TITLE: On the geometrical representation of classical statistical mechanics.

Georgios C. Boulougouris, *

"Laboratory of Computational Physical-Chemistry", Department of Molecular Biology and Genetics , University of Thrace, Alexandropouli, Greece.

Abstract: In this work a geometrical representation of equilibrium and near equilibrium statistical mechanics is proposed. Using a formalism consistent with the Bra-Ket notation and the definition of inner product as a Lebasque integral, we describe the macroscopic equilibrium states in classical statistical mechanics by "properly transformed probability Euclidian vectors" that point on a manifold of spherical symmetry. Furthermore, any macroscopic thermodynamic state "close" to equilibrium is described by a triplet that represent the "infinitesimal volume" of the points, the Euclidian probability vector at equilibrium that points on a hypersphere of equilibrium thermodynamic state and a Euclidian vector a vector on the tangent bundle of the hypersphere. The necessary and sufficient condition for such representation is expressed as an invertibility condition on the proposed transformation. Finally, the relation of the proposed geometric representation, to similar approaches introduced under the context of differential geometry, information geometry, and finally the Ruppeiner and the Weinhold geometries, is discussed. It turns out that in the case of thermodynamic equilibrium, the proposed representation can be considered as a Gauss map of a parametric representation of statistical mechanics.

INTRODUCTION:

The idea of using geometrical concepts in thermodynamics is probably as old as the foundations of Thermodynamics and Statistical Mechanics themselves. Furthermore, their importance has been certainly realized and emphasized by most of the founding fathers in both fields, (i.e. Gibbs[1], Clausius[2], and Caratheodory[3]). Notably, one of the first and probably best, uses of geometrical concepts is the axiomatic foundation of classical thermodynamics from Caratheodory. Within Clausius and Caratheodory's frameworks[3], the second law of thermodynamics is realized as a consequence of differential geometry (i.e. via the geometrical

* Electronic mail: *gbouloug@mbg.duth.gr*

properties of the Pfaffian differential). Similarly, geometry is in the heart of Gibbs's work. On the other hand, it seems that there are several novel approaches[4] using concepts from a variety of mathematical fields, (e.g. differential calculus, differential geometry, Riemannian geometry and Information Theory), which can provide additional mathematical tools in the study of thermodynamics. Characteristic examples are both the pioneer use of the Riemannian geometry in the work of Ruppeiner, as well as the introduction of a thermodynamic metric by Weinhold. Both these studies that turn out[5-7] to be intimately related to the notions of metric and statistical "distances" between probability distributions in the context of information theory[8].

The aim of this work is to extend and incorporate the original description of the dynamical response close to equilibrium for discrete systems[9], within the general context of statistical mechanics and additionally, to connect the proposed approach to similar attempts that have been reported in the literature[5-8, 10] .

The Eigenvector Representation of Observables and Probabilities in a High-dimensionaL Euclidean space (EROPHILE) was initially developed in a previous work by the author regarding the dynamic response close to equilibrium[9, 11], in discrete stochastic systems whose dynamics could be described by a master equation. In that case, the driving force was to understand the underlying similarities and differences, between different dynamic relaxation computational experiments close to equilibrium, within the context of statistical mechanics for the case of a system with discrete states[12-18]. The result was a geometrical representation of near equilibrium dynamics where both the dynamic response and all equilibrium thermodynamic averages could be represented via Euclidean vectors. Furthermore, it was shown that the common spectrum of near equilibrium dielectric relaxation and mechanical relaxation experiments of glassy polymers could be directly traced to the eigen values of the master equation, that describe the transitions between local potential energy minima, commonly referred as inherent structures. Interestingly, it turn out that within the context of EROPHILE[9] all statistical averages and variances of any stochastic variable could be expressed as projections in the form of inner products of Euclidean vectors.

In order to provide the basic steps that led to this work, a short introduction to the initial notions of EROPHILE as well as the basic building blocks of the ensemble approach in Statistical Mechanics, will also be provided in the next paragraphs, highlighting at the same time the relevance of each step to the proposed representation.

Elements of statistical mechanics of equilibrium ensembles

In this section, a sort description of the statistical mechanics representation of macroscopic thermodynamic equilibrium in the form of statistical ensembles over microstates, will be provided. The aim is to provide a bridge between basic concepts in the fields of statistical mechanics, information theory and differential geometry.

The statistical mechanics representation of macroscopic equilibrium starts on the realization that independent parameters are necessary and sufficient to uniquely define a macroscopic thermodynamic state. The origin of those quantities is intimately related to the notion of conserved extensive quantities and the way we separate the system under study from it's environment. The most common examples of such quantities are the energy, the number of molecules, and the volume, of a system. All of them are extensive, i.e. scale with the size of the system and at the same time are related to a conservation law. Interestingly, from the work of Clausius and Caratheodory we know, that it is essential that this number is greater or equal to two. In thermodynamics, this is essential for the existence of an integrating factor in the Pfaffian differential that is used to define heat. In the language of differential geometry, this is related to the definition of a complete differential form and how this is associated to the second exterior derivative of an orientable surface. The number of extensive independent quantities that are necessary to uniquely define a macroscopic thermodynamic state are the same in both the macroscopic thermodynamics and statistical mechanics. However, in macroscopic thermodynamics, the size dependence properties can be trivially evaluated based on a linear scale of the extensive properties with the system size that only appears in statistical mechanics at the thermodynamic limit of large systems. Most importantly in statistical mechanics each macroscopic thermodynamic state is realized as an ensemble of microscopic realization of the system called microstates. Each microstate is uniquely defined if all positions and velocities of a molecular system are set and it is characterized by a set of extensive variables and the probability of being observed in the ensemble. According to the original postulate by Boltzmann, in systems that do not exchange conserved quantities (i.e. energy E, number of particles N of each specie and volume V) with the environment, all microstates with the same E,N,V values are equally probable in the ensemble and no other microstate can be a member of this ensemble. As pointed out by Jaynes [19], Boltzmann postulate can be traced to the concept of assigning equal probabilities in events that we do not have any prior information on, in order to distinguish them (like the outcome of a head or tail experiment or the outcome of a fair dice). Different ensembles correspond to different rules for the exchange, or not, of those extensive conserved quantities between the system and it's environment, provided that at least one such extensive variable is fixed in order to preserve the size dependence of the thermodynamic state.

The relation between a thermodynamic state and the corresponding set of microstates is "quantified" by the concept of Entropy. As proposed by Boltzmann Entropy can be viewed as a measure of cardinality but at the same time via the work of Gibbs, Shannon and Jaynes [19], it can be also viewed, as an measure of information i.e. measure of the uncertainty imposed by the map, of a single macroscopic thermodynamics state, to a set of microstates.

When one (or more) of the extensive variables is allowed to be partitioned between the system and the environment then thermodynamic equilibrium is achieved once the conjugate "thermodynamic forces", in the system and in the environment become equal. Those forces are a function of intensive variables in both the system and the environment. In macroscopic thermodynamics, this corresponds to a change of the independent variables via a Legendre transformation. In statistical mechanics, this transformation can be realized either as a Laplace transformation, along with the application of saddle point approximation (in the thermodynamic limit), or equivalently as a constrained optimization of entropy, with Lagrange multipliers being a function of the intensive variables of the ensemble. The result is that the thermodynamic state is characterized by two sets of independent variables: a set of intensive variables and a set of extensive variables. In terms of statistical mechanics any microstate has a weight (i.e. the Boltzmann weight) of being observed in the ensemble that is no longer either one or zero. It is important to remember that the Boltzmann weight is again zero for all microstates that are not consistent with the values of the extensive variables that remain as part of the independent variables of the ensemble (i.e. they are not distributed between the system and the environment and therefore have a constant value). The probability of observing a microstate in the ensemble can be evaluated if one knows both the Boltzmann weight for this state and the normalization function that sums the Boltzmann weights of all the microstate of the ensemble.

In the general case, given the number (m) of all independent extensive quantities $\boldsymbol{\Phi}$ that are conserved and can be redistributed between the system and the environment. An ensemble is defined as a function of l ($l \geq 1$) external variables $\{\Phi_1, \ldots, \Phi_l\}\sigma$ and a set of m-l intensive variables $\{\ldots \varphi_k \ldots\}$, one for each extensive quantity that is allowed to be distributed between the system and the environment. In one component system m is expected to be 3 whereas Φ_{i} are the energy E, the volume V, and the number of molecules N of a system. Common examples of intensive variables φ_k are the temperature T, the pressure P of the system, and the chemical potentials μ *for each specie*. In order to provide a link with the field of information theory, the Greek letter θ will be used to describe such functions of intensive variables that appear in statistical ensembles as parameters in the so called exponential family of probabilities (i.e. θ_α can be one of $-1/k_{\mathrm{B}}T$, $-P/k_{\mathrm{B}}T$, $\mu/k_{\mathrm{B}}T$, where k_{B} is the Boltzmann constant). Therefore, a thermodynamic state will be represented in this work by the values of the set of extensive variables $\boldsymbol{\Phi}$: $\{\Phi_1, \dots, \Phi_{\mathrm{l}},\}$ and the set $\boldsymbol{\theta}$: $\{\dots, \theta_k, \dots\}$. For example, in the canonical ensemble $\boldsymbol{\Phi}$: $\{N, V\}$, $\boldsymbol{\varphi}$: $\{T\}$ and $\boldsymbol{\theta}$: $\{-1/k_{\mathrm{B}}T\}$ since the thermodynamic state is a function of the number of molecules N, the volume V and the temperature T (NVT ensemble). Given the set of independent thermodynamic variables, statistical mechanics describe an equilibrium thermodynamic state as an ensemble of microstates i by assigning a probability density $p_{i,(\boldsymbol{\theta},\boldsymbol{\Phi})}^{\mathrm{eq}}$ to all possible microstates. The probability density $p_{i,(\boldsymbol{\theta},\boldsymbol{\Phi})}^{\mathrm{eq}}$ is a function of the l extensive variables $\{\Phi_1, \dots, \Phi_l\}$ and k=m-l intensive thermodynamic forces $\boldsymbol{\theta}$: $\{\dots, \theta_\alpha, \dots\}$ (or equivalently of $\boldsymbol{\Phi}$ and $\boldsymbol{\varphi}$).

For each intensive variable function (θ_α) exists a conjugate extensive variable $X_{i,\alpha}$ for each "state" i of the ensemble, resulting in a set of conjugate extensive variables $\boldsymbol{X}_\alpha$ diffined for each microstate i (*i.e.* $X_{i,\alpha}$). In equilibrium the probability distribution can be understood as the result of maximizing the entropy function of this probability distribution under constraints for the average values of the extensive variables $< X_{i,\alpha} >_{\boldsymbol{p}_{(\boldsymbol{\theta},\boldsymbol{\Phi})}^{\mathrm{eq}}} = \sum_i \; p_{i,(\boldsymbol{\theta},\boldsymbol{\Phi})}^{\mathrm{eq}} X_{i,\alpha}$ being equal to the values of the k=m-l extensive variables $\{\Phi_{l+1}, \dots, \Phi_m\}$ that have been replased by the k intensive thermodynamic forces $\boldsymbol{\theta}$ $\left(\mathrm{i.e.} < X_{i,a} >_{\boldsymbol{p}_{(\boldsymbol{\theta},\boldsymbol{\Phi})}^{\mathrm{eq}}} = \Phi_{l+a}\right)$. In this formalism, thermodynamic forces $\boldsymbol{\theta}$ can be understood as Lagrange multipliers. It is important to note that under this representation there is an additional Lagrange multiplier that ensures that the equilibrium probability is normalized. This Lagrange multiplier is related to the partition function and therefore to the stationary thermodynamic potential of an ensemble. Another, equivalent way of looking at the derivation of an equilibrium ensemble is of course the notion of Laplace transformations starting from an isolated system. Under this framework, the derivation of $\boldsymbol{p}_{(\boldsymbol{\theta},\boldsymbol{\Phi})}^{\mathrm{eq}}$ involves a saddle point approximation and special attention should be given to the conditions of phase equilibrium. As an example, in the *NPT* ensemble where the number of molecules *N*, pressure *P* and Temperature *T*, is constant $\boldsymbol{\Phi}\ is\ \{\boldsymbol{N}\}$, $\boldsymbol{\theta}\ is\ \{{}^{-1}/_{k_{\mathrm{B}}T}, {}^{-P}/_{k_{\mathrm{B}}T}\}$, whereas $X_{i,1}$ is E_i and $X_{i,2}$ is V_i the energy and the volume of each state *i*.

