Stochastic thermodynamics of holonomic systems

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(Dated: May 31, 2019)

Stochastic thermodynamics is a recently introduced approach to deals with small systems in contact with one or more thermal baths. This theory has been applied to systems of unconstrained particles to investigate the role of the thermodynamics principles in micro- and nano-scale systems and to demonstrate some important fluctuations theorems. Nowadays, the manipulations of small systems with advanced nanotechnologies provided the experimental evidence of most of results based on stochastic thermodynamics. Here, this approach is generalized to consider arbitrary holonomic systems subjected to arbitrary external forces and described by Lagrange and Hamilton equations of motion. In both the underdamped and overdamped cases, the principles of thermodynamics are obtained in the out-of-equilibrium regime by giving microscopic interpretations of heat, energy and entropy. To do this, the Klein-Kramers (for the underdamped case) and Smoluchowski (for the overdamped case) equations are used in covariant form to be consistent with the Brownian motion on smooth manifolds. Moreover, explicit expressions for the entropy production have been obtained and can be applied to the non-equilibrium thermodynamics of holonomic systems.

I. INTRODUCTION

In the first decades of the 19th century, the experimental investigations on the motion of tiny particles suspensed in water [1, 2], and the observation of hydrodiffusion through membranes [3], gave a great impulse to the development of non-equilibrium statistical mechanics. Successively, the precise explanation of these phenomena was attained through the development of the diffusion theory [4, 5], the use of stochastic processes [6] and the introduction of the Langevin equation [7]. Importantly, these approaches led to the experimental evidence of the atomic hypothesis [8, 9]. Further, the Langevin stochastic equation was analysed through the probability distribution of the involved variables [10–14], laying the foundations of the Fokker-Planck methodology [15–19]. More recently, Sekimoto defined the concept of heat for a given stochastic solution of the Langevin equation [20, 21], leading to a thermodynamic interpretation of the Langevin approach and, consequently, to the origin of the stochastic thermodynamics. Similarly, the concepts of entropy and entropy production have been introduced for Langevin trajectories, substantiating the above suggested thermodynamic picture [22–24]. Grounded on these concepts, the stochastic approach to thermodynamics has been further developed for discrete systems (described by the master equation) and continuous ones (described by the Fokker-Planck equation), by eventually obtaining the thermodynamic principles directly derived from Langevin or Brownian paths [25–30]. Even more importantly, several fluctuation theorems have been derived, which quantitatively measure the effects of thermal fluctuations on entropy, entropy production, work, free energy and so on [31–36]. Concerning the thermodynamics of quantum systems, the evolution equation of the density matrix has been generalized to take into account the presence of a thermal bath [37–39], and additional fluctuation theorems have been established for arbitrary open quantum systems [40–42].

Thermal fluctuations play an important role in several applications ranging from soft matter and polymer theory to solid state physics and nanotechnology. A classical example deals with the thermal and elastic behavior of DNA [43, 44] and other polymer chains [45–47], which have been largely investigated with statistical methodologies. In addition, the conformational transitions observed in several macromolecules of biological origin (nucleic acids, proteins and so on) have been modeled with chains of bistable units [48–52]. In this context, the equivalence of the ensembles in the thermodynamic limit has been discussed to give a correct interpretation of isotensional (Gibbs) and isometric (Helmholtz) ensembles [53, 54]. Other important applications concern the physical understanding of molecular motors, using the chemical energy (supplied, e.g., by the ATP hydrolisis) to produce mechanical work in nanoscale systems subjected to thermal fluctuations [55–58]. Further, the dynamics of magnetization in ferromagnetic micro- and nano-particles is strongly influenced by the presence of a thermal bath. Therefore, the Landau-Lifshitz-Gilbert equation, governing the magnetization dynamics [59, 60], has been generalized with noise terms representing fluctuations [61–64]. This approach has been used to investigate different magnetic configurations, including memories and other devices, in order to better understand their stochastic behavior [19, 65–69].

