma^2 \,, \qquad \frac{\partial f_G}{\partial t} = 2\gamma \frac{\partial \gamma}{\partial t} \qquad (2)$$

$$\frac{\partial f_G}{\partial \mathbf{q}} = 2\gamma \frac{\partial \gamma}{\partial \mathbf{q}} \,, \quad \frac{\partial f_G}{\partial \mathbf{q}} = 2\gamma \frac{\partial \gamma}{\partial \mathbf{q}} \,, \quad \{H, f_G\} = 2\gamma \{H, \gamma\} \quad (3)$$

where $\{\cdot, \cdot\}$ denotes the Poisson bracket.

Among the phase-space functions that represent physical observables we focus on the conserved ones that we denote synthetically by the set

$$\{C_i\} = \{H, M_x, M_y, M_z, N_1, \ldots, N_r, I\} \qquad (4)$$

where H is the classical Hamiltonian function, M_j the momentum function for the j-th component, N_i the number-of-particle function for particles of type i, and $I = 1$ is the constant unity function, so that $\mathrm{Tr}(\gamma^2 H)$ represents the mean energy, $\mathrm{Tr}(\gamma^2 \mathbf{M})$

the mean momentum vector, $\mathrm{Tr}(\gamma^2 N_i)$ the mean number of particles of type i, and $\mathrm{Tr}(\gamma^2 I)$ the normalization condition on f_G.

The description of an irreversible diffusion-relaxation process in this framework can be done by assuming a evolution equation for the state f_G given by

$$\frac{d\gamma}{dt} = \Pi_\gamma \quad \text{where} \quad \frac{d}{dt} = \frac{\partial}{\partial t} - \{H, \cdot\} \qquad (5)$$

It is easy to verify that for $\Pi_\gamma = 0$ Eq. (5) reduces to Liouville's equation of classical reversible evolution. We do not make this assumption because we are interested in modeling irreversible evolution with energy, momentum, and particle numbers redistribution towards equilibrium, subject to the overall conservation of energy, momentum, number of particles of each kind, and normalization

$$\Pi_{C_i} = \frac{d}{dt}\mathrm{Tr}(\gamma^2 C_i) = (2\gamma C_i|\Pi_\gamma) = 0 \qquad (6)$$

The entropy state functional in this context is represented by

$$S(\gamma) = -k\mathrm{Tr}(f_G \ln f_G) = (-k\gamma \ln \gamma^2|\gamma) \qquad (7)$$

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

$$\Pi_S = -k\frac{d}{dt}\mathrm{Tr}(f_G \ln f_G) = (-2k\gamma \ln \gamma^2|\Pi_\gamma) \qquad (8)$$

Below, in the section on SAE/MEP dynamics, we construct an equation of motion for the square-root-of-density-of-phase distribution γ such that Π_S is maximal subject to the conservation constraints $\Pi_{C_i} = 0$ and a suitable additional constraint we discuss therein.

FRAMEWORK B: SMALL-SCALE AND RAREFIED GASES DYNAMICS

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

$$(A|B) = \mathrm{Tr}(AB) = \int_{\Omega_c} AB \, d\Omega_c \qquad (9)$$

where $\mathrm{Tr}(\cdot)$ 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 [11], the probability to find a particle at position $\mathbf{x}$ 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 $f(\mathbf{x}, \mathbf{c}, t) \, d\Omega_c / \int_{\Omega_c} f \, d\Omega_c$ where $f(\mathbf{x}, \mathbf{c}, t)$ is the local phase-density distribution which for every position $\mathbf{x}$ and time instant t is a function in $\mathscr{L}$.

Also in this framework, in order to easily impose the constraint of preservation of the nonnegativity of f during its time evolution, we introduce the local one-particle state representation not by f itself but by its square root, that we assume is a function in $\mathscr{L}$ that we denote by $\gamma = \gamma(\mathbf{x}, \mathbf{c}, t)$. Therefore, we have

$$f = \gamma^2 \,, \quad \frac{\partial f}{\partial t} = 2\gamma \frac{\partial \gamma}{\partial t}, \quad \frac{\partial f}{\partial \mathbf{x}} = 2\gamma \frac{\partial \gamma}{\partial \mathbf{x}}, \quad \frac{\partial f}{\partial \mathbf{c}} = 2\gamma \frac{\partial \gamma}{\partial \mathbf{c}} \quad (10)$$

Again, among the velocity-space functions that represent physical observables we focus on the conserved ones that we denote synthetically by the set

$$\{C_i\} = \left\{H = \tfrac{1}{2}m\mathbf{c} \cdot \mathbf{c}, M_x = mc_x, M_y = mc_y, M_z = mc_z, m\right\} \qquad (11)$$

of functions in $\mathscr{L}_c$ where H is the local kinetic energy function, M_x, M_y, M_z the components of the local momentum function, and m the particle mass, so that $\mathrm{Tr}(\gamma^2 H)$ represents the local kinetic energy density, $\mathrm{Tr}(\gamma^2 M_i)$ the i-th component of the local momentum density, and $\mathrm{Tr}(\gamma^2 m)$ the local mass density.

The 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

$$\frac{D\gamma}{Dt} = \Pi_\gamma \quad \text{where} \quad \frac{D}{Dt} = \frac{\partial}{\partial t} + \mathbf{c} \cdot \frac{\partial}{\partial \mathbf{x}} + \mathbf{a} \cdot \frac{\partial}{\partial \mathbf{c}} \quad (12)$$

and $\mathbf{a}$ denotes the particle acceleration due to external body forces.