In a nutshell, statistical mechanics via the above procedure, utilizes the first and second law of thermodynamics (i.e. the conservation of energy and the maximization of entropy in closed systems) resulting in expressing the probability of observing each microstate in an ensemble characterised by the values of $\boldsymbol{\theta}, \boldsymbol{\Phi}$ in the form of Eq (1).

$$p^{\mathrm{eq}}_{i,(\boldsymbol{\theta},\boldsymbol{\Phi})}\mathrm{d}v = \frac{e^{\Sigma_\alpha(\theta_\alpha X_{i,\alpha})}\mathrm{d}v}{\int \quad e^{\Sigma_\alpha\left(\theta_\alpha X_{\iota,\alpha}\right)}\mathrm{d}v} \approx \frac{e^{\Sigma_\alpha(\theta_\alpha X_{i,\alpha})}\mathrm{d}v}{\Sigma_\iota\, e^{\Sigma_\alpha\left(\theta_\alpha X_{\iota,\alpha}\right)}\mathrm{d}v} \qquad (1)$$

In an *NVT* ensemble eq (1) reads $p^{\mathrm{eq}}_{i,(-\beta,\{\boldsymbol{N},V\})}\mathrm{d}v = \frac{e^{-\beta U_i}\mathrm{d}v}{\int e^{-\beta U_i}\mathrm{d}v}$ and in an *NPT* ensemble $p^{\mathrm{eq}}_{i,(\{-\beta,-\beta P\},\mathrm{N})}\mathrm{d}v = \frac{e^{-\beta(U_i+PV_i)}\mathrm{d}v}{\int \quad e^{-\beta(U_i+PV_i)}\mathrm{d}v}$. The denominator of Eq (1) is a normalization factor that is commonly referred to as the partition function. Depending on the ensemble, it relates to a certain type of free energy. In an *NVT* and *NPT* ensemble, the partition functions are related to the Helmholtz and the Gibbs free energy, respectively, i.e. : $\beta(A_{NVT}) = -\ln\frac{1}{h^{3N}N!}\int e^{-\beta U_i}\, dv$ and $\beta G_{NPT} = -\ln\frac{1}{h^{3N}N!}\int e^{-\beta U_i}\, dv$

$$\Psi_{(\boldsymbol{\theta},\boldsymbol{\Phi})} = \int \; e^{\Sigma_\alpha\left(\theta_\alpha X_{\iota,\alpha}\right)}\mathrm{d}v \quad (2)$$

where h is the Plank constant and the *N*! is the “Correct Boltzmann counting” that “guaranties” the extensivety of the thermodynamic potentials and transforms integration over distinguishable particles to an integral over indistinguishable particles.

In the thermodynamic limit of large systems, the Gibbs, Boltzmann and Shannon definitions of entropy coincide in the form of Eq (3) for all ensembles provided that p_i is the probability of observing a microstate in the ensemble.

$$\frac{S}{k_{\mathrm{B}}} = -\int p\, ln(p)\mathrm{d}v \approx -\Sigma_i\; p_i ln(p_i)\mathrm{d}v \quad (3)$$

Note that as in Eq (1) the sum is over any microstate that has different values for the extensive variables $\{\Phi_1, \dots, \Phi_l\}$ has a zero weight in the integral. We should also note that in statistical mechanics it is possible to “embed” an ensemble with less intensive variables in an ensemble with more creating an "ensemble of ensembles". Then it is possible to express both entropy and the partition function as measures of a set of sets[9] an aspect that as mentioned is planned to be further elaborated in future work.

Finally, at thermodynamic equilibrium in the thermodynamic limit of large systems the equivalence of ensembles is well defined. Under this equivalence, the convergence for the expectation of the conjugate extensive or intensive variables reflects the relations between the first derivatives of the corresponding, to each ensemble, thermodynamic potential. On the other hand, the variances are different by construction, thus reflecting the relations of the second derivatives of the thermodynamic potentials under the constraints of each ensemble (i.e. the variance of the energy is by construction zero on an *NVE* ensemble and nonzero in an *NVT* ensemble). It will be shown that the variances of the conjugate extensive variables are an essential tool in the proposed representation, since they construct a base for the proposed tangent space.

The proposed geometrical representation of equilibrium and near equilibrium statistical ensembles.

The EROPHILE representation has been based [9] on two transformations that map probabilities and observables in vectors that span the same Euclidian space equipped with an Euclidian inner product operation.

Within the initial EROPHILE representation, any macroscopic "thermodynamic state" is realized as an ensemble of discrete set of n states. In the example given in the initial work on EROPHILE each state corresponded to "an inherent structure" i.e. local potential energy minima, of atomistic atactic Polyethylene (aPE) in the glassy state. Each ensemble is characterized by a probability vector $\boldsymbol{p} \equiv \{\ldots, p_i, \ldots, p_n\}$ whose components are the probabilities of observing each state *i* in the ensemble. For a memoryless stochastic system consisting of discrete states, the probability vector can be evaluated given an initial condition and the elements of a transition matrix that govern the transitions between states. In dynamical systems consisting of discrete states with memoryless stochastic transitions the dynamical evolution of this vector is expressed in the form of a master equation Eq (4) . The solution of such a master equation can be expressed in the general form of Eq (5) as a function of the rate matrix $\bar{\bar{\boldsymbol{K}}}$ whose elements are constants for the case of memoryless transitions. Similarly, in the more general case of a stochastic Markovian system a similar solution can be expressed in terms of the transition matrix $\bar{\bar{\boldsymbol{\Pi}}}$ of the process [20, 21].

$$\frac{d\boldsymbol{p}_{(t)}}{dt} = \overline{\overline{\boldsymbol{K}}}\boldsymbol{p}_{(t)} \quad (4)$$

$$\boldsymbol{p}_{(\tau)} = e^{\overline{\overline{\boldsymbol{K}}}\tau}\boldsymbol{p}_{(t=0)} \quad (5)$$

$$\boldsymbol{p}_{(s)} = \overline{\overline{\boldsymbol{\Pi}}}^{s}\boldsymbol{p}_{(0)} \quad (6)$$

For Markovian systems it is quite convenient to express such solutions in the form of an eigenvalue-eigenvector decomposition of the rate or the transition matrices.

Within the EROPHILE representation[9], the set of probabilities $\boldsymbol{p}$ is mapped on to an Euclidian vector $\widetilde{\boldsymbol{p}}$ via the transformation $\tilde{p}_{i,(t)} = p_{i,(t)} \big/ \sqrt{p_i^{\mathrm{eq}}}$, that can be written in a matrix or a bra-ket notation in the form of Eq (7) and has as a unique requirement the existence of positive $p_i^{\mathrm{eq}} > 0$ for all states of the ensemble. Furthermore, for stochastic systems with transitions that obey the balance condition, the equilibrium probabilities p_i^{eq} can be guaranteed to be the outcome of the evolution as time goes to infinity $p_i^{\mathrm{eq}} = p_{i,(t=\infty)}$.

$$\widetilde{\boldsymbol{p}}_{(t)} \equiv |\widetilde{\boldsymbol{p}}_{(t)}\rangle = \overline{\overline{\boldsymbol{M}}}^{-\mathbf{1}}|\boldsymbol{p}_{(t)}\rangle \quad (7)$$

where $\overline{\overline{\boldsymbol{M}}} = \begin{bmatrix} \sqrt{p_1^{\mathrm{eq}}} & 0 & 0 \\ 0 & \sqrt{p_i^{\mathrm{eq}}} & 0 \\ 0 & 0 & \sqrt{p_n^{\mathrm{eq}}} \end{bmatrix}$ is a diagonal n x n matrix and $\overline{\overline{\boldsymbol{M}}}^{-\mathbf{1}}$ its inverse. It is important to note at this point that the requirement for the invertibility of $\overline{\overline{\boldsymbol{M}}}$ should be further investigated at the conditions of phase equilibrium or in cases where one of the extensive variables of the ensemble has been changed.

Based on this transformation of Eq (7) the master equation can be written [9] in the form :

$$\frac{d|\widetilde{\boldsymbol{p}}_{(t)}\rangle}{dt} = \overline{\overline{\overline{\boldsymbol{K}}}}|\widetilde{\boldsymbol{p}}_{(t)}\rangle \quad (8)$$

where $\overline{\overline{\overline{\boldsymbol{K}}}} = \overline{\overline{\boldsymbol{M}}}^{-\mathbf{1}}\overline{\overline{\boldsymbol{K}}}\,\overline{\overline{\boldsymbol{M}}}$. As a result, the $\overline{\overline{\overline{\boldsymbol{K}}}}$ is symmetric and has the same set of real eigenvalues as $\overline{\overline{\boldsymbol{K}}}$. Furthermore, the left end right eigenvectors of $\overline{\overline{\boldsymbol{K}}}$ can be evaluated from the eigenvectors of $\overline{\overline{\overline{\boldsymbol{K}}}}$. The transformation of the probabilities in the form of Eq (7) is a similarity transformation that also serves as a procedure that provides stability in the numerical solution of the eigenvector problem for systems whose dynamics can be described by the master equation (Eq (4)) when the rate constants obey the detailed balance conditions.

Although the initial casting of the EROPHILE representation was developed in an effort to understand the dynamics of relaxation experiments, what is of essence in this work is not the actual dynamics or even the evolutionary properties of the stochastic systems but rather the existence of a stationary equilibrium distribution indicating that the proposed representation is generally applicable in all cases that $\bar{\bar{\boldsymbol{M}}}$ is invertible.

The novelty of the initial EROPHILE representation was mainly due to the second proposed transformation, namely that observables can be transformed in to Euclidian vectors that span the same Euclidian space as the eigenvectors of a properly symmetrized rate matrix. More precisely, for any observable X that has a unique value for each state i of the ensemble the macroscopic thermodynamic quantity is estimated from the average value over the ensemble in the form of Eq (9) that results in Eq (10) in the case of thermodynamic equilibrium. For example, observable X_i can be the total Energy E_i, the Volume V_i, the number of molecules N_i or even any other property whose value is uniquely set for each microstate like the virial contribution to the pressure from each microstate.

$$\langle X \rangle_t = \sum p_{i,(t)} x_\iota \quad (9)$$

$$\langle X \rangle_{\mathrm{eq}} = \sum \quad p_{i,(\infty)} x_\iota = \sum \quad p_i^{\mathrm{eq}} x_\iota \quad (10)$$

In the EROPHILE representation the array of those x_ι values are transformed in Euclidean vectors $\widetilde{\boldsymbol{x}}$ via the map $x_i \rightarrow \tilde{x}_i = x_i \sqrt{p_i^{\mathrm{eq}}}$ that results in expressing the estimation of ensemble averages as inner products. In a vector-matrix notation where observables are written as row vectors (bra-)and probabilities as column vectors (ket-) the transformation and the expectation values can be expressed in the form of Eqs (11)-(13).

$$\widetilde{\boldsymbol{x}} \equiv \langle \widetilde{\boldsymbol{x}} | = \boldsymbol{x} \bar{\bar{\boldsymbol{M}}} \qquad (11)$$

$$\langle X \rangle_{(t)} = \boldsymbol{x} \bar{\bar{\boldsymbol{M}}} \bar{\bar{\boldsymbol{M}}}^{-1} \boldsymbol{p}_{(t)} = \widetilde{\boldsymbol{x}} \bullet \widetilde{\boldsymbol{p}}_{(t)} \equiv \langle \widetilde{\boldsymbol{x}} | | \widetilde{\boldsymbol{p}}_{(t)} \rangle \qquad (12)$$

$$\langle X \rangle_{eq} = \widetilde{\boldsymbol{x}} \bullet \widetilde{\boldsymbol{p}}^{\mathrm{eq}} \equiv \langle \widetilde{\boldsymbol{x}} | | \widetilde{\boldsymbol{p}}^{\mathrm{eq}} \rangle \quad (13)$$

Note that it is also possible to express the Euclidian observable $\widetilde{\boldsymbol{x}}$ as the product of $\langle \widetilde{\boldsymbol{p}}^{\mathrm{eq}} |$ with a diagonal matrix $\bar{\bar{\mathbf{X}}}$ (who’s diagonal elements are $\bar{\bar{X}}_{ii} = x_i$) if one would like to make a link of the proposed representation to that Dirac [22] and von Neumann [23] formulation of Quantum Mechanics in the form of metrics.

From Eq (13) it can be seen that the expectation values of thermodynamic state properties at equilibrium (like energy, temperature, pressure, volume, but also free energy [24-26] and entropy) correspond to a projection (i.e. inner products) on the equilibrium vector (i.e. the normal to the tangent plane vector). In this work, the bra-ket notation is introduced in order to provide a common framework for both the finite discrete and the continuous vector spaces.

Similarly, variances and autocorrelations at equilibrium can be viewed again as projections. In those quantities, the part that is normal to the tangent plane has been projected out. As a result, variances and autocorrelations can be expressed as a linear combination of the vector base that spans the tangent plane.

$$\langle (X-\langle X\rangle)^2\rangle_{\mathrm{eq}} = \left(\langle \widetilde{\boldsymbol{x}}| - \left(\langle \widetilde{\boldsymbol{x}}||\widetilde{\boldsymbol{p}}^{\mathrm{eq}}\rangle\right)\langle \widetilde{\boldsymbol{p}}^{\mathrm{eq}}|\right)^2 \quad (14)$$

Given a system of n microstates, a convenient base can be formed by the n eigenvectors $\widetilde{\boldsymbol{u}_h} \equiv \langle\widetilde{\boldsymbol{u}_h}| = |\widetilde{\boldsymbol{u}_h}\rangle$,(for *h*=0,n-1) of the symmetrized transition matrix, where one of them, will have to correspond to the equilibrium vector ($\widetilde{\boldsymbol{u}_0} \equiv \langle\widetilde{\boldsymbol{u}_0}| = |\widetilde{\boldsymbol{p}}^{\mathrm{eq}}\rangle$). Hopefully, even when it is not possible to solve the eigenvalue problem as in the original application [9, 11], it may still be possible to use other basis sets, or even try to construct basis sets (for example using Gram–Schmidt, Krylov or any other similar method).