In this paper, we retrace the development of the stochastic thermodynamics by giving emphasis to the holonomic character of the systems under investigation. It means that we take into consideration holonomic systems, described by a set of generalized coordinates, and in contact with a thermal bath. Hence, the starting point

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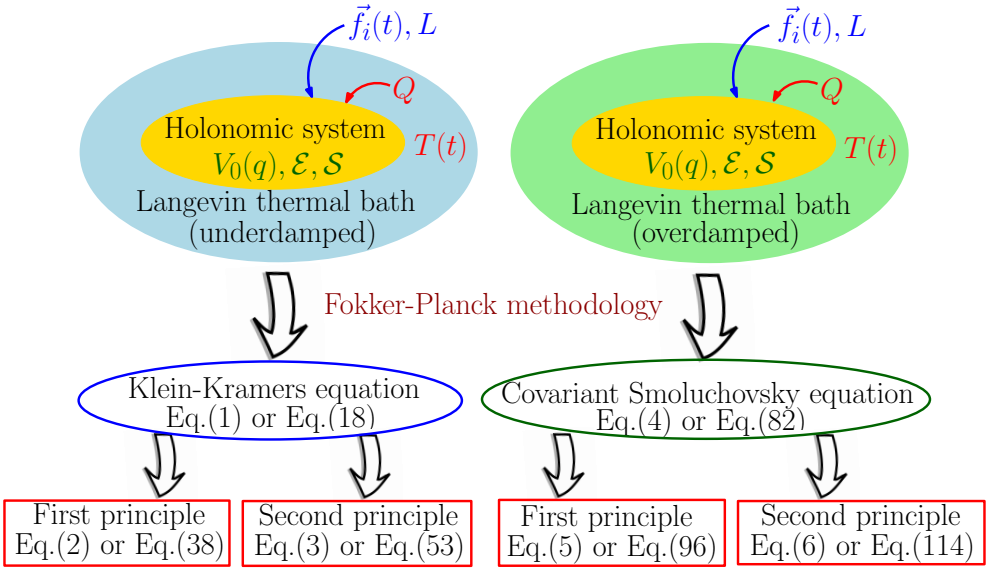

FIG. 1. Scheme of the structure of the paper concerning the two approaches (underdamped and overdamped) for introducing the stochastic thermodynamics of a holonomic system. We apply to the system the forces $\vec{f}_i(t)$ doing a work L and we embed the system in a thermal bath at temperature $T(t)$ transferring the heat Q. The system is described by a potential energy $V_0(q)$, an internal energy $\mathcal{E}$ and an entropy $\mathcal{S}$. The two approaches lead to the principles of the thermodynamics provided that we perform a correct identification of all observables.

is represented by the set of equations of the analytical mechanics, namely Lagrange and Hamilton equations, suitably modified to take into account the influence of thermal fluctuations. To do this, we implemented the Langevin thermal bath based on two additional force terms, i. e. the dissipative force and the random force. Of course, it means that we assume the Langevin scheme as a simple modeling of the real collision mechanisms, governing the non-equilibrium dynamics and the relaxation processes.

The objective of this work is to investigate the stochastic thermodynamics of holonomic systems under both underdamped and overdamped conditions. In the first case we elaborate a Klein-Kramers equation for an arbitrary holonomic system, with an arbitrary value of the friction coefficient. It means that we work in the whole phase space composed of generalized coordinates and momenta. Interestingly, this Klein-Kramers equation for the density $W(q,p,t)$ assumes the following form based on the Poisson brackets

$$\frac{\partial W}{\partial t} = \{\mathcal{H}, W\} + \beta \left\{q^k, p_k W\right\} + D a_{ij} \left\{q^i, \left\{q^j, W\right\}\right\}, \tag{1}$$