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

$$\Pi_{C_i} = \frac{\partial \text{Tr}(fC_i)}{\partial t} + \nabla \cdot \text{Tr}(f \mathbf{c} C_i) = (2\gamma C_i | \Pi_\gamma) = 0 \quad (13)$$

The local entropy density functional in this context is represented by

$$S(\mathbf{x}, t) = -k\text{Tr}(f \ln f) = (-k\gamma \ln \gamma^2 | \gamma) \quad (14)$$

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

$$\Pi_S = -k\frac{\partial \text{Tr}(f \ln f)}{\partial t} - k\nabla \cdot \text{Tr}(f \mathbf{c} \ln f) = (-2k\gamma \ln \gamma^2 | \Pi_\gamma) \quad (15)$$

Below, in the section on SAE/MEP dynamics, we construct a new 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 a suitable additional constraint we discuss therein.

The resulting new 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 BGK model as well as with Monte Carlo simulations of the original Boltzmann equation for hard spheres [12]. In addition to the strong thermodynamics consistency even far from stable equilibrium, Ref. [12] gives a proof that in the near-equilibrium limit the SEA model reduces to the BGK model.

FRAMEWORK C: STATISTICAL OR INFORMATION THEORETIC MODELS OF RELAXATION TO EQUILIBRIUM

Let $\mathscr{L}$ be the set of all $n \times n$ real, diagonal matrixes $A = \text{diag}(a_j)$, $B = \text{diag}(b_j)$, ... ($n \leq \infty$), equipped with the inner product $(\cdot | \cdot)$ defined by

$$(A|B) = \text{Tr}(AB) = \sum_{j=1}^{n} a_j b_j \quad (16)$$

In Information Theory [13], the probability assignment to a set of n events, p_j being the probability of occurrence of the j-th event is represented by $\rho = \text{diag}(p_j)$. Again, in order to easily impose the constraint of preservation of the nonnegativity of the probabilities during their time evolution, we adopt the description in terms of the square-root of ρ that we denote by

$$\gamma = \text{diag}(\sqrt{p_j}) \quad (17)$$

Typically we consider a set of conserved features of the process

$$\{C_i\} = \{H, N_1, \ldots, N_r, I\} \quad (18)$$

of diagonal matrixes $H = \text{diag}(e_j)$, $N_1 = \text{diag}(n_{1j})$, ..., $N_r = \text{diag}(n_{rj})$, $I = \text{diag}(1)$ in $\mathscr{L}$ representing characteristic features of the events in the set, which for the j-th event take on respectively the values e_j, n_{1j}, ..., n_{rj}. The corresponding expectation values are $\text{Tr}(\rho H) = \sum_{j=1}^{n} p_j e_j$, $\text{Tr}(\rho N_1) = \sum_{j=1}^{n} p_j n_{1j}$, ..., $\text{Tr}(\rho N_r) = \sum_{j=1}^{n} p_j n_{rj}$, and $\text{Tr}(\rho I) = \sum_{j=1}^{n} p_j = 1$ thus providing the normalization condition on ρ.

The time evolution of the square-root probability distribution γ is the solution of the rate equation

$$\frac{d\gamma}{dt} = \Pi_\gamma \quad (19)$$

where in order to satisfy the constraints of conservation of the expectation values $\text{Tr}(\rho C_i)$ the term Π_γ must be such that

$$\Pi_{C_i} = \frac{d}{dt}\text{Tr}(\rho C_i) = (2\gamma C_i | \Pi_\gamma) = 0 \quad (20)$$

The entropy functional in this context is represented by

$$S(\gamma) = -k\text{Tr}(\rho \ln \rho) = (-k\gamma \ln \gamma^2 | \gamma) \quad (21)$$

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

$$\Pi_S = -k\frac{d}{dt}\text{Tr}(\rho \ln \rho) = (-2k\gamma \ln \gamma^2 | \Pi_\gamma) \quad (22)$$

Below, in the section on SAE/MEP dynamics, we construct a model for the rate term Π_γ such that Π_S is maximal subject to the conservation constraints $\Pi_{C_i} = 0$ and a suitable additional constraint we discuss therein.

An attempt along the same lines has been presented in [14].

FRAMEWORK D: RATIONAL EXTENDED THERMODYNAMICS, MACROSCOPIC NON-EQUILIBRIUM THERMODYNAMICS, AND CHEMICAL KINETICS

Let $\mathscr{L}$ be the set of all $n \times n$ real, diagonal matrixes $A = \text{diag}(a_j)$, $B = \text{diag}(b_j)$, ... ($n \leq \infty$), equipped with the inner product $(\cdot | \cdot)$ defined by

$$(A|B) = \text{Tr}(AB) = \sum_{j=1}^{n} a_j b_j \quad (23)$$

In Rational Extended Thermodynamics [15], the local state at position $\mathbf{x}$ and time t of the continuum under study is represented by an element γ in $\mathscr{L}$, i.e.,

$$\gamma(\mathbf{x}, t) = \text{diag}[\alpha(\mathbf{x}, t)] \quad (24)$$

Thus, $\gamma(\mathbf{x}, t)$ represents the set of fields 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 it is assumed that their local densities and their local fluxes are all given by particular functions of γ that we denote synthetically by

$$\{C_i(\gamma)\} = \{E(\gamma), M_x(\gamma), M_y(\gamma), M_z(\gamma), m(\gamma)\} \quad (25)$$

$$\{\mathbf{J}_{C_i}(\gamma)\} = \{\mathbf{J}_E(\gamma), \mathbf{J}_{M_x}(\gamma), \mathbf{J}_{M_y}(\gamma), \mathbf{J}_{M_z}(\gamma), \mathbf{J}_m(\gamma)\} \quad (26)$$

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

$$\frac{DC_i}{Dt} = \frac{\partial C_i}{\partial t} + \nabla \cdot \mathbf{J}_{C_i} = \Pi_{C_i} = 0 \quad (27)$$

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

$$S(\gamma) \quad \text{and} \quad \mathbf{J}_S(\gamma) \quad (28)$$

so that the entropy balance equation takes the form

$$\frac{DS}{Dt} = \frac{\partial S}{\partial t} + \nabla \cdot \mathbf{J}_S = \Pi_S \quad (29)$$

where Π_S is the local production density.