In the initial work [9] on the EROPHILE it was shown that it is possible to use the eigenvalues λ_h and the eigenvectors of the symmetrized master equation in order to express both variances $\langle (X-\langle X\rangle)^2\rangle_{\mathrm{eq}}$ and autocorrelations ($\langle X_{t=0}X_{t=\tau}\rangle_{\mathrm{eq}} - \langle X \quad \rangle_{\mathrm{eq}}^2$) for any observable X, as shown in Eqs (15) and (16) respectively.

$$\langle (X-\langle X\rangle)^2\rangle_{\mathrm{eq}} = \sum_{h\neq 0} (\langle \widetilde{\boldsymbol{x}}||\widetilde{\boldsymbol{u}_h}\rangle)^2 \quad (15)$$

$$\langle X_{\mathrm{t=0}}X_{\mathrm{t=\tau}}\rangle_{\mathrm{eq}} - \langle X\rangle_{\mathrm{eq}}^2 = \sum_{\mathrm{h}\neq 0} (\langle \widetilde{\boldsymbol{x}}||\widetilde{\boldsymbol{u}_h}\rangle)^2 \mathrm{e}^{\lambda_h \tau} \quad (16)$$

This work is based on an important realization for the geometrical perspective of the transformation properties introduced in Eq (4) that comes in the form of the normalization condition of the probability distribution away and at equilibrium, and can be expressed as an inner product of vectors as shown in Eqs (17), (18).

$$1 = \widetilde{\boldsymbol{p}}^{\mathrm{eq}}_{(\boldsymbol{\theta},\boldsymbol{\Phi})} \bullet \widetilde{\boldsymbol{p}}^{\mathrm{eq}}_{(\boldsymbol{\theta},\boldsymbol{\Phi})} \equiv \left\langle \widetilde{\boldsymbol{p}}^{\mathrm{eq}}_{(\boldsymbol{\theta},\boldsymbol{\Phi})} \middle|\middle| \widetilde{\boldsymbol{p}}^{\mathrm{eq}}_{(\boldsymbol{\theta},\boldsymbol{\Phi})} \right\rangle \quad (17)$$

$$1 = \widetilde{\boldsymbol{p}}^{\mathrm{eq}}_{(\boldsymbol{\theta},\boldsymbol{\Phi})} \bullet \widetilde{\boldsymbol{p}}_{(\boldsymbol{\theta},\boldsymbol{\Phi})} \equiv \left\langle \widetilde{\boldsymbol{p}}^{\mathrm{eq}}_{(\boldsymbol{\theta},\boldsymbol{\Phi})} \middle|\middle| \widetilde{\boldsymbol{p}}_{(\boldsymbol{\theta},\boldsymbol{\Phi})} \right\rangle \quad (18)$$

Equations (15) and (16) imply that any possible realization of the ensemble out of equilibrium must lie on the hyperplane with normal unit vector the equilibrium vector $\widetilde{\boldsymbol{p}}^{\mathrm{eq}}_{(\boldsymbol{\theta},\boldsymbol{\Phi})}$. On the other hand, all equilibrium realizations characterized by the vectors $\widetilde{\boldsymbol{p}}^{\mathrm{eq}}_{(\boldsymbol{\theta},\boldsymbol{\Phi})}$ must lie on a hypersphere of radius 1. Amazingly, the only restriction is that the matrix $\bar{\bar{\boldsymbol{M}}}$ must be invertible and that the non-equilibrium ensemble should consist of microstates that have common values of the extensive variables of the ensemble $\boldsymbol{\Phi}$.

Another important realization is that the proposed transformation can be understood as a coordinate system transformation to an orthonormal base. The new base vectors are the “pure states” where the ensemble consists of a single state. The orthonormality property of the new coordinate system, implies that the covariant and contravariant space can be spanned by the same set of base vectors $\widetilde{\boldsymbol{e}_\iota} \equiv |e_i\rangle \equiv \left[0, \ldots, \quad \underbrace{,\sqrt{1},}_{i^{th}} \quad \ldots, 0\right]^T$, $\widetilde{\boldsymbol{e}^\iota} \equiv |e_i\rangle^T = \langle e_i|$ i.e. the orthogonality condition expressed as $\widetilde{\boldsymbol{e}_\iota} \bullet \widetilde{\boldsymbol{e}_J} = \widetilde{\boldsymbol{e}^\iota} \bullet \widetilde{\boldsymbol{e}^\iota} = \delta_{ij}$ (where δ_{ij} is the Dirac delta function that is unity, if the indexes are equal and zero otherwise).

In order to provide a visual example of the proposed representation, the normalizing conditions in the case of a 3-state toy system are presented for two cases. In Fig. 1a. for the case $\widetilde{\boldsymbol{p}}^{\mathrm{eq}} \equiv |\widetilde{\boldsymbol{p}}^{\mathrm{eq}}\rangle = \left\{\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}\right\}^T$, and in Fig. 1b for the case $\widetilde{\boldsymbol{p}}^{eq} \equiv |\widetilde{\boldsymbol{p}}^{\mathrm{eq}}\rangle = \left\{\sqrt{\frac{1}{6}}, \sqrt{\frac{2}{6}}, \sqrt{\frac{3}{6}}\right\}^T$.

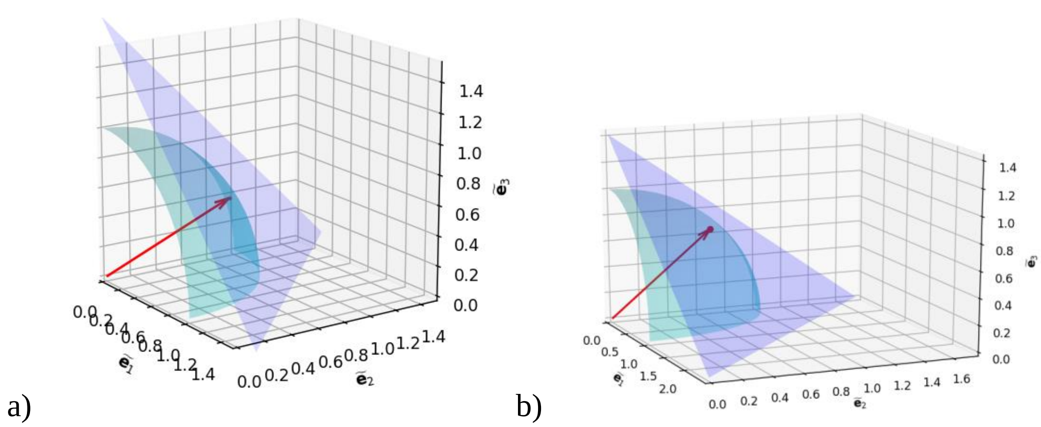

FIG. 1: A visual representation of the hypersurfaces of a toy 3-state system: All possible equilibrium states have to lie on the sphere of unit 1. Given specific thermodynamic conditions, $|\tilde{\boldsymbol{p}}^{\mathrm{eq}}\rangle$ specifies a single point , and the vectors that describe equilibrium and all non-equilibrium realizations $\tilde{\boldsymbol{p}} \equiv |\tilde{\boldsymbol{p}}\rangle$ have to line on the tangent plane at the given equilibrium vector $\vec{\tilde{p}}^{eq}$.a) The tangent plane at equilibrium state $\tilde{\boldsymbol{p}}^{\mathrm{eq}} \equiv |\tilde{\boldsymbol{p}}^{\mathrm{eq}}\rangle = \left\{\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}\right\}^T$, b) The tangent plane at equilibrium state $\tilde{\boldsymbol{p}}^{\mathrm{eq}} \equiv |\tilde{\boldsymbol{p}}^{\mathrm{eq}}\rangle = \left\{\sqrt{\frac{1}{6}}, \sqrt{\frac{2}{6}}, \sqrt{\frac{3}{6}}\right\}^T$ .As it is shown in the text, the manifold of spherical symmetry can be viewed as the Gauss map of both the constrain $\tilde{\boldsymbol{p}}^{\mathrm{eq}} \bullet \tilde{\boldsymbol{p}}^{\mathrm{eq}}$ and of the parametric hypersurface of equilibrium free energy (times -$k_{\mathrm{B}}T$) in a orthonormal coordinate system span by "pure state" ensembles $|e_i\rangle$. By virtue of the Gauss map the tangent hyper planes in this figure are also tangent hyper planes to the parametric curve at each equilibrium point.

By assigning a value in each of the 3-states for an observable X ($\boldsymbol{x} = \{2,1,0\}$) in our 3-state toy system at equilibrium state $|\tilde{\boldsymbol{p}}^{\mathrm{eq}}\rangle = \left\{\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}\right\}^{\mathrm{T}}$ as presented in Fig. 1a, it is possible to provide the visual representation of the Euclidian vectors that are involved in the estimation of the expectation value and the variance of the observable (Fig. 2). The original "constant field" $\boldsymbol{x} = \{2,1,0\}$ is first mapped on to $\tilde{\boldsymbol{x}} \equiv \langle\tilde{\boldsymbol{x}}| = \left\{\frac{1}{\sqrt{3}}2, \frac{1}{\sqrt{3}}1, \frac{1}{\sqrt{3}}0\right\}$ for that equilibrium point. The normal and in plane projections of this Euclidian vector measures the equilibrium average and variance as dictated by Eqs (11) and (12). Note that the magnitude of $\langle\tilde{\boldsymbol{x}}| - \left(\langle\tilde{\boldsymbol{x}}||\tilde{\boldsymbol{p}}^{\mathrm{eq}}\rangle\right)\langle\tilde{\boldsymbol{p}}^{\mathrm{eq}}|$ is invariant to the addition of a constant in the original filed (i.e. if $\tilde{\boldsymbol{x}}$ represents the energy at each state, then the magnitude of the projection to the tangent plain does not depend on the reference energy value).

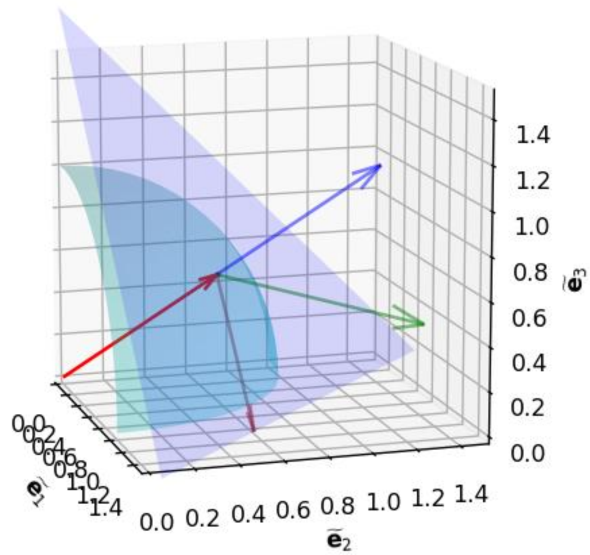

FIG. 2: A visual representation of the Euclidian vectors that represent averages and variances in a toy 3-state system at an equilibrium state $\widetilde{\boldsymbol{p}}^{\mathrm{eq}} \equiv |\widetilde{\boldsymbol{p}}^{\mathrm{eq}}\rangle = \left\{\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}\right\}^T$ The vectors, on and normal, to the tangent plane are $\left(\langle\widetilde{\boldsymbol{x}}|\left|\widetilde{\boldsymbol{p}}^{\mathrm{eq}}\right\rangle\right)\langle\widetilde{\boldsymbol{p}}^{\mathrm{eq}}|$ and $\langle\widetilde{\boldsymbol{x}}| - \left(\langle\widetilde{\boldsymbol{x}}|\left|\widetilde{\boldsymbol{p}}^{\mathrm{eq}}\right\rangle\right)\langle\widetilde{\boldsymbol{p}}^{\mathrm{eq}}|$ and represent the average and the variance of an observable $\boldsymbol{x} = \{2,1,0\}$ that is mapped to the Euclidian vector $\widetilde{\boldsymbol{x}} \equiv \langle\widetilde{\boldsymbol{x}}| = \left\{\frac{1}{\sqrt{3}}2, \frac{1}{\sqrt{3}}1, \frac{1}{\sqrt{3}}0\right\}$ for the given equilibrium point.

EROPHILE as inner product in a bra-ket formulation

In the language of differential geometry, the transformations of Eq (7) and (11) imply a covariant and a contravariant relation between dual vector spaces. If those vectors are real (as it is assumed in this work) this transformation is expected to be also homomorphic.

In order to extend the EROPHILE approach to the statistical ensembles of microstates used in statistical mechanics, a general framework for the inner product will be attempted in two ways, an informal (for conceptual reasons) and a formal based on the bra-ket formalism.

In the informal approach, a classical statistical ensemble is defined over a microstate that are points in a multidimensional hypervolume defined by the positions and the velocities of all atoms. It is well known from the application of molecular simulation that the sampling of such space can be handled as a vector matrix multiplication procedure simply by replacing the discrete probability P_i with $P_i d\xi$ where $d\xi$ is the infinitesimal volume element. Since in this work we are dealing with cases where dv is constant it follows that treating classical ensembles using a vector representation is a valid approach. Furthermore in molecular simulation it is common to group a set of microstates and performed Monte Carlo simulations by introducing transition matrixes of the form of Eq. (6) between those ensemble of microstates. Such example is the Monte Carlo simulations in the canonical ensemble. Whereas a microstate is unequally defined by the values of both the positions and the momentum of all atoms in Monte Carlo simulations we «ignore» the momentum space and perform simulations only in the configurational space. The idea behind that is that we can integrate over the momentum space and that will result in a constant contribution to the Boltzmann weight in all configurations that will eventually trop out since the probabilities are normalized and will appear only as an additive constant in the entropy and the free energies. In a simplified language, the probability of being in a microstate i ($P_i \mathrm{d}\xi$) is being expressed as $p_i \rho dv$ where the index i now runs on all possible configurations and ρ includes the integration over the momentum space. As a conscience the term "microstate" has a more general use. In the proposed geometrical representation we can follow the same approach as in Monte Carlo and incorporate the constant contributions to the Boltzmann weight in to the "infinitesimal volume" $\mathrm{d}\xi$ of the EROPHILE space. Finally, we know from our work[27] on reaching ensemble averages in Monte Carlo that it is possible to estimate the equilibrium ensembles by linking "microstates" via alternative "ghost" Markovian Webs. That is, to take configurations from a Molecular Dynamics trajectory and perform "ghost" Monte Carlo Moves by attempting a transition to nearby configuration that may lead to significant enrichment of the ensemble average. Based on this work [27] we know that it is possible to introduce a base of vectors in the equilibrium tangent space by introducing any valid "ghost" Markovian Webs even where the actual dynamics are unknown.