where we introduced the Hamiltonian function of the system as $\mathcal{H} = \frac{1}{2}a^{kh}p_k p_h + V = \frac{1}{2}a^{kh}p_k p_h + V_0 - \sum_{i=1}^{N} \vec{f}_i \cdot \vec{r}_i$, where $V_0(q)$ represents the potential energy of the system and $\vec{f}_i(t)$ are the external forces applied to the system. Here, the three terms of drift (Liouville), friction (depending on the coefficient β) and noise (depending on the coefficient $D = K_B T \beta$) can be easily recognized. We observe that the diffusion term is based on the metric tensor of the system a_{ij}. Then, we prove the coherence of the trajectories in this phase space with the first and second principles of the thermodynamics. To do this, we consider the external set of forces $\vec{f}_i(t)$ applied to the system (doing a work on the system) and an arbitrarily time varying temperature $T(t)$ of the thermal bath where the system is embedded (representing an arbitrary thermodynamic transformation). Coherently, the concepts of work, heat, energy and entropy are discussed for a system described by generalized coordinates and momenta. In addition, the explicit form of the entropy production is written in terms of the metric tensor of the system. Concerning the first principle, it is obtained from Eq.(1) in the form

$$\begin{aligned} \frac{d\mathcal{E}}{dt} &= \sum_{i=1}^{N} \mathbb{E}\left\{\vec{f}_i \cdot \vec{v}_i\right\} + 2\beta \left(\frac{1}{2} n K_B T - \mathbb{E}\left\{K_0\right\}\right) \\ &= \frac{d\mathbb{E}\left\{L\right\}}{dt} + \frac{d\mathbb{E}\left\{Q\right\}}{dt}, \end{aligned} \tag{2}$$

where we identify the rate of average work $\frac{d\mathbb{E}\{L\}}{dt}$ done on the system with the average power $\sum_{i=1}^{N} \mathbb{E}\left\{\vec{f}_i \cdot \vec{v}_i\right\}$ and the remaining term with the rate of average heat $\frac{d\mathbb{E}\{Q\}}{dt}$ entering the system (being K_0 the kinetic energy of the system). We will thoroughly discuss the interpretation of this last term in connection with the equipartition law of thermodynamics. The second principle of the thermodynamics is based on the definition of the entropy $\mathcal{S} = -K_B \mathbb{E}\left\{\log W\right\}$. Again, starting with Eq.(1), we

can prove that

$$\frac{d\mathcal{S}}{dt} = \frac{1}{T}\frac{d\mathbb{E}\{Q\}}{dt} + \frac{1}{\beta T}\int_{\mathbb{R}^n}\int_{\mathcal{A}} \frac{a^{kh}\mathcal{J}_k\mathcal{J}_h}{W} dqdp, \quad (3)$$

where $\mathcal{J}_k$ represents the probability current density due to the friction and noise forces. The second term in Eq.(3) represents the entropy production, which is manifestly non negative being represented by a positive definite quadratic form. Therefore, we can write the second principle in the classical form $\frac{d\mathcal{S}}{dt} \geq \frac{1}{T}\frac{d\mathbb{E}\{Q\}}{dt}$. Finally, the two principles of thermodynamics can be rigorously obtained in the framework of the stochastic thermodynamic also for system with an arbitrary set of constraints.