In general the balance equation for each of the underlying field properties is

$$\frac{D\alpha_j}{Dt} = \frac{\partial \alpha_j}{\partial t} + \nabla \cdot \mathbf{J}_{\alpha_j} = \Pi_{\alpha_j} \quad (30)$$

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

$$\frac{D\gamma}{Dt} = \frac{\partial \gamma}{\partial t} + \nabla \cdot \mathbf{J}_\gamma = \Pi_\gamma \quad (31)$$

where $\mathbf{J}_\gamma = \mathrm{diag}[\mathbf{J}_{\alpha_j}]$ and $\Pi_\gamma = \mathrm{diag}[\Pi_{\alpha_j}]$.

It is then further assumed that there exist functions $\Phi_{\alpha_j}(\gamma)$ (Liu's Lagrange multipliers [16]) that we denote here in matrix form by

$$\Phi = \mathrm{diag}(\Phi_{\alpha_j}) \tag{32}$$

such that the local entropy production density can be written as

$$\Pi_S = \sum_{j=1}^n \Phi_{\alpha_j} \Pi_{\alpha_j} = (\Phi | \Pi_\gamma) \tag{33}$$

and must be nonnegative everywhere.

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

$$\Psi_i = \mathrm{diag}(\Psi_{i\alpha_j}) \tag{34}$$

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

$$\Pi_{C_i} = \sum_{j=1}^n \Psi_{i\alpha_j} \Pi_{\alpha_j} = (\Psi_i | \Pi_\gamma) \tag{35}$$

Typically, but not necessarily, the first five underlying fields $\alpha_j(\mathbf{x},t)$ for $j = 1,\dots,5$ are conveniently chosen to coincide with the energy, momentum, and mass densities, so that Eqs. (30) for $j = 1,\dots,5$ coincide with Eqs. (27) because $\Pi_{\alpha_j} = 0$ for this subset of conserved fields.

The above framework reduces to the traditional Onsager theory of macroscopic Non-Equilibrium 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 $X_{\alpha_j} = -\Phi_{\alpha_j}$ the "thermodynamic forces" and Π_{α_j} the "thermodynamic currents".

The same framework reduces to the standard scheme of Chemical Kinetics (CK) if the α_j's are taken to represent the local reaction coordinates, Π_{α_j} the local rate of advancement of reaction j, Φ_{α_j} its entropic affinity, C_i the local concentration of atomic elements of kind i, $\Pi_{C_i} = 0$ their local production density.

Below, in the section on SAE/MEP dynamics, we construct an equation of motion for γ such that Π_S is maximal subject to the conservation constraints $\Pi_{C_i} = 0$ and a suitable additional constraint we discuss therein.

FRAMEWORK E. MESOSCOPIC NON-EQUILIBRIUM THERMODYNAMICS

Let $\mathscr{L}$ be the set of all $n \times n$ diagonal matrixes $A = \mathrm{diag}(a_j(\gamma))$, $B = \mathrm{diag}(b_j(\gamma))$, ... whose entries $a_j(\gamma)$, $b_j(\gamma)$, ... are real, square-integrable functions of a set of mesoscopic properties usually denoted by $\alpha_1,\dots,\alpha_m$ that here we denote synthetically by defining the matrix

$$\gamma = \mathrm{diag}(\alpha_1,\dots,\alpha_m) \tag{36}$$

and denoting its m-dimensional range by Ω_γ, usually called the $\boldsymbol{\alpha}$-space. Let $\mathscr{L}$ be equipped with the inner product $(\cdot|\cdot)$ defined by

$$(A|B) = \sum_{i=1}^n \mathrm{Tr}(a_i b_i) = \sum_{i=1}^n \int_{\Omega_\gamma} a_i(\gamma) b_i(\gamma)\, d\Omega_\gamma \tag{37}$$

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

In Mesoscopic Non-Equilibrium Thermodynamics (MNET) (see, e.g., [6]) the α_j's are the set of mesoscopic (coarse grained) local extensive properties assumed to represent the local non-equilibrium state of the portion of continuum under study. The mesoscopic description of the local state at position $\mathbf{x}$ and time t is in terms of a probability density on the $\boldsymbol{\alpha}$-space Ω_γ, that we denote by $P(\gamma;\mathbf{x},t)$. $P(\gamma;\mathbf{x},t)\, d\Omega_\gamma$ represents the probability that the values of the underlying fields are between γ and $\gamma + d\gamma$.

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

$$\frac{DP}{Dt} = \frac{\partial P}{\partial t} + \mathbf{c} \cdot \nabla P = -\nabla_\gamma \cdot \Pi_\gamma \tag{38}$$

where $\mathbf{c} = \mathbf{c}(\gamma)$ 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) and we define for shorthand

$$\Pi_\gamma = \mathrm{diag}(\Pi_{\alpha_j}) \quad \text{and} \quad \nabla_\gamma = \mathrm{diag}\left(\frac{\partial}{\partial \alpha_j}\right) \tag{39}$$

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

The conserved fields $C_i(\mathbf{x},t)$ have an associated underlying extensive property which can be expressed in terms of the mesoscopic coordinates as $\psi_i(\gamma)$. They obey the balance equation

$$\frac{DC_i}{Dt} = \frac{\partial C_i}{\partial t} + \nabla \cdot \mathbf{J}_{C_i} = \Pi_{C_i} = 0 \tag{40}$$