The formal extension is based on the definition of the inner product as a Lebasque integral, as introduced by Brody and Rivier in their approach [4] to link parametric statistics with the Riemannian formalism of Rupinder's approach to statistical fluctuations, and the bra-ket formalisms of measurable vector spaces that have been extensively used in the proof of the quasi ergodic hypothesis by von Neumann [28] and on the foundation of quantum mechanics by Dirac. In this work we will use those notions slightly different, adjusted for systems where an underlying stochastic process with transition that obey detailed balance can be assumed, allowing us to restrict our self's in a Hilbert space of real functions due to the symmetries imposed by the condition of detailed balance. Therefore, we will need to utilize the formalism of inner product only in real vector spaces resulting in the general from of Eq (19).

$$\langle f||g\rangle \equiv \int f^* * g\,\mathrm{d}\xi \underbrace{=}_{f,g\,real} \int f * g\,\mathrm{d}\xi = \int f * g * \rho \mathrm{d}v \quad (19)$$

where in the Lebasque integral of Eq (19) ξ (in $\mathrm{d}\xi = \rho \mathrm{d}v$) is the measure of the points in the supporting space. In the equilibrium microstate representation of statistical mechanics, $\mathrm{d}v$ is the "infinitesimal volume" that eventually relates to the reference ideal gas state and ρ is the constant contribution to the "microstates". Note that that ρ has to be consistent with the values of the extensive parameters of the ensemble or zero otherwise. If v is not expressed as a function of the cartesian coordinates and conjugate momentum of the atoms, then ρ also incorporates the Jacobian of the transformation. In general, $\rho \mathrm{d}v$ is expected to be a measure of the cardinality of the infinitesimal volume elements of the integral in the definition of the partition functions. In this work, $\rho \mathrm{d}v$ is consider a constant for all microstates that belong to the ensemble and zero for all other microstates that do not fulfil the hard constraints imposed by the values of the extensive variables of the ensemble $\boldsymbol{\Phi}$: $\{\Phi_1, \ldots, \Phi_l,\}$.

It should be noticed that in the present work it could have been chosen to avoid dealing explicitly with the infinitesimal measure ($\mathrm{d}\xi = \rho dv$) of the supporting space of the microstate since it remains constant upon changing the intensive parameters of a statistical ensemble (i.e. the type of changes that we investigate in this work). However, it is included in the description due to its expected importance in extending the representation in cases where such a condition is no longer valid, for example in a system where dissipation can be attributed to the contraction of phase space. Similarly, the change in the volume of the supporting space is expected to be of significant importance in cases where the extensive variables are to be changed. Although such changes are not dealt with in this work due to the known equivalence of ensembles, we expect that many of the geometrical aspects described herein can be extended in processes that change the values of the average of the conjugate extensive variables instead of changing the intensive variables. One way to do this is to follow the approaches that has been proposed [7] in the content of the Ruppeiner [29] and the Weinhold [30, 31] geometries. Finally, it should be stated that the use of complex eigenfunctions will become essential in studying the dynamical response of systems where the time evolution operator has complex eigenfunctions as in the case of the full Liouville operator of molecular dynamics. Another reason that the inner product should retain the complex conjugate nature is the inability of expressing the ensemble as the result of an underline stochastic process with the property of detailed balance, due to the fact that the necessary and sufficient condition for the existence of an equilibrium ensemble is the condition of balance and not that of a detailed balance (that is a sufficient but not a necessary condition).

The proposed Euclidian representation of statistical mechanics

As in the case of the equilibrium thermodynamic states, it is proposed that macroscopic thermodynamic states away from equilibrium can also be represented via an ensemble. Those non-equilibrium ensembles are also characterised by a set of extensive and a set of intensive variables along with the probability of observing the system in each microstate consistent with the constrains imposed by the values of the extensive variables of the ensemble. The difference between equilibrium and non-equilibrium ensembles is the uniqueness of the equilibrium distribution. The equilibrium distribution is uniquely determined as the result of maximization of the entropy under the given constraints on the average values of the extensive variables $\boldsymbol{X}$ conjugate to the intensive parameters $\boldsymbol{\theta}$ of the ensemble. In a non-equilibrium distribution, the probability of observing the system in a microstate can have any value provided that this microstate is consistent with the values of the remaining extensive variables of the ensemble $\boldsymbol{\Phi}$.

The objective is to provide a geometrical representation of such a non-equilibrium ensemble casted as the combination of a manifold of spherical symmetry and its tangent space bundle, consistent to the approach we have proposed for the representation of glassy dynamics (EROPHILE).

In Chart 1 we present a schematic of the proposed map of such statistical mechanics ensembles on to points in a Euclidian space characterized by a triplet : $\left(\mathrm{d}\xi, |\widetilde{\boldsymbol{p}}^{\mathrm{eq}}\rangle, |\widetilde{\boldsymbol{p}}\rangle - |\widetilde{\boldsymbol{p}}^{\mathrm{eq}}\rangle\right)$ i.e. The "volume" of the points $d\mu$, the Euclidian vector at equilibrium $|\widetilde{\boldsymbol{p}}^{\mathrm{eq}}\rangle$ that spans a hypersphere and a Euclidian vector $|\widetilde{\boldsymbol{p}}\rangle - |\widetilde{\boldsymbol{p}}^{\mathrm{eq}}\rangle$ that measures the deviation from equilibrium and belongs to the tangent space of the hypersphere at that equilibrium point.

Upon the proposed mapping all the thermodynamic equilibrium states that correspond to the same values for the extensive ($\boldsymbol{\Phi}$) and different values for the intensive variables ($\boldsymbol{\varphi}$), lie in a sub manifold of a hypersphere of radius 1. The dimensionality of this submanifold is equal to the number of the intensive variables. The points in the tangent space bundle of this submanifold represent all possible realizations of the macroscopic system that are consistent with the constraints imposed by the extensive variables of the ensemble. Each point in the tangent bundle is represented by a tuple of two vectors, the vector that points at the equilibrium condition on the submanifold and a vector on the tangent space that represents the displacement from equilibrium. In order to provide a physical interpretation of our approach two extreme limiting cases are considered, for starting from an equilibrium state and changing the values of the ensemble intensive variables $\vec{\varphi}$ (and therefore $\boldsymbol{\theta_{\varphi}}$): a) quasi statically (and reversibly) and b) infinitely fast (irreversible). In both cases, the physical meaning of the change in the values of the intensive variables corresponds to changes on the environment that is in contact with the system for example a change of the temperature of the thermostat or the pressure of the barostat. In the limit that this change is made gradually with infinitely slow rate at infinite number of steps, the process is reversible and at any given time the system is in equilibrium with its environment and the intensive properties $\boldsymbol{\theta_{\varphi}}$ of the system are equal to the corresponding intensive properties of the environment. On the other hand, if the intensive properties of the environment are to be changed abruptly from an initial value to a new value for a system that was initially in equilibrium the resulting process will be an irreversible process and the second law of thermodynamics will be expressed as an inequality.

Gibbs equilibrium statistics: m, Macroscopic Thermodynamic conditions leads to l, hard constrained extensive ensemble variables $\boldsymbol{\Phi} = \{\Phi_1, \dots, \Phi_l\}$ and m-l, soft constraints expressed via m-l functions $\boldsymbol{\theta} = \{\dots, \theta_k, ..\}$ of conjugate intensive ensemble variables $\{\dots, \varphi_k, ..\}$. Entropy maximization under those constrains of leads to the

$$\underbrace{\{\Phi_1, \dots, \Phi_l\}}_{Extensive}, \underbrace{\{\dots, \varphi_k, ..\}}_{intensive} \to \; p^{\mathrm{eq}}_{i,(\boldsymbol{\Phi},\boldsymbol{\theta}_{\boldsymbol{\varphi}})}\mathrm{d}\xi$$

Equilibrium distribution for each microstate $p^{\mathrm{eq}}_{i,(\boldsymbol{\Phi},\boldsymbol{\theta}_{\boldsymbol{\varphi}})}\mathrm{d}\xi$ i.e. the probability for each microstate consistent with the ensemble constrains.

Euclidian Representation of Observables and Probabilities in a HIgh-dimensionaL vEctor space. Each point the EROPHILE space is describe by $\mathrm{d}\xi, |\widetilde{\mathbf{p}}^{\mathrm{eq}}_{\square}\rangle, |\widetilde{\mathbf{p}}\rangle$ (i.e. "the size of the point", the vector that point in the hypersphere of equilibrium states (with same $\boldsymbol{\Phi}$ but different $\boldsymbol{\varphi}$), the vector on the tangent bundle) :

$$\{\Phi_1, \dots, \Phi_l\}, \{\dots, \theta_k, ..\}, p^{\mathrm{eq}}_{i,(\boldsymbol{\Phi},\boldsymbol{\theta}_{\boldsymbol{\varphi}})}\mathrm{d}\xi \to$$

$$\left(\mathrm{d}\xi, \sqrt{p^{\mathrm{eq}}_{i,(\boldsymbol{\Phi},\boldsymbol{\theta}_{\boldsymbol{\varphi}})}}, \frac{p^{\square}_{i,(\boldsymbol{\Phi},\boldsymbol{\theta}_{\boldsymbol{\varphi}})} - p^{\mathrm{eq}}_{i,(\boldsymbol{\Phi},\boldsymbol{\theta}_{\boldsymbol{\varphi}})}}{\sqrt{p^{\mathrm{eq}}_{i,(\boldsymbol{\Phi},\boldsymbol{\theta}_{\boldsymbol{\varphi}})}}}\right) \equiv$$

$$\left(\mathrm{d}\xi, |\widetilde{\boldsymbol{p}}^{\mathrm{eq}}_{\square}\rangle, |\widetilde{\boldsymbol{p}}\rangle - |\widetilde{\boldsymbol{p}}^{\mathrm{eq}}_{\square}\rangle\right)$$

CHART 1. The essential steps of the proposed geometrical representation of equilibrium and near equilibrium statistical ensembles in respect to the Gibbs approach of statistical ensembles.

In Fig. 3 we depict the locus of the equilibrium points that corresponds in changing one intensive variable (temperature) in our toy 3-state representation of a canonical ensemble.

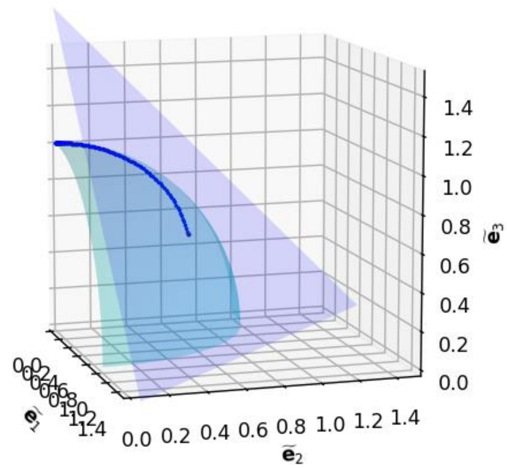

FIG. 3 : The locus of the equilibrium points that corresponds in changing one intensive variable (Temperature) in our toy 3-state representation of a canonical ensemble. (see text for more details). The vector and the normal plane correspond to infinite temperature whereas the other side of the curve end up at zero temperature.

In this 3 state toy system the equilibrium probability of each of the 3-states is $p_{i,(\boldsymbol{\theta},\boldsymbol{\Phi})}^{\mathrm{eq}} \mathrm{d}v = \frac{e^{\boldsymbol{\theta} \boldsymbol{X}_i dv}}{\sum_{i=1}^{3} e^{\boldsymbol{\theta} \boldsymbol{X}_i dv}}$ (i.e $\boldsymbol{\theta}\ is\ \left\{{-1}/{k_b T}\right\}$ and $\boldsymbol{X}_i\ is\ \{E_i\}$) with $\{E_1, E_2, E_3\} = \{0, -1, -2\}$.