In the overdamped conditions, the system is analyzed in the so-called high friction limit hypothesis with a negligible system inertia. The validity and the accuracy of the overdamped approximation have been recently discussed [70], and the overdamped stochastic thermodynamics has been further generalized to systems with multiple reservoirs [71]. The first step of our analysis concerns the elaboration of the overdamped Langevin equation and the corresponding Smoluchowski equation. This is a nontrivial task for an arbitrary holonomic system since it is difficult to directly identify in the underdamped Langevin equation the negligible terms for high values of the friction coefficient [72]. To approach the problem, we reduced the number of noise terms used in the underdamped case ($3N$ for a system with N particles) to $n < 3N$ where n is the number of degrees of freedom (*i.e.* the number of generalized coordinates). Thus, the system naturally evolves on a differential manifold of dimension n, without the necessity to adopt an embedding in a larger space (dimension $3N$). The final Langevin equation for the overdamped case defines the trajectories in the reduced configurational space, with only the generalized coordinates. While in the underdamped case the stochastic trajectories are given by geodetic lines on the differential manifold suitably modified by the applied forces and by the thermal bath, in the overdamped case, the trajectories are represented by a Brownian motion on the same differential manifold (as rigorously defined in the mathematical literature). Accordingly, the generally covariant version of the Smoluchowski equation is derived, confirming that the overdamped dynamics can be precisely interpreted with a Brownian motion on a Riemannian manifold. By considering the probability density $W(q,t)$ on the configurational space, we can define $P(q,t) = \frac{1}{\sqrt{\det(\mathbf{a})}}W(q,t)$, which is coherent with a covariant setting since the measure element $d\mu = \sqrt{\det(\mathbf{a})}dq$ leads to $\int_{\mathcal{A}} P d\mu = 1$. The covariant Smoluchowski equation eventually assumes the form

$$\frac{\partial P}{\partial t} = \frac{1}{\beta}\frac{1}{\sqrt{\det(\mathbf{a})}}\frac{\partial}{\partial q^k}\left(a^{kh}\frac{\partial V}{\partial q^h}\sqrt{\det(\mathbf{a})}P\right) + \frac{K_B T}{\beta}\nabla^2 P, \quad (4)$$

where we introduced the effective potential energy $V = V_0 - \sum_{i=1}^{N}\vec{f}_i\cdot\vec{r}_i$. Here, the symbol ∇^2 represents the Laplace-Beltrami operator, equivalent to the standard Laplace operator on a differential manifold. Then, we proved that this picture is perfectly coherent with the first and second principles of the thermodynamics, provided that we properly define the thermodynamic quantities under the overdamped assumption. For instance, we prove that the definition of entropy must be modified to attain the covariant character and to be invariant to any coordinates change. We prove that it must be defined as $\mathcal{S} = -K_B\mathbb{E}\{\log P\}$, as largely discussed in Section V. The first principle is eventually obtained from Eq.(4) in the form

$$\begin{aligned}\frac{d\mathcal{E}}{dt} &= \sum_{i=1}^{N}\vec{f}_i\cdot\frac{d\mathbb{E}\{\vec{r}_i\}}{dt} + \int_{\mathcal{A}}\frac{\partial V}{\partial q^k}\mathcal{J}^k\sqrt{\det(\mathbf{a})}dq \\ &= \frac{d\mathbb{E}\{L\}}{dt} + \frac{d\mathbb{E}\{Q\}}{dt}, \end{aligned} \quad (5)$$

where the second term in both lines represent the heat rate entering the system. Here, as before, $\mathcal{J}_k$ represents the probability current density due to the friction and noise forces. Concerning the second principle, we will obtain the final form of the entropy balance as

$$\frac{d\mathcal{S}}{dt} = \frac{1}{T}\frac{d\mathbb{E}\{Q\}}{dt} + \frac{\beta}{T}\int_{\mathcal{A}} a_{kh}\mathcal{J}^k\mathcal{J}^h\frac{\sqrt{\det(\mathbf{a})}}{P}dq, \quad (6)$$

where the second term describing the entropy production is always non-negative and we can write the second principle of the thermodynamics as $\frac{d\mathcal{S}}{dt} \geq \frac{1}{T}\frac{d\mathbb{E}\{Q\}}{dt}$, where the equality is satisfied only for quasi-static transformations. In both Eqs.(3) and (6), we observe the role of the metric tensor of the system, taking into account the applied constraints, on the entropy production term. Importantly, also in the case of overdamped dynamics, the two principles of thermodynamics can be directly proved by means of the motion equation of the probability density, given in Eq.(4). Further properties and details concerning the equations anticipated in this Introduction will be explained in the main text of this work.