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

$$C_i(\mathbf{x},t) = \int_{\Omega_\gamma} \psi_i(\gamma) P(\gamma;\mathbf{x},t)\, d\Omega_\gamma$$

$$\mathbf{J}_{C_i}(\mathbf{x},t) = \int_{\Omega_\gamma} \psi_i(\gamma) \mathbf{c}(\gamma) P(\gamma;\mathbf{x},t)\, d\Omega_\gamma$$

$$\Pi_{C_i}(\mathbf{x},t) = \int_{\Omega_\gamma} \psi_i(\gamma) \frac{DP}{Dt}(\gamma;\mathbf{x},t)\, d\Omega_\gamma$$

$$= -\int_{\Omega_\gamma} \psi_i(\gamma) \nabla_\gamma \cdot \Pi_\gamma d\Omega_\gamma$$

$$= \int_{\Omega_\gamma} \Pi_\gamma \cdot \nabla_\gamma \psi_i(\gamma)\, d\Omega_\gamma$$

$$= (\Psi_i | \Pi_\gamma) \tag{41}$$

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

$$\Psi_i = \nabla_\gamma \psi_i(\gamma) \tag{42}$$

The entropy balance equation takes the form

$$\frac{DS}{Dt} = \frac{\partial S}{\partial t} + \nabla \cdot \mathbf{J}_S = \Pi_S \tag{43}$$

where the local density $S(\mathbf{x},t)$, the local flux $\mathbf{J}_S(\mathbf{x},t)$ and the local production density $\Pi_S(\mathbf{x},t)$ are defined in terms of the associated extensive property expressed in terms of the mesoscopic coordinates as

$$\phi(\gamma) = -k \ln P(\gamma) \tag{44}$$

as follows

$$S(\mathbf{x},t) = \int_{\Omega_\gamma} \phi(\gamma) P(\gamma;\mathbf{x},t)\, d\Omega_\gamma$$

$$\mathbf{J}_S(\mathbf{x},t) = \int_{\Omega_\gamma} \phi(\gamma) \mathbf{c}(\gamma) P(\gamma;\mathbf{x},t)\, d\Omega_\gamma$$

$$\Pi_S(\mathbf{x},t) = \int_{\Omega_\gamma} \phi(\gamma) \frac{DP}{Dt}(\gamma;\mathbf{x},t)\, d\Omega_\gamma$$

$$= -\int_{\Omega_\gamma} \phi(\gamma) \nabla_\gamma \cdot \Pi_\gamma d\Omega_\gamma$$

$$= \int_{\Omega_\gamma} \Pi_\gamma \cdot \nabla_\gamma \phi(\gamma)\, d\Omega_\gamma$$

$$= (\Phi | \Pi_\gamma) \tag{45}$$

where again in the next to the last equation we integrated by parts and we defined

$$\Phi = \nabla_\gamma \phi(\gamma) \qquad (46)$$

Below, in the section on SAE/MEP dynamics, we construct an equation of motion for γ such that Π_S is maximal subject to the conservation constraints $\Pi_{C_i} = 0$ and a suitable additional constraint we discuss therein. The result, when introduced in Eq. (38) will yield the Fokker-Planck equation for $P(\gamma; \mathbf{x}, t)$ which is also related (see, e.g., [17]) to the GENERIC structure [18]. The formalism can also be readily extended to the family of Tsallis [19] entropies in the frameworks of non-extensive thermodynamic models [20].

FRAMEWORK F: QUANTUM STATISTICAL MECHANICS, QUANTUM INFORMATION THEORY, QUANTUM THERMODYNAMICS, MESOSCOPIC NON-EQUILIBRIUM QUANTUM THERMODYNAMICS, AND INTRINSIC QUANTUM THERMODYNAMICS

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

$$(A|B) = \text{Tr}\left(A^\dagger B + B^\dagger A\right)/2 \qquad (47)$$

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

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 nonnegative-definite element of $\mathscr{L}$.

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; 3; 4; 5] in order to easily impose the constraints of preservation of both the nonnegativity and the self-adjointness of ρ during its time evolution. Therefore, we assume that the state representative is an element γ in $\mathscr{L}$ from which we can compute the density operator as follows

$$\rho = \gamma \gamma^\dagger \qquad (48)$$

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

$$\frac{d\rho}{dt} = \gamma \frac{d\gamma^\dagger}{dt} + \frac{d\gamma}{dt}\gamma^\dagger \qquad (49)$$

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

$$\{C_i\} = \left\{H, M_x, M_y, M_z, N_1, \ldots, N_r, I\right\} \qquad (50)$$

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

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[1] In simplified models, the set $\{C_i\}$ is often restricted to only $\{H, I\}$. Operators M_x, M_y, M_z are the components of the momentum operator. Operator N_i, for $i = 1, \ldots, r$, is the number operator for particles of type i in the system. If the system is closed to particle exchange, it has a fixed number n_i of particles of type i, then $N_i = n_i I$, i.e., it is a c-number operator, where I is the identity operator on $\mathscr{H}$. If the system is open to particle exchange, then the Hilbert space $\mathscr{H}$ is a Fock space, i.e.,

$$\mathscr{H} = \bigoplus_{j_1=0}^{\infty} \cdots \bigoplus_{j_r=0}^{\infty} \mathscr{H}_{j_1 j_2 \ldots j_r} \text{ and } N_i = \sum_{j_1=0}^{\infty} \cdots \sum_{j_r=0}^{\infty} j_i I_{j_1 j_2 \ldots j_r}$$

where $I_{j_1 j_2 \ldots j_r}$ is the projector operator onto the subspace $\mathscr{H}_{j_1 j_2 \ldots j_r}$ belonging to the composition with j_1 particles of type 1, j_2 particles of type 2, and so on.