In the limit of infinite temperature all 3 microstates have equal probability of being observed where at the limit of zero temperature only the one with the lowest energy is observed. Changing the Temperature in a reversible way corresponds in moving along the hypersurface of the spherical symmetry along the vector $\frac{d|\widetilde{\boldsymbol{p}}^{\mathrm{eq}}\rangle}{dT} = \frac{d\theta_1}{dT}\frac{d|\widetilde{\boldsymbol{p}}^{\mathrm{eq}}\rangle}{d\theta_1}$ where it can be easily shown that $\frac{d|\widetilde{\boldsymbol{p}}^{\mathrm{eq}}\rangle}{d\theta_1} = \frac{1}{2}\langle\widetilde{\boldsymbol{E}}| - \left(\langle\widetilde{\boldsymbol{E}}||\widetilde{\boldsymbol{p}}^{\mathrm{eq}}\rangle\right)\langle\widetilde{\boldsymbol{p}}^{\mathrm{eq}}|$ i.e. is a vector that lies on the tangent plane (since $\frac{d|\widetilde{\boldsymbol{p}}^{\mathrm{eq}}\rangle}{d\theta_1} \bullet |\widetilde{\boldsymbol{p}}^{\mathrm{eq}}\rangle = 0$). In the case that the ensemble has more than one intensive variables the directional derivatives can be represented as Euclidian vectors of the form of Eq. (20) that are the half of the Euclidian vectors whose norm is a variance of the conjugate extensive variable $\boldsymbol{X}_a$. Note that $\frac{d|\widetilde{\boldsymbol{p}}^{\mathrm{eq}}\rangle}{d\theta_a}$ are vectors that lie on the tangent plane by construction (since $\frac{d|\widetilde{\boldsymbol{p}}^{\mathrm{eq}}\rangle}{d\theta_a} \bullet |\widetilde{\boldsymbol{p}}^{\mathrm{eq}}\rangle = 0$). Another important direct consequence of the transformation is that the second derivative of the partition function 's logarithm $ln\Psi_{\boldsymbol{\Phi},\boldsymbol{\theta}}$ with respect to the intensive variables can be represented as a Euclidian vector as shown in Eq (21).

$$\left.\frac{d|\widetilde{\boldsymbol{p}}^{\text{eq}}\rangle}{d\theta_a}\right|_{\boldsymbol{\Phi},\boldsymbol{\theta}_{b\neq a}} = \frac{1}{2}\langle\widetilde{\boldsymbol{X}_a}| - \left(\langle\widetilde{\boldsymbol{X}_a}||\widetilde{\boldsymbol{p}}^{\text{eq}}\rangle\right)\langle\widetilde{\boldsymbol{p}}^{\text{eq}}| \qquad (20)$$

$$\left.\frac{d|\widetilde{\boldsymbol{p}}^{\text{eq}}\rangle}{d\theta_a}\right|_{\boldsymbol{\Phi},\boldsymbol{\theta}_{b\neq a}} \bullet \left.\frac{d|\widetilde{\boldsymbol{p}}^{\text{eq}}\rangle}{d\theta_a}\right|_{\boldsymbol{\Phi},\boldsymbol{\theta}_{b\neq a}} = \frac{1}{4}\langle\boldsymbol{X}_a - \langle\boldsymbol{X}_a\rangle\rangle^2 = \frac{1}{4}\left.\frac{d^2 ln\Psi_{\boldsymbol{\Phi},\boldsymbol{\theta}}}{d\theta_a^2}\right|_{\boldsymbol{\Phi},\boldsymbol{\theta}_{b\neq a}} \qquad (21)$$

The quasi-static process of changing the values of intensive variables depicted, in Fig. 3, can be understood as the limit of infinitely slow, reversible change and is essential in understanding reversible thermodynamics. On the other hand, the picture provided by the proposed representation is probably more useful in the case of the other limiting case, that of an infinitely fast change between two values of an intensive variable. As is shown in Fig. 4, changing the value of an intensive variable instantly moves the equilibrium vector from the old equilibrium point on the hypersphere to a new equilibrium point again on the hypersphere and along the submanifold of quasi-static changes depicted in Fig. 3. In the limit that the change is "instantaneous" the ensemble is mapped on a non-equilibrium point that now belongs in the tangent plane of the new equilibrium point. If the system is left to relax on the new conditions the system will move on this plane (due to the restriction of Eq (18)) independent of the nature of the dynamics. If the dynamics are of a Markovian nature then the movement in the plane can be easily modelled by the eigenvectors and the eigenvalues of the process[9]. If additionally the stochastic transitions also obey detailed balance then the proposed transformations leads to real eigenvalues and eigenvectors and all observables can be expressed as projections in the proposed Euclidian space[9]. If, on the other hand, the transitions do not obey detailed balance (i.e. the dynamics in microstate representation is expected to obey balance but not necessary detailed balance) the movement on the tangent plane will be characterised by the spectrum of the time evolution operator and its symmetries. This leads to a covariant and contravariant based complex vector, space spanned by the left and the write eigenvectors of the operator as in the case of quantum mechanical operators.

It is easy to see that by changing the values of the intensive variables of the ensemble from $\boldsymbol{\theta}^{\text{old}}$ to $\boldsymbol{\theta}^{\text{new}}$ in an "irreversible" way,(i.e. by changing only the environment) and requiring that the relative probabilities $|\boldsymbol{p}\rangle$ of observing a microstate in the ensemble of the system remain at their previous values, will lead in the transformation of Eq (22).

$$|\boldsymbol{p}\rangle = \overline{\overline{\boldsymbol{M}}}_{\boldsymbol{\theta}^{\text{old}}}\left|\widetilde{\boldsymbol{p}}^{\text{eq}}_{\boldsymbol{\theta}^{\text{old}}}\right\rangle = \overline{\overline{\boldsymbol{M}}}_{\boldsymbol{\theta}^{\text{new}}}\left|\widetilde{\boldsymbol{p}}_{\boldsymbol{\theta}^{\text{new}}}\right\rangle \rightarrow$$

$$\left|\widetilde{\boldsymbol{p}}_{\boldsymbol{\theta}^{\text{new}}}\right\rangle = \overline{\overline{\boldsymbol{M}}}^{-\mathbf{1}}_{\boldsymbol{\theta}^{\text{new}}}\overline{\overline{\boldsymbol{M}}}_{\boldsymbol{\theta}^{\text{old}}}\left|\widetilde{\boldsymbol{p}}^{\text{eq}}_{\boldsymbol{\theta}^{\text{old}}}\right\rangle = \overline{\overline{\boldsymbol{M}}}_{\boldsymbol{\theta}^{\text{old}}\rightarrow\boldsymbol{\theta}^{\text{new}}}\left|\widetilde{\boldsymbol{p}}^{\text{eq}}_{\boldsymbol{\theta}^{\text{old}}}\right\rangle \qquad (22)$$

where $\bar{\bar{\boldsymbol{M}}}_{\boldsymbol{\theta}^{\text{old}}\to\boldsymbol{\theta}^{\text{new}}} = \begin{bmatrix} \frac{\sqrt{p^{\text{eq}}_{1,\boldsymbol{\theta}^{\text{old}}}}}{\sqrt{p^{\text{eq}}_{1,\boldsymbol{\theta}^{\text{new}}}}} & 0 & 0 \\ 0 & \frac{\sqrt{p^{\text{eq}}_{i,\boldsymbol{\theta}^{\text{old}}}}}{\sqrt{p^{\text{eq}}_{i,\boldsymbol{\theta}^{\text{new}}}}} & 0 \\ 0 & 0 & \frac{\sqrt{p^{\text{eq}}_{n,\boldsymbol{\theta}^{\text{old}}}}}{\sqrt{p^{\text{eq}}_{n,\boldsymbol{\theta}^{\text{new}}}}} \end{bmatrix}$ is a diagonal n x n matrix. Our choice to investigate a change of the intensive variables of the ensemble away from conditions of phase transitions, guarantees that $\bar{\bar{\boldsymbol{M}}}_{\boldsymbol{\theta}^{\text{old}}\to\boldsymbol{\theta}^{\text{new}}}$ has an non zero determinant and is therefore invertible with $\bar{\bar{\boldsymbol{M}}}_{\boldsymbol{\theta}^{\text{new}}\to\boldsymbol{\theta}^{\text{old}}} = \bar{\bar{\boldsymbol{M}}}^{-\mathbf{1}}_{\boldsymbol{\theta}^{\text{old}}\to\boldsymbol{\theta}^{\text{new}}}$.

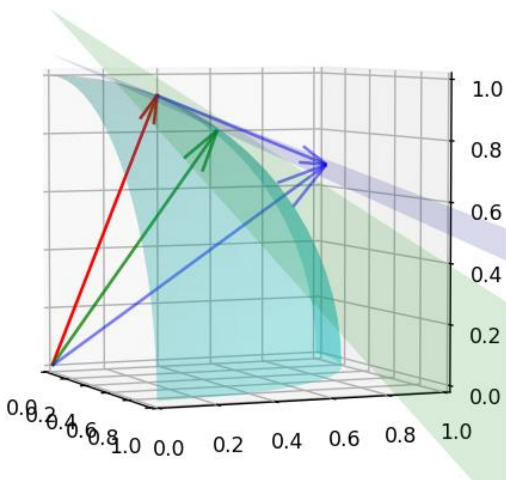

FIG. 4: A geometrical representation of a non-equilibrium change that is the result of changing the value of an intensive variable (e.g. Temperature). Upon an “irreversible adiabatic” change of the intensive variable an equilibrium point that was initially a point in the hypersphere is mapped on to the tangent plane of the new equilibrium state and the new non-equilibrium state is represented by: the measure of the supporting space, the equilibrium vector at the new conditions, and a vector on the tangent space that measures the displacement from the equilibrium $(d\xi, |\widetilde{\boldsymbol{p}}^{\text{eq}}\rangle, |\widetilde{\boldsymbol{p}}\rangle - |\widetilde{\boldsymbol{p}}^{\text{eq}}\rangle)$.

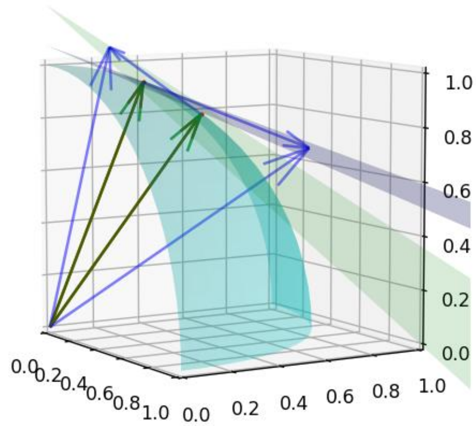

FIG. 5: Schemetic representation of the effect of $\bar{\bar{\boldsymbol{M}}}_{\boldsymbol{\theta}^{\text{old}}\to\boldsymbol{\theta}^{\text{new}}}$ *and* $\bar{\bar{\boldsymbol{M}}}_{\boldsymbol{\theta}^{\text{new}}\to\boldsymbol{\theta}^{\text{old}}}$ on the equiibrium vectors $\left|\widetilde{\boldsymbol{p}}^{\text{eq}}_{\boldsymbol{\theta}^{\text{old}}}\right\rangle$ and $\left|\widetilde{\boldsymbol{p}}^{\text{eq}}_{\boldsymbol{\theta}^{\text{new}}}\right\rangle$ respectively.

Note that as shown in Fig. 5 and as expected, the non-equilibrium mapping of going from one state to the other is not symmetrical. The length of the in plane displacement from equilibrium $\left(\text{i.e. of the Euclidian norm } ||\widetilde{\boldsymbol{p}}\rangle - |\widetilde{\boldsymbol{p}}^{\text{eq}}\rangle|\right)$ due to its relation to the “information content”[10] is a measure of the irreversibility introduced by each sudden change of the intensive variables, irrespective of the path that the dynamics return the system to equilibrium, as is has been shown for the information content . The “information content”[10] in k_{B} units is the K-L divergence of the non-equilibrium distribution p relative the new equilibrium p_{eq} ::: $D_{KL}(p \ \ |p_{\text{eq}}) = \int \ p \ \ \ln\left(\frac{p}{p_{\text{eq}}}\right) d\xi$. The K-L divergence has been recognized as a very important quantity in non-equlibrium statistical mechanics[6, 10], (i.e. a measure of irreversibility) since it accounts for the total change in entropy of both the system and its environment when the system is relaxed to a new equilibrium state characterized by p_{eq} form a non-equilibrium state characterised by a probability distribution p . In appendix B we summarize the main steps that have been used to link[6, 10] the $D_{KL}(p \ \ |p_{\text{eq}})$ to the second law of thermodynamics mainly for reasons of clarity. Amazingly, for small deviations from equilibrium the information content and therefore the manifestation of the irreversibility as the increase of the total entropy (the entropy of the system plus the entropy of the environment) is a linear function of the square of the Euclidian distance $\left(\text{i.e. of the Euclidian norm } ||\widetilde{\boldsymbol{p}}\rangle - |\widetilde{\boldsymbol{p}}^{\text{eq}}\rangle|\right)$ on our tangent hyperplains, and the actual dynamics do not play any role in the amount of total entropy increase. At significant deviations from equilibrium the amount of irreversible total entropy increase is a nonlinear but still monotonic function of the Euclidian distance on our tangent hyperplanes and is again independent of the path that returns the system to equilibrium. Obviously, although the change of the total entropy does not depend on the path, the entropy production rate does depend on the dynamics.

Finally, a connection of the proposed Euclidian representation with the notions of thermodynamic length and the Riemannian metric representation proposed by the work of Weinhold and Ruppineer, along with a link to the equivalent statistical measure as it has been realized by a series of relevant works [4, 6, 7, 10], is provided. As it has been shown in these works [4, 6, 7, 10], the main tool in order to derive a proper metric in statistics is the K-L divergence [32] and the Fisher information matrix. In the field of differential geometry [8, 33, 34], the K-L divergence provides a tool for defining a metric for probabilities, i.e. a semidefinite measure of how "far" one distribution is from another distribution, but it also provides a physical measure of irreversibility and the second law of thermodynamics. Before using the K-L divergence as a tool to link our parametric representation of statistical mechanics to the work of Weinhold and Ruppineer, we should also mention some important differences in our approach. In this work we deal with changes on the intensive variables of a statistical ensemble whereas the works of Weinhold and Ruppineer, have been based on the extensive representations of the macroscopic and statistical thermodynamics, expressing either the entropy or the energy as a function of extensive variables. The proposed work hints at a Gauss approach on the parametric representation of hypersurfaces whereas Weinhold and Ruppineer approach is based on the Riemannian view point. Nevertheless given that the Riemann and Gauss representations agree, we expect that the same "equivalence" can be established in our case too. Several works have shown that not only the two representations are equivalent but that it is possible to connect the matrix of the second derivatives in respect to the extensive variables to include intensive variables too [7]. Therefore, the link has to be the Riemannian metric that measures "thermodynamic lengths" and coincides with the Fisher information metric that is based on the derivation of the K-L divergence. The K-L divergence, although it is not a distance as it is not symmetrical it is a very handy tool as it quantifies the difference between any two distributions $p^{(\mathrm{o})}$ and $p^{(\mathrm{n})}$ with the important property of being semi positive definite ($D_{KL}\left(p^{(\mathrm{n})}|\mathrm{p}^{(\mathrm{o})}\right) \geq 0$), and being zero only in the case that the two distributions are identical. The K-L divergence, finds numerous uses is in many fields: e.g. in inference statistics, information theory and information geometry [34]. As already mentioned, in terms of statistical mechanics it has been shown that it is strongly related to the second law of thermodynamics, to irreversibility and to the ability to produce work [6, 10].