It is worth noticing that constraints in a mechanical systems can be introduced in a different way, namely by considering a free system subjected to a potential energy able to force the constraints when one or more parameters assume specific values (typically zero or infinity). For instance, to fix the distance d between two particles, we can use the potential energy $V(\vec{r}_1,\vec{r}_2) = \frac{1}{2}\kappa(\|\vec{r}_1 - \vec{r}_2\| - d)^2$, with $\kappa \to \infty$. This approach can be adopted to mimic an arbitrary holonomic system and it is frequently used to develop numerical methods (e.g., in molecular dynamics) [73–75].

The structure of the paper is the following (see Fig.1). In Section II, the Langevin and Klein-Kramers equation are written in the whole phase space of a holonomic system. When the system relaxes towards the thermodynamic equilibrium, we prove the coherence of these equations with the canonical Gibbs distribution. In Section III, the stochastic thermodynamics is developed for a holonomic system within the underdamped assumption

(arbitrary value of the friction coefficient). The principles of the thermodynamics are discussed and obtained in this context. In Section IV, the covariant Langevin and Smoluchovsky equations are elaborated in the configurational space of a holonomic system under the hypothesis of overdamped relaxation (high friction limit). In this case, the trajectories live on a differential manifold defined by the metric tensor of the system and the obtained equations have been proved to be consistent with the configurational Gibbs distribution, when the system relax towards the thermodynamic equilibrium. In Section V, the stochastic thermodynamics is developed in the configurational space of an overdamped holonomic system. Also in this case, the principles of the thermodynamics have been obtained with an ad-hoc definition of the thermodynamic quantities. In addition, an example is discussed to better explain the meaning of these quantities. Finally, a Section with some conclusions and perspectives closes the paper.

II. LANGEVIN AND KLEIN-KRAMERS EQUATIONS IN THE PHASE SPACE OF A HOLONOMIC SYSTEM

We consider a system composed of N particles with masses $m_i\,(i=1,\dots,N)$ subjected to holonomic scleronomous constraints. The coordinates of the particles $\vec{r}_1,\dots,\vec{r}_N$ must satisfy the relations $f_\alpha(\vec{r}_1,\dots,\vec{r}_N)=0$ $(\forall\alpha=1,\dots,p)$. Such constraints concern only the positions of the particles and they do not depend on time [76]. So, the degrees of freedom of the system are $n=3N-p$. Therefore, we introduce the generalized coordinates $q=(q^1,\dots,q^n)$ such that the positions are given by $\vec{r}_i=\vec{r}_i(q^1,\dots,q^n)$ and the velocities by $\vec{v}_i=\frac{d}{dt}\vec{r}_i=\frac{\partial\vec{r}_i}{\partial q^k}\dot{q}^k$. The implicit Einstein convention is assumed for the sums over the n degrees of freedom. However, we maintain explicit notation for the sums over the N particles. The Newton motion equations are given by $\vec{F}_i+\vec{\Phi}_i=m_i\vec{a}_i$, where $\vec{F}_i$ are the total forces applied to the particles, $\vec{\Phi}_i$ are the reaction forces, and $\vec{a}_i$ are the acceleration vectors. From the virtual work principle $\sum_{i=1}^N\vec{\Phi}_i\cdot\vec{v}_i=0$, the classical Lagrangian approach delivers [76]

$$\frac{d}{dt}\left(\frac{\partial K_0}{\partial\dot{q}^k}\right)-\frac{\partial K_0}{\partial q^k}=\sum_{i=1}^N\vec{F}_i\cdot\frac{\partial\vec{r}_i}{\partial q^k}\triangleq\mathcal{Q}_k, \tag{7}$$

where $\mathcal{Q}_1,...,\mathcal{Q}_n$ are the so-called generalized forces [76] and the quantity K_0 is the kinetic energy

$$K_0=\sum_{i=1}^N\frac{1}{2}m_i\vec{v}_i\cdot\vec{v}_i=\frac{1}{2}a_{kh}(q)\dot{q}^k\dot{q}^h, \tag{8}$$

with

$$a_{kh}(q)=\sum_{i=1}^N m_i\frac{\partial\vec{r}_i}{\partial q^k}\cdot\frac{\partial\vec{r}_i}{\partial q^h}. \tag{9}$$