The semi-empirical description of an irreversible relaxation process is done in this framework by assuming an evolution equation for the state γ given by the equations

$$\frac{d\gamma}{dt} + \frac{i}{\hbar}H\gamma = \Pi_\gamma \qquad (51)$$

$$\frac{d\gamma^\dagger}{dt} - \frac{i}{\hbar}\gamma^\dagger H = \Pi_{\gamma^\dagger} \qquad (52)$$

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

$$\frac{d\rho}{dt} + \frac{i}{\hbar}[H, \rho] = \Pi_\gamma \gamma^\dagger + \gamma \Pi_{\gamma^\dagger} \qquad (53)$$

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

$$\Pi_{\gamma^\dagger} = \Pi_\gamma^\dagger \quad \text{and} \quad \Pi_\gamma = \Pi_{\gamma^\dagger}^\dagger \qquad (54)$$

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

$$\Pi_{C_i} = \frac{d}{dt}\text{Tr}(\rho C_i) = \text{Tr}(C_i\Pi_\gamma \gamma^\dagger + \gamma \Pi_{\gamma^\dagger} C_i) = (2C_i\gamma|\Pi_\gamma) = 0 \qquad (55)$$

The entropy functional in this context is represented by

$$S(\gamma) = -k\text{Tr}(\rho \ln \rho) = (-k(\ln \gamma\gamma^\dagger)\gamma|\gamma) \qquad (56)$$

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

$$\Pi_S = -k\frac{d}{dt}\text{Tr}(\rho \ln \rho) = (-2k(\ln \gamma\gamma^\dagger)\gamma|\Pi_\gamma) \qquad (57)$$

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 $\mathscr{H}$ and operators $\{H, N_1, \ldots, N_r\}$) 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 $\mathscr{H}$. 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. (53) with $\Pi_\gamma = 0$ so that Eq. (53) reduces to von Neumann's equation of quantum reversible 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 sections for ρ represents a model for the rates of change of 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 below), thus essentially extends to the quantum landscape the same statistical or information theoretic non-equilibrium problem we defined above as Framework C.

In Quantum Thermodynamics (QT), instead, the density operator takes on a more fundamental physical meaning. It is not any longer related to the heterogeneity of the ensemble, and it is not any longer assumed that the individual member systems of the ensemble are in pure states.

The prevailing interpretation of QT 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-bath composite is assumed to be in a pure quantum mechanical state $\mathscr{H} \otimes \mathscr{H}_R$ and reduces to the density operator ρ on the system's space $\mathscr{H}$ when we partial trace over the bath's space $\mathscr{H}_R$.

The semi-empirical description of an irreversible relaxation process is done in this framework by assuming for Π_ρ in Eq. (53) the Lindblad-Gorini-Kossakowski-Sudarshan (LGKS) [21; 22]

$$\Pi_\rho = \sum_j \left(V_j \rho V_j^\dagger - \frac{1}{2} \{V_j^\dagger V_j, \rho\} \right) \qquad (58)$$

where $\{\cdot, \cdot\}$ denotes the anticommutator and operators V_j are to be chosen so as to properly model the system-bath interaction. The justification and modeling assumptions that lead to the general form of Eq. (58) are well known.

In the framework of QT the SEA equation of motion we construct in the next sections for ρ represents 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 a suitable additional constraint, see below). In some cases this could be simpler than the LGKS model and it has the advantage of a strong built-in thermodynamics consistency.

Mesoscopic Non-Equilibrium 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. The essential elements of this proof have actually already been given [4], but only for the particular case corresponding to Eq. (62) below (Fisher-Rao metric).

An even more fundamental physical meaning is assumed within the theory that we originally called Quantum Thermodynamics [2; 3; 23; 24; 25; 26] but more recently renamed Intrinsic Quantum Thermodynamics (IQT) to avoid confusion with the QT model just outlined.

IQT assumes that the second law of thermodynamics should complement the laws of mechanics even at the single particle level [23]. 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 non-idempotent ρ's. This way, the entropy functional $S(\rho)$ becomes in IQT an intrinsic fundamental property.[2]

In the framework of IQT the SEA equation of motion (53)

for ρ which results from the expression for Π_γ we construct in the next section represents a strong implementation of the MEP principle at the fundamental quantum level and generalizes the original framework in which we developed the SEA formalism about 30 years ago by making it compatible, at least in the near-equilibrium limit with MNEQT.

Even the brief discussion above shows clearly that the differences between QSM, QIT, QT, and IQT 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 they share on the mathematical basis, can find in the different theories different physical interpretations and applications.

STEEPEST-ENTROPY-ASCENT/MAXIMAL-ENTROPY-PRODUCTION DYNAMICS. UNIFIED VARIATIONAL FORMULATION FOR FRAMEWORKS A TO F

In the preceding sections we formulated the non-equilibrium problem in various different frameworks in a unifying way that allows us to represent their dissipative parts in a single formal way. In essence, the state is represented by an element γ of a suitable vector space $\mathscr{L}$ 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 $\mathscr{L}$ which determines the rate of entropy production according to the relation

$$\Pi_S = (\Phi | \Pi_\gamma) \qquad (59)$$

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

$$\Pi_{C_i} = (\Psi_i | \Pi_\gamma) \qquad (60)$$

Except for the RET Framework D, where we have no explicit expressions for Φ and Ψ_i, in Frameworks A, B, C we found that $\Phi = -k(\ln \gamma^2)\gamma$ and $\Psi_i = 2C_i\gamma$, in Framework F we found that $\Phi = -k(\ln \gamma \gamma^\dagger)\gamma$ and $\Psi_i = 2C_i\gamma$.

The formulation in terms of square roots of probabilities in Framework C, of the phase density in Frameworks A and B, of the density operator in Framework F takes care of the important condition that for the evolution law to be well defined it must conserve the nonnegativity of probabilities, phase densities and density operators (which must also remain self adjoint).