In this work, the change of the K-L divergence is considered under two different types of displacements: i) one along the hypersphere of the equilibrium states and ii) along the tangent plane. The first type corresponds to quasi static processes of changing the values for the intensive variables of the ensemble, whereas the second corresponds to displacements from equilibrium. In this work we chose to use a minor modification to the notion of the Extended K-L Divergence [35] ($D_{EKL}\left(p^{(\mathrm{n})}|p^{(\mathrm{o})}\right)=\int p^{(\mathrm{n})}\ln\left(\frac{p^{(\mathrm{n})}}{p^{(\mathrm{o})}}\right)d\xi-\int p^{(\mathrm{n})}d\xi+\int p^{(\mathrm{o})}d\xi$), that is identical for most part to the original definition of K-L divergence ($D_{KL}\left(p^{(\mathrm{n})}|p^{(\mathrm{o})}\right)=\int \ p^{(\mathrm{n})}\ln\left(\frac{p^{(\mathrm{n})}}{p^{(\mathrm{o})}}\right)d\xi$) but it yields somehow more compact results when it is being differentiated, as it has been shown in the field of information geometry [35]. For most practical purposes of this work the reader can treat the two divergences as identical but it may useful to consider the extended Divergence in cases where an analogous geometrical representation needs extension in order to utilize the more general notions of divergences [35].

The basic building block of Weinhold geometry that turns out to be relevant to our approach, is the notion of a metric that results in the definition of a Thermodynamic length (L_{Weinhold}) given in the form of Eq (23).

$$L_{\mathrm{Weinhold}} = \int \sqrt{\sum_a \sum_b \frac{dX_a}{dt}\frac{d^2S_X}{dX_a dX_b}\frac{dX_b}{dt}}dt \qquad (23)$$

Equation (23) at a first glance expresses Weinhold’s thermodynamic length as a function of macroscopic extensive variables X_a. X_a in a typical one-component system represents extensive variables like the Energy, the volume and the number of particles, but from the work of Salamon, Nulton and Berry [7], it turns out that Weinhold thermodynamic distance (L_{Weinhold}) is equal to the statistical distance L_{SNB} .

$$L_{\mathrm{SNB}} = \int \sqrt{\sum_i \sum_j \frac{dp_i}{dt}\frac{d^2S_{Shannon}}{dp_i dp_j}\frac{dp_j}{dt}}dt \qquad (24)$$

Notably, the statistical distance can also be derived in the context of the informational geometry based on the metric g_{ab} introduced in the second order expansion of the KL-Divergence $D_{KL}\left(p_{\theta_0}|p_{\theta_0+\delta}\right)=\frac{1}{2}g_{ab}d\theta_{\mathrm{a}}\,d\theta_{\mathrm{b}}$, where $g_{ab}=\int p_{\theta_0}\left(\sum_a \sum_b \frac{\partial \ln(p_{\theta_0})}{\partial\theta_{\mathrm{a}}}\frac{\partial \ln(p_{\theta_0})}{\partial\theta_{\mathrm{b}}}\right)d\xi$ are the elements of the Fisher information matrix that is a metric tensor in the context of Riemannian geometry [4]. Therefore, statistical distance (and therefore thermodynamic length) can be understood as arclengths of a curve lying on a Riemannian manifold. Interestingly it is not the length of the curve but rather the "energy" of the curve that is of thermodynamic interest due to its relation with the actual relative entropy difference.

Our investigation reveals two type of distances:

- the arclength along the hypersphere of equilibrium thermodynamic states $L_{\mathrm{Eq-E\rho}}$
- the distance on a tangent plane $L_{\mathrm{NEq-E\rho}}$ of a system out of equilibrium

The arclength $L_{\mathrm{Eq-E\rho}}$ measures the length of the arc on the proposed unit hypersphere that links equilibrium distributions with one dimensional path. Since it is an one dimensional reversible path, it can be parametrized by a single variable (t) by expressing the ensemble parameters $\boldsymbol{\theta}$ as a function of t (i.e. $\boldsymbol{\theta}(t)$) . An example of such path is given in Fig. 3 where the locus of equilibrium states with different temperatures from infinity to zero are shown. Note that this arclength is invariant on the parametrization and that the arc is not necessary geodesic for an arbitrary process $\boldsymbol{\theta}(t)$.

On the other hand, $L_{\mathrm{NEq-E\rho}}$ measures the distance of a nonequilibrium point $\left|\boldsymbol{p}_{\boldsymbol{\theta}}\right\rangle$ from the corresponding equilibrium $\left|\widetilde{\boldsymbol{p}}_{\boldsymbol{\theta}}^{\mathrm{eq}}\right\rangle$ (i.e. the point on the hypersphere with the same values for all $\boldsymbol{\theta}$). This distance is the Euclidean norm of the $\left|\boldsymbol{p}_{\boldsymbol{\theta}}\right\rangle-\left|\widetilde{\boldsymbol{p}}_{\boldsymbol{\theta}}^{\mathrm{eq}}\right\rangle$ vector that lie on the tangent plane at $\left|\widetilde{\boldsymbol{p}}_{\boldsymbol{\theta}}^{\mathrm{eq}}\right\rangle$ and is a measure of irreversibility. It is also a monotonic function of the "information content" and the "potential work" as it is masseters via the K-L Divergence. Example of such distances are shown in in Figs 4-5.

The infinitesimal arclength $\mathrm{d}s_{\mathrm{Eq-E\rho}}$ along a parametric line curve embedded on the unit hypersphere where all equilibrium vectors $\left|\widetilde{\boldsymbol{p}}_{\boldsymbol{\theta}(t)}^{\mathrm{eq}}\right\rangle$ have to lie can be evaluated from the square root of the inner product of the tangent vector $\frac{d\left|\widetilde{\boldsymbol{p}}_{\boldsymbol{\theta}(t)}^{\mathrm{eq}}\right\rangle}{dt}$ in the from of Eq (25):

$$\mathrm{d}s_{\mathrm{Eq-E\rho}}=\sqrt{\frac{d\left|\widetilde{\boldsymbol{p}}_{\boldsymbol{\theta}(t)}^{\mathrm{eq}}\right\rangle}{dt}\bullet\frac{d\left|\widetilde{\boldsymbol{p}}_{\boldsymbol{\theta}(t)}^{\mathrm{eq}}\right\rangle}{dt}}\,\mathrm{d}t=\sqrt{\left(\sum_a\frac{\partial\left|\widetilde{\boldsymbol{p}}_{\boldsymbol{\theta}(t)}^{\mathrm{eq}}\right\rangle}{\partial\theta_\alpha}\frac{\partial\theta_\alpha}{\partial t}\right)\bullet\left(\sum_a\frac{\partial\left|\widetilde{\boldsymbol{p}}_{\boldsymbol{\theta}(t)}^{\mathrm{eq}}\right\rangle}{\partial\theta_\alpha}\frac{\partial\theta_\alpha}{\partial t}\right)}\,\mathrm{d}t=$$

$$\sqrt{\sum_a\sum_\beta\left(\frac{\partial\left|\widetilde{\boldsymbol{p}}_{\boldsymbol{\theta}(t)}^{\mathrm{eq}}\right\rangle}{\partial\theta_\alpha}\bullet\frac{\partial\left|\widetilde{\boldsymbol{p}}_{\boldsymbol{\theta}(t)}^{\mathrm{eq}}\right\rangle}{\partial\theta_\beta}\frac{\partial\theta_\alpha}{\partial t}\frac{\partial\theta_b}{\partial t}\right)}\,\mathrm{d}t \quad (25)$$

In terms of differential geometry Eq (25) is an expression of the infinitesimal arclength of a parametric surface as a function of the first fundamental form. Note that since this arclength is on a unit hypersphere (that is a Gauss map of another surface) the first and the second fundamental forms of the unit hypersphere are identical and that the arclength on a Gauss map is in fact integral over the curvature measured in rad. It is important to note that the tangent vectors of any parametric representation of statistical mechanics has to lie on the tangent bundle of hyperplanes on the proposed hypersphere tangent plane at $\left|\tilde{\boldsymbol{p}}^{\mathrm{eq}}_{\boldsymbol{\theta}(t)}\right\rangle$ and can be written as a function of a base formed from the vectors $\frac{\partial\left|\tilde{\boldsymbol{p}}^{\mathrm{eq}}_{\boldsymbol{\theta}(t)}\right\rangle}{\partial\theta_a}$, with θ_a spaning the set of intensive variables of the ensemble, that is to say that the proposed representation is a Gauss map of the statistical ensemble approach introduced by Gibbs.

The arclength $L_{\mathrm{Eq-E\rho}}$ along a curve $\boldsymbol{\theta}(t)$ can be measured as the line integral of the form of Eq (26):

$$L_{\mathrm{Eq-E\rho}} = \int \sqrt{\frac{d\left|\tilde{\boldsymbol{p}}^{\mathrm{eq}}_{\boldsymbol{\theta}(t)}\right\rangle}{dt} \bullet \frac{d\left|\tilde{\boldsymbol{p}}^{\mathrm{eq}}_{\boldsymbol{\theta}(t)}\right\rangle}{dt}}\mathrm{d}t = \int \sqrt{\sum_\alpha \sum_\beta \left(\frac{\partial\left|\tilde{\boldsymbol{p}}^{\mathrm{eq}}_{\boldsymbol{\theta}(t)}\right\rangle}{\partial\theta_\alpha} \bullet \frac{\partial\left|\tilde{\boldsymbol{p}}^{\mathrm{eq}}_{\boldsymbol{\theta}(t)}\right\rangle}{\partial\theta_\beta}\frac{\partial\theta_\alpha}{\partial t}\frac{\partial\theta_\beta}{\partial t}\right)}\mathrm{d}t \qquad (26)$$

It turns out the arclength $L_{\mathrm{Eq-E\rho}}$ on our hypersphere is equal to the half of the arclength on the hypersurface of the E-K-L divergence as it can be seen in Eq (27):

$$L_{\mathrm{EKL}} = \int \sqrt{\sum_a \sum_b \frac{\partial\tilde{p}^{eq}_{i,\theta_a}}{\partial t}\frac{\partial^2 D_{EKL}(p_{\dot{\theta}}|p_{\theta})}{\partial\tilde{p}^{eq}_{i,\theta_0}\partial\tilde{p}^{eq}_{j,\theta_0}}\bigg|_{\boldsymbol{\theta}}\frac{\partial\tilde{p}^{eq}_{i,\theta_b}}{\partial t}}\mathrm{d}t = 2\int\sqrt{\frac{\partial\left|\tilde{p}^{eq}_{\boldsymbol{\theta}}\right\rangle}{\partial t}\bullet\frac{\partial\left|\tilde{p}^{eq}_{\boldsymbol{\theta}}\right\rangle}{\partial t}}\mathrm{d}t = 2L_{\mathrm{Eq-E\rho}} \quad (27)$$

where we have taken in to account that $\frac{\partial^2 D_{EKL}(p_{\dot{\theta}}|p_{\theta})}{\partial\sqrt{p_{i,\theta}}\partial\sqrt{p_{j,\theta}}}\bigg|_{\theta} = \frac{\partial^2 D_{EKL}(p_{\dot{\theta}}|p_{\theta})}{\partial\sqrt{p_{i,\dot{\theta}}}\partial\sqrt{p_{j,\dot{\theta}}}}\Bigg|_{\boldsymbol{\theta}} = 4\delta_{ij}$ as shown in appendix A.

In the case that we choose to parameterize the curve via a single ensemble parameter θ_a, then the infinitesimal length can be express similarly in the form of Eq (28).

$$\mathrm{d}s_{Eq-E\rho} = \sqrt{\frac{\partial\left|\tilde{\boldsymbol{p}}^{eq}\right\rangle}{\partial\theta_a}\bigg|_{\boldsymbol{\Phi},\boldsymbol{\theta}_{\beta\neq a}} \bullet \frac{\partial\left|\tilde{\boldsymbol{p}}^{eq}\right\rangle}{\partial\theta_a}\bigg|_{\boldsymbol{\Phi},\boldsymbol{\theta}_{\beta\neq a}}}\mathrm{d}\theta_a = \sqrt{\frac{1}{4}\langle X_a - \langle X_a\rangle\rangle^2}\mathrm{d}\theta_a = \sqrt{\frac{1}{4}\frac{\partial^2 ln\Psi_{\boldsymbol{\Phi},\boldsymbol{\theta}}}{\partial\theta_a^2}\bigg|_{\boldsymbol{\Phi},\boldsymbol{\theta}_{\beta\neq a}}}\mathrm{d}\theta_a \quad (28)$$

where we have used the fact that the tangent vectors $\left.\frac{d|\tilde{p}^{eq}\rangle}{d\theta_a}\right|_{\vec{\Phi},\theta_{\beta\neq a}}$ are equal to ½ of the projections of the vector that describes the conjugate extensive variable $\langle\widetilde{\boldsymbol{X}_{\boldsymbol{a}}}|$ on the tangent plane as shown in Eq (20). Since the thermodynamic length under similar conditions, can be measured [4, 36] as $L_{C,BR} = \int \sqrt{\frac{\mathrm{d}\theta_a}{\mathrm{d}t} \left.\frac{\partial^2 ln\Psi_{\boldsymbol{\Phi},\boldsymbol{\theta}}}{\partial\theta_a^2}\right|_{\boldsymbol{\Phi},\boldsymbol{\theta}_{\beta\neq a}} \frac{\mathrm{d}\theta_a}{\mathrm{d}t}}\,\mathrm{d}t$, integrating $\mathrm{d}s_{Eq-E\rho}$, will resalt in ½ of the thermodynamic Length.

As Brody and Rivier have shown [4] the second derivative of the logarithm of the equilibrium ensemble partition $ln\Psi_{\boldsymbol{\Phi},\boldsymbol{\theta}}$ in respect to the intensive parameter θ_a is in fact a Fisher metric tensor. As in the case of Weinhold's thermodynamic Length (L_{Weinhold}) and Salamon, Nulton and Berry [7], statistical distance L_{SNB}, the definition of an energy of action of the curve would lead to an expression directly related to the free energy differences[36].

Summarizing the arclength on our unit hypersphere is half of the length as measured by Weinhold's thermodynamic length (L_{Weinhold}) , Salamon, Nulton and Berry [7] referenced as statistical distance L_{SNB} and Crooks-Brody and Rivier thermodynamic measure[4, 36] L_{C-BR}. The reader should also have in mind, that this equivalence "implies" an equivalence in representing a thermodynamic state with different ensamples and therefore may be subject to the distance from the thermodynamic limit in finite systems. In the thermodynamic limit, thermodynamic lengths may be constructed with alternative but equivalent metric tensors as has been show by Weinhold [30].

Concerning the tangent distance of nonequilibrium points from the corresponding equilibrium point ($L_{\mathrm{NEq-E\rho}} = \int \mathrm{d}s_{\mathrm{NEq-E\rho}}$) , it is possible to express $\mathrm{d}s_{\mathrm{NEq-E\rho}}$ in the form of a Taylor expansion. A second order expansion of $\mathrm{d}s_{\mathrm{NEq-E\rho}}$ is proportional to the square of the Euclidian distance on the tangent plain. In order to verify this one has to express the displacement of the divergence on an orthonormal base on the tangent plane at $|\tilde{\boldsymbol{p}}^{\mathrm{eq}}_{\boldsymbol{\theta}^o}\rangle$. The orthonormal base would make up the columns of a matrix $\overline{\overline{\boldsymbol{U}}}$ that can describe any perturbation from $|\tilde{\boldsymbol{p}}^{\mathrm{eq}}_{\boldsymbol{\theta}^o}\rangle$ that satisfies the normalization condition, and therefore lie on the tangent plane. For any infinitesimal deviation $\boldsymbol{\delta\beta} \equiv \{\dots, \delta\beta_l, \dots\}$ along any of the base vectors the change in the EKL Divergence will be given from Eq (29).

$$\lim_{\overrightarrow{\delta\beta}\to\vec{0}} D_{GKL}\left(\left|\widetilde{\boldsymbol{p}}_{\boldsymbol{\theta}^o}^{\mathrm{eq}}\right\rangle + \boldsymbol{\delta\beta}\overline{\overline{\boldsymbol{U}}}\middle|\left|\widetilde{\boldsymbol{p}}_{\boldsymbol{\theta}^o}^{\mathrm{eq}}\right\rangle\right) = \frac{1}{2}\sum_l \ (\delta\beta_l)^2 = \ \frac{1}{2}\mathrm{d}s_{\mathrm{NEq-E\rho}}^2 \quad (29)$$

As it has been demonstrated for both the infinitesimal arclength on the proposed hypersphere $\mathrm{d}s_{\mathrm{Eq-E\rho}}$ and the infinitesimal distance on the tangent plane $\mathrm{d}s_{\mathrm{NEq-E\rho}}$ is intimately related with the infinitesimal change of the EKL Divergence. Note that although the infinitesimal differentials along the hypersphere and the tangent plain have are equal norm $\left\|\mathrm{d}s_{\mathrm{NEq-E\rho}}\right\| = \left\|\mathrm{d}s_{\mathrm{Eq-E\rho}}\right\|$ the integration that leads to arclengths on the hypersphere and the tangent planes are different. Therefore, the physical interpretation of the proposed representation is intimately linked with the physical interpretation of the KL Divergence. Out of the different aspects of the physical interpretation of the KL Divergence (and equivalently the EKL Divergence) we should point out the works on “information content”, “potential work”, and the notion of exergy. The physical importance of the KL Divergence is probably best understood as the measure of irreversibility for a system that returns to equilibrium $p_{(\boldsymbol{\Phi},\boldsymbol{\theta})}^{eq}$ from an arbitrary distribution $p_{(\boldsymbol{\Phi},\boldsymbol{\theta})}$ since it measures the total entropy increase in both the system and the environment, as shown in the Eq (30) and explained in appendix B.

$$D_{\mathrm{EKL}}\left(\mathrm{p}_{(\boldsymbol{\Phi},\boldsymbol{\theta})}|\mathrm{p}_{(\boldsymbol{\Phi},\boldsymbol{\theta})}^{\mathrm{eq}}\right) \geq 0 \rightarrow \frac{S_{(\boldsymbol{\Phi},\boldsymbol{\theta})}^{\mathrm{eq}} - S_{(\boldsymbol{\Phi},\boldsymbol{\theta})}}{\mathrm{k_B}} - \frac{Q}{\mathrm{k_B T}} \geq 0 \quad (30)$$

Where Q is the amount of heat exchanged with its environment characterized by the values of thermodynamic forces $\boldsymbol{\theta}$. We should note that since the exchange of work and heat is exchanged with a reservoir of constant intensive variables (set by $\boldsymbol{\theta}$), Q is consistent with the definition of being equal to the difference in internal energy minus the exchanged work. Similarly, since the heat exchanges with the environment is a measure of the entropy increases of the environment, the semipositive definiteness of the K-L divergence accounts for the irreversible nature of total entropy increase as dictated by the second law of thermodynamics.

CONCLUSIONS

The present manuscript reports on a novel geometrical representation for reversible and irreversible changes in the values of the intensive variable in the context of the statistical mechanical representation proposed by Gibbs. This representation satisfies the invertibility requirement that appears in the EROPHILE transformations (Eq (7) and Eq (11)). This requirement along with the restriction that the supporting phase space volume does not change are the necessary and sufficient conditions for the proposed formulation. The additional assumption of a stochastic process that obeys detailed balance can provide the proposed framework to express fluctuations and variances with the same base, namely that of the tangent manifold.

Within the proposed framework, any possible distribution of states is expressed as a Euclidean vector with deviations from the equilibrium distribution represented as points on a Euclidean hyperplane. The tangent vector of this hyperplane represents the equilibrium distribution. Furthermore, within the proposed framework, a state can be defined in a general manner that is not limited to the classical notion of a micro or a microstate, but can include the notion of coarse-grained states as the disjoint (mutually exclusive) sets of microstate with common properties. In this general sense, each generalized state is a separate statistical ensemble of microstates that can be represented by its own Euclidean space.

In this work the planes introduced in EROPHILE are shown to be tangent to a hypersphere, which comprises of all possible equilibrium points. It is important to keep in mind that within the proposed representation, even though all possible equilibrium thermodynamic states are points on this hypersphere, only a subset of these hypersphere points, may in general, correspond to thermodynamic states compatible to a given statistical ensemble. The dimensionality of the hypersphere's sub-manifold, where equilibrium thermodynamic states lie, is equal to the number of intensive variables of the ensemble. Thus, in the case of the microcanonical ensemble, the dimensionality is zero and a single point on the hypersphere may be related to an equilibrium thermodynamic state. On the other hand, in the case of a canonical ensemble the dimensionality is equal to one and all equilibrium points lie on a single line, whereas for a grand canonical or an isothermal-isobaric NPT ensemble the dimensionality is two, and equilibrium points lie on a two-dimensional surface. All other possible distributions must lie outside the hypersphere, on tangent planes in one of those equilibrium points. In the language of differential geometry, the proposed framework implies a parametric representation of equilibrium statistical mechanics as a Gauss map [37].

Specifically, statistical ensembles with at least one intensive variable (e.g. temperature) are examined. Under this condition, a change of an intensive variable can be described by an arc on a Euclidian hypersurface of spherical symmetry. For the description of the arc length, the metric for tangent spaces taken from the field of differential geometry is introduced, and completed to the "thermodynamic length" and the statistical distance [7, 31] and to the Remanian approach via the information Fisher metric in the field of information geometry. The “action” of a curve along this hyper surface is a measure of the change of the Kullback–Leibler divergence between the initial and final equilibrium state. As such, it is a measure of the change in exergy when the system moves from an initial equilibrium to a final equilibrium by changing the values of the intensive variables of the ensemble. Finally, we have demonstrated that the distances in the proposed representation are also related to the “thermodynamic length” and the statistical distance first introduced [5, 7, 31] in the Weinhold and Ruppeiner geometries.

The arclength on the proposed equilibrium manifold has been shown to be consistent with the Weinhold (thermodynamic) length, providing a link to the work of Weinhold who has proposed a novel representation of thermodynamics by an abstract vector space for the second derivative with respect to extensive variables. This can also be understood on the basis of a Riemannian geometry[31]. It should be noted that the original representation of Weinhold has been shown to be equivalent to the Ruppeiner approach that was based in the Riemannian treatment of Einstein theory subsystem fluctuations of extensive variables. Amazingly both approachs have been found to be consistent with the notions based on Information theory as has been demonstrated in several relevant works [5, 7, 10] that have been able to connect the macroscopic thermodynamic with the probabilistic representation of a system. A very important tool in linking the probabilistic representation[5, 7, 10] and the microscopic thermodynamic processes has been proven to be the K-L divergence that is also the base of the modern discipline of information geometry [8, 33, 34]. As it has been shown the metric on our Euclidean space is also related to the K-L divergences and is consistent with the previous results.

In our representation the space is Euclidian and equilibrium is represented as a manifold on a hypersphere embedded in the Euclidean space, whereas non-equlibrium state live on it’s tangent bundle along with the variances of the conjugate extensive variables of the ensemble.

Currently we were able to map Equilibrium and non-equilibrium processes that change the value of intensive variables, but we hope that it will be possible to extend the formalism in following changes of extensive variables analogous to the frameworks proposed by Weinhold and Ruppeiner.

Finally, we hope that the proposed representation can be the bases of further development in order to be able to provide analogous geometrical representations for systems where our two basic requirements (the invertibility of transformation matrix $\bar{\bar{\boldsymbol{M}}}$, and the conservation of the volume of the supporting microstate phase space dv) is no longer valid (i.e. in the case of phase transitions and in dissipative systems). Especially in the case of phase transitions we feel that this work can provide a significant advantage in the description of phase equilibrium due the relation of the Gauss map to the catastrophe theory via the condition of zero Gaussian curvature.

It is important to stress, that the Weinhold and Ruppeiner approaches to describe thermodynamic equilibrium along with the further developments and applications that have been reported by several other authors, have been formulated and can be understood in the context of the Riemannian geometry. The proposed work is better understood within the context of Gauss parametric representation of surfaces. Whereas this relation indicates that the results should be consistent, it is strongly suggested that the new approach can be very promising in describing deviations from equilibrium having a conceptual advantage due to the Euclidian nature of the tangent space in this representation. Our aim was to provide a formal framework that respects the subtle notions of Gibbs statistical mechanics (e.x. the deference's in extensive and intensive variables) and at the same time provide a physical picture of the equilibrium and rear equilibrium process. Most importantly, it has been shown how to uniquely describe an non equilibrium state as a triplet : $\left(d\xi, |\widetilde{\boldsymbol{p}}^{\mathrm{eq}}\rangle, |\widetilde{\boldsymbol{p}}\rangle - |\widetilde{\boldsymbol{p}}^{\mathrm{eq}}\rangle\right)$, by quantifying all possible non-equilibrium states that satisfy a set of well defined conditions the invertibility of a transformation matrix $\bar{\bar{\boldsymbol{M}}}$. Finally, the proposed framework allows a quantitative description for the return to equilibrium by admitting a map to the tangent bundle of the proposed equilibrium hypersphere, based on the "spectral decomposition" of any underling stochastic process that can be used to model the "dynamics" of the system.

ACKNOWLEDGMENTS

Dr Loukas Peristeras, Dr Konstantinos Papavasiliou and Dr Vasileios Michalis, are acknowledged for careful proof reading of the manuscript. Finally, the acronym EROPHILE was initially derived from "Eigenvector Representation of Observables and Probabilities in a HIgh-dimensionaL Euclidean space" in honour of my daughter Erofili. Since it turns out that the use of eigenvectors is not essential in the more general approach proposed in this work I retained the use of the same acronym in the form of "Euclidian Representation of Observables and Probabilities in a HIgh-dimensionaL vEctor space".

APPENDIX

APPENDIX A: Derivatives of the KL and GLK Divergence.