Our next objective is to implement the MEP principle. We do this by assuming that the time evolution of the state γ follows the path of steepest entropy ascent in $\mathscr{L}$. 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 norm of Π_γ. Hence, we must do the maximization at constant norm of Π_γ.

The norm of Π_γ represents the square of the distance $d\ell$ traveled by γ in the state space $\mathscr{L}$ 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 SAE/MEP direction at each state γ looks at all possible

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[2]In a sense it accomplishes the conceptual program, so intensely sought for also by Ilya Prigogine and coworkers [27], 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 perceived by John Maddox in 1985 [28].

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 SAE/MEP path until we equip the space $\mathscr{L}$ with a metric 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 $\mathscr{L}$. 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. [29; 30; 31]). According to this metric, the distance between two states γ_1 and γ_2 is given by

$$d(\gamma_1, \gamma_2) = \sqrt{2}\arccos(\gamma_1|\gamma_2) \tag{61}$$

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

$$d\ell = 2\sqrt{(\Pi_\gamma|\Pi_\gamma)}\, dt \tag{62}$$

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

However, here we will adopt a more general metric, which in Framework F generalizes our previous work and in the other frameworks provides a most general formulation. We assume the following expression for the distance traveled along a trajectory in state space

$$d\ell = \sqrt{(\Pi_\gamma|\hat{G}|\Pi_\gamma)}\, dt \tag{63}$$

where $\hat{G}$ is a real, symmetric, and positive-definite operator on $\mathscr{L}$ that we call the metric tensor, (super)matrix, or (super)operator depeding on the framework. In Framework F, since $\mathscr{L}$ is the space of operators on the Hilbert space $\mathscr{H}$ of the quantum system, $\hat{G}$ is a superoperator on $\mathscr{H}$. However, a simple case is when $\hat{G}|A) = |GA)$ with G some self-adjoint positive-definite operator in $\mathscr{L}$.

We may now finally state **the SAE/MEP 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 $(d\ell/dt)^2 = \dot{\varepsilon}^2 =$ prescribed. The last constraint keeps the norm of Π_γ constant so that we maximize only with respect to its direction. From Eq. (63) it amounts to keeping fixed the value of $(\Pi_\gamma|\hat{G}|\Pi_\gamma)$ at some small positive constant $\dot{\varepsilon}^2$. The solution is easily obtained by the method of Lagrange multipliers. We seek the unconstrained maximum, with respect to Π_γ, of the Lagrangian

$$\Upsilon = \Pi_S - \sum_i \beta_i \Pi_{C_i} - \tau\left[(\Pi_\gamma|\hat{G}|\Pi_\gamma) - \dot{\varepsilon}^2\right] \tag{64}$$

where β_i and τ are the Lagrange multipliers. They must be independent of Π_γ but can be functions of the state γ. Using Eqs. (59) and (60), we rewrite (64) as follows

$$\Upsilon = (\Phi|\Pi_\gamma) - \sum_i \beta_i(\Psi_i|\Pi_\gamma) - \tau\left[(\Pi_\gamma|\hat{G}|\Pi_\gamma) - \dot{\varepsilon}^2\right] \tag{65}$$

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

$$\frac{\delta\Upsilon}{|\delta\Pi_\gamma)} = |\Phi) - \sum_i \beta_i|\Psi_i) - \tau\hat{G}|\Pi_\gamma) = 0 \tag{66}$$

Thus, we obtain the SEA/MEP general evolution equation (the main result of this paper)

$$|\Pi_\gamma) = \hat{L}|\Phi - \sum_j \beta_j \Psi_j) \tag{67}$$

where we define for convenience

$$\hat{L} = \frac{1}{\tau}\hat{G}^{-1} \tag{68}$$

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/MEP. 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 entails Onsager reciprocity.

Inserting Eq. (67) into the conservation constraints (60) yields the important system of equations which defines the values of the Lagrange multipliers β_j,

$$\sum_j (\Psi_i|\hat{L}|\Psi_j)\beta_j = (\Psi_i|\hat{L}|\Phi) \tag{69}$$

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. When Cramer's rule is worked out explicitly, the SEA equation (67) takes the form of a ratio of determinants with which we presented it in the IQT framework [24; 25; 26; 5].

We can now immediately prove the general consistence with the thermodynamic principle of entropy non-decrease (H-theorem in Framework B). Indeed, subtracting Eqs. (60) each multiplied by the corresponding β_j's from Eq. (59) and then inserting Eq. (67) yields the following explicit expression for rate of entropy production

$$\Pi_S = (\Phi|\Pi_\gamma) = (\Phi - \sum_j \beta_j \Psi_j|\Pi_\gamma)$$
$$= (\Phi - \sum_i \beta_i \Psi_i|\hat{L}|\Phi - \sum_j \beta_j \Psi_j) \geq 0 \tag{70}$$

which is clearly nonnegative-definite by virtue, again, of the nonnegativity 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/MEP path. This amounts to inserting Eq. (67) into the additional constraint $(d\ell/dt)^2 = \dot{\varepsilon}^2 =$ prescribed. We readily find

$$\frac{d\ell^2}{dt^2} = (\Pi_\gamma|\hat{G}|\Pi_\gamma)$$
$$= \frac{1}{\tau^2}(\Phi - \sum_i \beta_i \Psi_i|\hat{G}^{-1}\hat{G}\hat{G}^{-1}|\Phi - \sum_j \beta_j \Psi_j) \tag{71}$$

$$= \frac{1}{\tau}\Pi_S = \dot{\varepsilon}^2 \tag{72}$$

from which we see that the Lagrange multiplier τ is related to the entropy production rate and the speed $d\ell/dt$. In other words, through τ we may specify either the speed at which γ evolves along the SEA/MEP trajectory in state space or the instantaneous rate of entropy production. Indeed, using Eq. (71), we obtain

$$\tau = \frac{\sqrt{(\Phi - \sum_i \beta_i \Psi_i|\hat{G}^{-1}|\Phi - \sum_j \beta_j \Psi_j)}}{d\ell/dt} \tag{73}$$

$$= \frac{(\Phi - \sum_i \beta_i \Psi_i|\hat{G}^{-1}|\Phi - \sum_j \beta_j \Psi_j)}{\Pi_S} \tag{74}$$

Hence, using τ given by Eq. (74) the evolution equation Eq. (67) will produce a SEA/MEP trajectory in state space with the prescribed entropy production Π_S. Eq. (74) also clearly supports the interpretation of τ as the "overall relaxation time".

In general, we may interpret the vector

$$|\Lambda) = \hat{G}^{-1/2}|\Phi - \sum_i \beta_i \Psi_i) \qquad (75)$$

as a vector of "generalized partial affinities". In terms of this vector, Eq. (67) rewrites as

$$\hat{G}^{1/2}|\Pi_\gamma) = \frac{1}{\tau}|\Lambda) \qquad (76)$$

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 we have an equilibrium state or a non-dissipative limit cycle. In fact, that 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 $\Phi - \sum_j \beta_j \Psi_j$, represents a measure of the "overall degree of disequilibrium". 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 non-equilibrium states.

Eq. (74) rewrites as

$$\Pi_S = \frac{(\Lambda|\Lambda)}{\tau} \qquad (77)$$

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 non-linear evolution equation that is well defined and reasonable 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 F for an isolated system), i.e., when the entropy balance equation reduces to $dS/dt = \Pi_S$, Eq. (72) may be rewritten as

$$\frac{d\ell}{dt/\tau} = \frac{dS}{d\ell} \qquad (78)$$

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 entropy gradient along the trajectory.

If the state γ moves only due to the dissipative term Π_γ (for example in Framework F 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

$$\ell(t) = \int_0^t \sqrt{(\Pi_\gamma|\hat{G}|\Pi_\gamma)}\,dt \qquad (79)$$

and, correspondingly, we may also define the "non-equilibrium action"

$$\Sigma = \frac{1}{2}\int_0^t (\Pi_\gamma|\hat{G}|\Pi_\gamma)\,dt = \frac{1}{2}\int_0^t \frac{\Pi_S}{\tau}\,dt = \frac{1}{2}\int_0^t \frac{(\Lambda|\Lambda)}{\tau^2}\,dt \quad (80)$$

where for the last two equalities we used Eq. (72) and Eq. (77), respectively.

The explicit expressions of the SEA/MEP dynamical equations that result in the six different frameworks treated here can be readily obtained but will be given elsewhere.

PICTORIAL REPRESENTATIONS

Let us give pictorial representations of the vectors that we defined in the SEA/MEP 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 $|\Psi_i)$'s and the orthogonal projection of $|\Phi)$ which defines the Lagrange multipliers β_i in
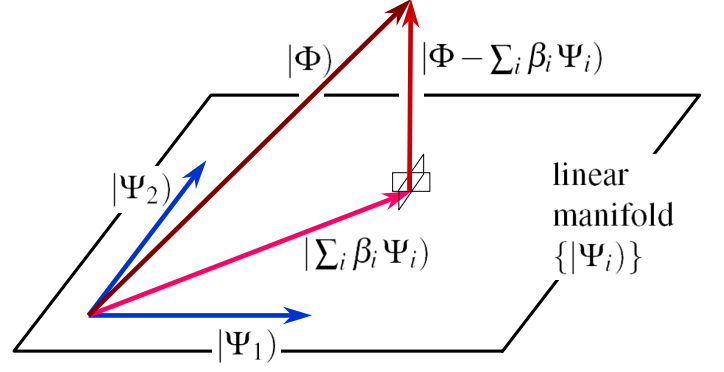

Figure 1. Pictorial representation of the linear manifold spanned by the vectors $|\Psi_i)$ and the orthogonal projection of $|\Phi)$ onto this manifold which defines the Lagrange multipliers β_i in the case of a uniform metric $\hat{G} = \hat{I}$. The construction defines also the generalized affinity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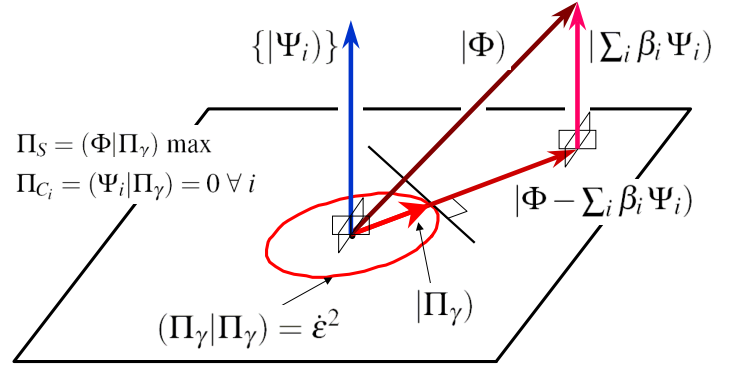

Figure 2. Pictorial representation of the SEA/MEP variational construction in the case of a uniform metric $\hat{G} = \hat{I}$. The circle represents the condition $(\Pi_\gamma|\Pi_\gamma) = \dot{\varepsilon}^2$. The vector $|\Pi_\gamma)$ must be orthogonal to the $|\Psi_i)$'s in order to satisfy the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

the case of uniform metric, i.e., the orthogonality conditions $(\Psi_j|\Phi - \sum_i \beta_i \Psi_i) = 0$ for every j, which is Eq. (69) with $\hat{L} = \hat{I}$. The construction defines also the generalized affinity vector, which in this case is $|\Lambda) = |\Phi - \sum_i \beta_i \Psi_i)$ and is orthogonal to the linear manifold spanned by the vectors $|\Psi_i)$'s.