The KL and GLK Divergence are given from the following relations

$D_{KL}(p^n|p^o) = \sum \;\; p^n \ln\left(\frac{p^n}{p^o}\right)$ (A1)

$D_{EKL}(p^n|p^o) = \sum \;\; p^n \ln\left(\frac{p^n}{p^o}\right) - \sum \;\; p^n + \sum \;\; p^o$ (A2)

Given two distributions $\boldsymbol{p}, \boldsymbol{q}$ characterized by potentially different values for a set of parameters $\boldsymbol{\theta}$, the Taylor expansion of the EKL Divergence can be evaluated as :

$$D_{\mathrm{EKL}}\left(\boldsymbol{p} + \boldsymbol{\delta}\sqrt{\boldsymbol{p}}|\sqrt{\boldsymbol{q}}\;\right) = D_{\mathrm{EKL}}(\boldsymbol{p}|\boldsymbol{q}) + \frac{1}{2}\sum_i \frac{\partial^2 D_{EKL}(p_i|q_i)}{\partial\sqrt{p_i}\partial\sqrt{p_i}}\;\delta\sqrt{p_i}\delta\sqrt{p_i} \quad \text{(A3)}$$

The evaluation of the deviation from equilibrium along the tangent hyperplane can be measured by expressing any possible deviation from equilibrium as a linear combination over a base that span the tangent plane as $|\tilde{p}_{i,\theta_0}\rangle = \left|\tilde{p}_{i,\theta_0}^{eq}\right\rangle + \sum_l \;\; \beta_l|\tilde{u}_l\;\rangle$. Then one can evaluate the derivative of the divergence along any possible direction on the plane resulting in :

$$\frac{\partial D_{EKL}(\boldsymbol{p}|\boldsymbol{q})}{\partial\beta_k} = \sum \;\; u_{k,i}\sqrt{p_{i,\theta_0}^{eq}}\left(\ln\left(1 + \frac{\left(\sum_l \;\beta_l u_{l,i}\right)}{\sqrt{p_{i,\theta_0}^{eq}}}\right)\right) \quad \text{(A4)}$$

And

$$\frac{\partial^2 D_{EKL}(\boldsymbol{p}|\boldsymbol{q})}{\partial\beta_l\partial\beta_k} = \delta_{l,k}\sum u_{l,i}u_{l,i}\frac{\sqrt{p_{i,\theta_0}^{eq}}}{\sqrt{p_{i,\theta_0}^{eq}} + \sum_l \;\beta_l u_{l,i}} \quad \text{(A5)}$$

Therefore, the first and the second derivatives at the point of equilibrium $\boldsymbol{\beta} = 0$ are give as :

$$\left.\frac{\partial \;\; D_{EKL}(\boldsymbol{p}|\boldsymbol{q})}{\partial\beta_l}\right|_{\boldsymbol{\beta}=0} = 0 \quad \text{(A6)}$$

$$\left.\frac{\partial^2 D_{EKL}(\boldsymbol{p}|\boldsymbol{q})}{\partial\beta_l\partial\beta_k}\right|_{\boldsymbol{\beta}=0} = \delta_{l,k}\langle\tilde{u}_l\;|\tilde{u}_l\;\rangle = \delta_{l,k} \quad \text{(A7)}$$

Thus, the second order Taylor expansion of the EKL divergence for any infinitesimal deviation from equilibrium is given as ½ the square of the infinitesimal distance in the tangent space.

$$D_{EKL}\left(\tilde{p}_{i,\theta_0}^{eq} + \boldsymbol{\delta\beta}\overline{\overline{\boldsymbol{U}}}|\tilde{p}_{i,\theta_0}^{\mathrm{eq}}\right) = \frac{1}{2}\sum_l \;(\delta\beta_l)^2 = \frac{1}{2}(\boldsymbol{\delta\beta})^2 \quad \text{(A8)}$$

APPENDIX B: On the K-L divergence and the second law of thermodynamics:

As it has been shown in literature it is possible to relate the second law of thermodynamics in the form of a monotonic increase of the total entropy of a system and its environment with the positive definiteness of the K-L divergence. We reproduce the basic steps of this relation for clarity reasons.

$$D_{EKL}\left(p_{(\boldsymbol{\Phi},\boldsymbol{\theta})}|p^{\text{eq}}_{(\boldsymbol{\Phi},\boldsymbol{\theta})}\right)=D_{KL}\left(p_{(\boldsymbol{\Phi},\boldsymbol{\theta})}|p^{\text{eq}}_{(\boldsymbol{\Phi},\boldsymbol{\theta})}\right)=\sum_i p_{i,(\boldsymbol{\Phi},\boldsymbol{\theta})}\ln\left(\frac{p_{i,(\boldsymbol{\Phi},\boldsymbol{\theta})}}{p^{\text{eq}}_{i,(\boldsymbol{\Phi},\boldsymbol{\theta})}}\right)\geq 0\rightarrow$$

$$\sum_i\left[p_{i,(\boldsymbol{\Phi},\boldsymbol{\theta})}\ln\left(p_{i,(\boldsymbol{\Phi},\boldsymbol{\theta})}\right)-p_{i,(\boldsymbol{\Phi},\boldsymbol{\theta})}\ln\left(\frac{e^{\sum_\alpha\theta_\alpha X_{i,\alpha}}}{\Psi^{eq}_{(\boldsymbol{\Phi},\boldsymbol{\theta})}}\right)\right]\geq 0\rightarrow$$

$$\frac{-S_{(\boldsymbol{\Phi},\boldsymbol{\theta})}}{k_{\mathrm{B}}}+\ln\left(\Psi^{\text{eq}}_{(\boldsymbol{\Phi},\boldsymbol{\theta})}\right)-\sum_i p_{i(\boldsymbol{\Phi},\boldsymbol{\theta})}\left(\sum\nolimits_\alpha\theta_\alpha X_{i,\alpha}\right)\geq 0\rightarrow$$

$$\frac{S^{eq}_{(\boldsymbol{\Phi},\boldsymbol{\theta})}-S_{(\boldsymbol{\Phi},\boldsymbol{\theta})}}{k_{\mathrm{B}}}+\sum_\alpha\theta_\alpha\left[\sum_i\left(p^{\text{eq}}_{i,(\boldsymbol{\Phi},\boldsymbol{\theta})}-p_{i,(\boldsymbol{\Phi},\boldsymbol{\theta})}\right)X_{i,\alpha}\right]\geq 0\rightarrow$$

$$D_{\mathrm{EKL}}\left(p_{(\boldsymbol{\Phi},\boldsymbol{\theta})}|p^{\text{eq}}_{(\boldsymbol{\Phi},\boldsymbol{\theta})}\right)\geq 0\rightarrow\frac{S^{\text{eq}}_{(\boldsymbol{\Phi},\boldsymbol{\theta})}-S_{(\boldsymbol{\Phi},\boldsymbol{\theta})}}{k_B}-\frac{Q}{k_BT}\geq 0$$

$$\rightarrow\frac{\Delta S^{\text{sys}}}{k_{\mathrm{B}}}+\frac{\Delta S^{\text{env}}}{k_{\mathrm{B}}}\geq 0\quad\text{(B1)}$$

Note that the following relations have been used:

$\frac{S_{(\boldsymbol{\Phi},\boldsymbol{\theta})}}{k_{\mathrm{B}}}=-\sum_i p_{i,(\boldsymbol{\Phi},\boldsymbol{\theta})}\ln\left(p_{i(\boldsymbol{\Phi},\boldsymbol{\theta})}\right)$ even away from equilibrium.

$p^{\text{eq}}_{i,(\boldsymbol{\Phi},\boldsymbol{\theta})}=e^{\sum_\alpha\theta_\alpha X_{i,\alpha}-\ln\left(\Psi^{\text{eq}}_{(\boldsymbol{\Phi},\boldsymbol{\theta})}\right)}$ and at the same time $\ln\left(\Psi^{\text{eq}}_{(\boldsymbol{\Phi},\boldsymbol{\theta})}\right)=\sum_\alpha\theta_\alpha<X_\alpha>_{\text{eq}}+\frac{S^{\text{eq}}_{(\boldsymbol{\Phi},\boldsymbol{\theta})}}{k_B}$ as expected from equilibrium statistical mechanics for a single state system.

$\ln\left(\frac{p_{i,(\boldsymbol{\Phi},\boldsymbol{\theta})}}{p^{\text{eq}}_{i,(\boldsymbol{\Phi},\boldsymbol{\theta})}}\right)<\infty\ for\ every\ i$ which means that if $p_{i,(\boldsymbol{\Phi},\boldsymbol{\theta})}\neq 0$ then $p^{\text{eq}}_{i,(\boldsymbol{\Phi},\boldsymbol{\theta})}\neq 0$ has to hold (i.e. the matrix $\bar{\bar{\boldsymbol{M}}}$ must be invertible).

$\frac{Q}{k_{\mathrm{B}}T}=\sum_\alpha\theta_\alpha\left[\sum_i\left(p_{i,(\boldsymbol{\Phi},\boldsymbol{\theta})}-p^{\text{eq}}_{i,(\boldsymbol{\Phi},\boldsymbol{\theta})}\right)X_{i,\alpha}\right]=\sum_\alpha\theta_\alpha\left[<X_a>-<X_a>_{\text{eq}}\right]$, where Q is positive when it enters the system and work is measured as the product of the thermodynamic forces of the environment (that remains constant) times the change of the conjugate extensive “displacements”.

$\frac{\Delta S^{\text{env}}}{k_{\mathrm{B}}}\geq-\frac{Q}{k_{\mathrm{B}}T}$ with the equality representing a reversible change on the environment. Since the same steps can be made where $p_{(\boldsymbol{\Phi},\boldsymbol{\theta})}$ is the equilibrium distributions at a different thermodynamic state (with the same values for $\boldsymbol{\Phi}$) the semidefinite nature of D_{KL} has be intimately linked with the second low of thermodynamics in both reversible and irreversible process.

Note that changing the values of an extensive variable requires more attention in order to include the difference in the number of microstates as a function of the difference values of the extensive variable as it is evident in the free energy perturbation method.

REFERENCES

1. J. W. Gibbs, H. A. Bumstead and R. G. Van Name, *The Scientific papers of J. Willard Gibbs ... vol. 1, vol. 1*, Longmans, Green, London; New York, 1906.
2. R. Clausius, *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 1866, **32**, 1-17.
3. C. Carathéodory, *Mathematische Annalen*, 1909, **67**, 355-386.
4. D. Brody and N. Rivier, *Physical Review E*, 1995, **51**, 1006-1011.
5. F. Schlögl, *Zeitschrift für Physik B Condensed Matter*, 1985, **59**, 449-454.
6. F. Schlögl, *Zeitschrift für Physik B Condensed Matter*, 1983, **52**, 51-60.
7. P. Salamon, J. D. Nulton and R. S. Berry, *The Journal of Chemical Physics*, 1985, **82**, 2433-2436.
8. S.-I. Amari, *Ann. Statist.*, 1982, **10**, 357-385.
9. G. C. Boulougouris and D. N. Theodorou, *J. Chem. Phys.*, 2009, **130**, 044905-044907.
10. I. Procaccia and R. D. Levine, *The Journal of Chemical Physics*, 1976, **65**, 3357-3364.
11. G. C. Boulougouris and D. N. Theodorou, *J. Chem. Phys.*, 2007, **127**, 084903-084907.
12. N. Lempesis, G. G. Vogiatzis, G. C. Boulougouris, L. C. A. van Breemen, M. Hütter and D. N. Theodorou, *Molecular Physics*, 2013, **111**, 3430-3441.
13. N. Lempesis, G. C. Boulougouris and D. N. Theodorou, *Journal of Chemical Physics*, 2013, **138**.
14. N. Lempesis, D. G. Tsalikis, G. C. Boulougouris and D. N. Theodorou, *Journal of Chemical Physics*, 2011, **135**, 17.
15. D. G. Tsalikis, N. Lempesis, G. C. Boulougouris and D. N. Theodorou, *Journal of Physical Chemistry B*, 2010, **114**, 7844-7853.
16. D. G. Tsalikis, N. Lempesis, G. C. Boulougouris and D. N. Theodorou, *J. Chem. Theory Comput.*, 2010, **6**, 1307–1322.
17. D. G. Tsalikis, N. Lempesis, G. C. Boulougouris and D. N. Theodorou, *J. Phys. Chem. B*, 2008, **112**, 10628-10636.
18. D. G. Tsalikis, N. Lempesis, G. C. Boulougouris and D. N. Theodorou, *J. Phys. Chem. B*, 2008, **112**, 10619-10627.
19. E. T. Jaynes, *Annual Review of Physical Chemistry*, 1980, **31**, 579-601.
20. *Understanding Molecular Simulation: From Algorithms to Applications*, Academic Press, Inc., 1996.
21. M. P. Allen and D. J. Tildesley, in *Computer simulation of liquids*, Clarendon Press, Oxford, 1 edn., 1987, pp. 212-219.
22. P. A. M. Dirac, *Mathematical Proceedings of the Cambridge Philosophical Society*, 2008, **35**, 416-418.
23. J. von Neumann and R. T. Beyer, *Mathematical Foundations of Quantum Mechanics New Edition*, NED - New edition edn., Princeton University Press, 2018.
24. G. C. Boulougouris, *Journal of Computational Chemistry*, 2014, **35**, 1024-1035.
25. G. C. Boulougouris, *J. Chem. Phys.*, 2013, **138**, 114111.
26. G. C. Boulougouris, *J. Phys. Chem. B*, 2012, **116**, 997-1006.
27. G. C. Boulougouris and D. Frenkel, *J. Chem. Theory Comput.* , 2005, **1**, 389-393.
28. J. v. Neumann, *Proceedings of the National Academy of Sciences of the United States of America*, 1932, **18**, 70-82.

29. G. Ruppeiner, *Reviews of Modern Physics*, 1995, **67**, 605-659.
30. F. Weinhold, *Physics Today*, 1976, **29**.
31. F. Weinhold, *The Journal of Chemical Physics*, 1975, **63**, 2479-2483.
32. S. Kullback and R. A. Leibler, *The Annals of Mathematical Statistics*, 1951, **22**, 79-86.
33. S.-i. Amari, *Entropy*, 2014, **16**, 2131.
34. S. Amari and A. Cichocki, 2010, **58**, 183.
35. H. Zhu and R. Rohwer, *Neural Processing Letters*, 1995, **2**, 28-31.
36. G. E. Crooks, *Physical Review Letters*, 2007, **99**, 100602.
37. C. F. Gauss, A. M. Hiltebeitel and J. C. Morehead, *General Investigations of Curved Surfaces of 1827 and 1825: Translated with Notes and a Bibliography by James Caddall Morehead and Adam Miller Hiltebeitel*, University Library, 1902.