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

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

Next, we consider the more general scenario of a non-uniform metric tensor $\hat{G}$. Figure 3 gives a pictorial representation of the linear manifold spanned by the vectors $\hat{G}^{-1/2}|\Psi_i)$
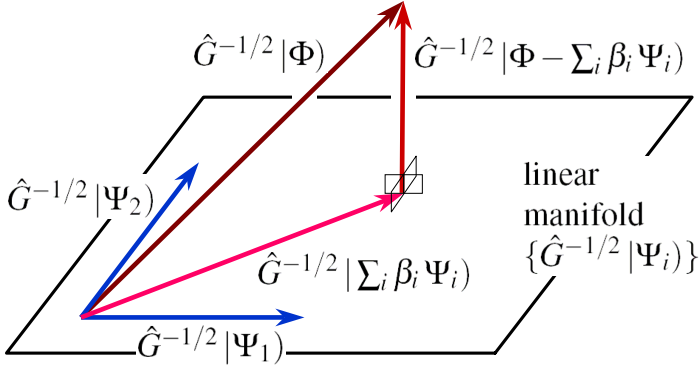
Figure 3. Pictorial representation of the linear manifold spanned by the vectors $\hat{G}^{-1/2}\Psi_i$ and the orthogonal projection of $\hat{G}^{-1/2}|\Phi)$ onto this manifold which defines the Lagrange multipliers β_i in the case of a non-uniform metric $\hat{G}$. The construction defines also the generalized affinity vector $|\Lambda) = \hat{G}^{-1/2}|\Phi - \sum_i \beta_i \Psi_i)$.
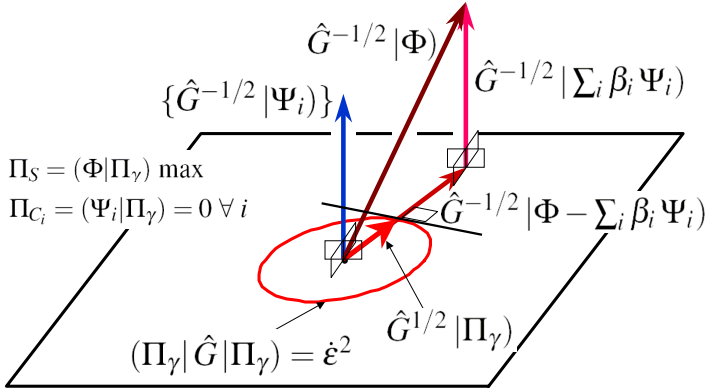

Figure 4. Pictorial representation of the SEA/MEP variational construction in the case of a non-uniform metric $\hat{G}$. The circle represents the condition $(\Pi_\gamma|\hat{G}|\Pi_\gamma) = \dot{\varepsilon}^2$, corresponding to the norm of vector $\hat{G}^{1/2}|\Pi_\gamma)$. This vector must be orthogonal to the $\hat{G}^{-1/2}|\Psi_i)$'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 $\hat{G}^{1/2}|\Pi_\gamma)$ must have the same direction as $|\Lambda) = \hat{G}^{-1/2}|\Phi - \sum_i \beta_i \Psi_i)$.

and the orthogonal projection of $\hat{G}^{-1/2}|\Phi)$ which defines the Lagrange multipliers β_i in the case of non-uniform metric $\hat{G}$, where the orthogonality conditions that define the β_i's are $(\Psi_j|\hat{G}^{-1}|\Phi - \sum_i \beta_i \Psi_i) = 0$ for every j, which is Eq. (69). The construction defines also the generalized affinity vector $|\Lambda) = \hat{G}^{-1/2}|\Phi - \sum_i \beta_i \Psi_i)$ which is orthogonal to the linear manifold spanned by the vectors $\hat{G}^{-1/2}|\Psi_i)$'s.

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

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

line orthogonal to $|\Phi - \sum_i \beta_i \Psi_i)$.

The compatibility with the conservation constraints $\Pi_{C_i} = (\Psi_i|\Pi_\gamma) = 0$ requires that $\hat{G}^{1/2}|\Pi_\gamma)$ lies in subspace orthogonal to the $\hat{G}^{-1/2}|\Psi_i)$'s. To take the SEA/MEP direction, the vector $\hat{G}^{1/2}|\Pi_\gamma)$ 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 $|\Pi_\gamma)$ has the same direction as the generalized affinity vector $|\Lambda) = \hat{G}^{-1/2}|\Phi - \sum_i \beta_i \Psi_i)$.

CONCLUSIONS

In this paper, we review the essential mathematical elements of the formulations of six different approaches to the description of non-equilibrium dynamics. At the price of casting some of them in a somewhat unusual notation, we gain the possibility to set up a unified formulation, which allows us to investigate the locally Maximum Entropy Production (MEP) principle in all these contexts. It is a generalization to non-homogeneous cases of the local Steepest Entropy Ascent (SEA) concept whereby the time evolution the state is assumed to follows a path in state space which, with respect to an underlying metric, is always tangent to the direction of maximal entropy production compatible with the conservation constraints.

The present SEA/MEP 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. Actually, the present formulation constitutes a generalization even in the quantum thermodynamics framework and constitutes a natural generalization to the far-nonequilibrium domain of Mesoscopic Non-Equilibrium Quantum Thermodynamics.

The analysis emphasizes that in the SEA/MEP implementation of the MEP principle, 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.

We conclude that in most of the existing theories of non-equilibrium the time evolution of the 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/MEP 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 appear 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 SEA/MEP.

Far from equilibrium the resulting unified family of SAE/MEP dynamical models is a very fundamental as well as practical starting point because it features an intrinsic consistency with the second law of thermodynamics. The proof of nonnegativity of the local entropy production density is a general and straightforward 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 non-equilibrium states.

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