Now, we suppose that $\vec{F}_i$ takes into account the following terms: (i) a conservative force field describing the system structure, (ii) an external force field representing the work done on the system, (iii) a friction force mimicking the energy transfer from the particles to the thermal bath, and (iv) a noise term mimicking the energy transfer from the bath to the system. If we sum the mechanical power of previous points (iii) and (iv), we obtain the heat rate exchanged between system and environment (see Section III for a rigorous demonstration) [20, 21]. We then postulate

$$\vec{F}_i=-\frac{\partial V_0}{\partial\vec{r}_i}+\vec{f}_i(t)-m_i\beta\vec{v}_i+\sqrt{Dm_i}\vec{n}_i(t), \tag{10}$$

where β is the friction coefficient (per unit mass) and D is the diffusion coefficient (per unit mass). As usual, we assume the following hypotheses on the noises: $\vec{n}_i(t)\in\mathbb{R}^3$ are Gaussian stochastic processes, $\mathbb{E}\{\vec{n}_i(t)\}=0$, and $\mathbb{E}\{\vec{n}_i(t_1)\otimes\vec{n}_j^T(t_2)\}=2\delta_{ij}\mathbf{I}_3\delta(t_1-t_2)$ (here $\mathbb{E}$ means "expected value", T means "transposed", δ_{ij} is the Kronecker delta, $\delta(.)$ is the Dirac delta function, $\otimes$ is the tensor product of vectors and $\mathbf{I}_3$ is the 3×3 identity matrix). We will prove that this approach is coherent with the canonical distribution at equilibrium and the first and second thermodynamics principles during the out-of-equilibrium system evolution. The stochastic differential equation described by Eqs.(7) and (10) will be understood by means of the Stratonovich approach for two main reasons: firstly, the usual rules of calculus (for derivatives and integrals) remain unchanged and, secondly, the Stratonovich approach is the most convenient interpretation within the physical sciences since it can be obtained as the limiting process of a coloured noise (with finite noise energy) towards an uncorrelated white one (with diverging energy). Indeed, the white process is a mathematical idealization useful when the typical time-scale of the noise is much shorter than any other time-scale of the system [19]. Later on, also the Itô interpretation will be introduced to better understand the Brownian motion on a Riemannian manifold (see Section IV).

In order to obtain a first order differential system, we consider the Hamilton equations equivalent to Eqs.(7) and (10)

$$\dot{q}^k=a^{kh}p_h, \tag{11}$$

$$\dot{p}_k=-\frac{1}{2}\frac{\partial a^{ij}}{\partial q^k}p_ip_j-\frac{\partial V_0}{\partial q^k}+\sum_{i=1}^N\vec{f}_i(t)\cdot\frac{\partial\vec{r}_i}{\partial q^k}$$
$$-\beta p_k+\sum_{i=1}^N\sqrt{Dm_i}\vec{n}_i(t)\cdot\frac{\partial\vec{r}_i}{\partial q^k}, \tag{12}$$

where we used the standard notation $a^{kh}=(a^{-1})_{kh}$ for the inverse matrix, and we introduced the generalized momenta p_k. These equations describe a holonomic system under the effects of a conservative field, an external field and embedded into a thermal bath. From the

mathematical point of view, they represent a stochastic differential problem with multiplicative noise.

We can now apply the Fokker-Planck methodology, which is briefly presented here for an arbitrary interpretation of the stochastic calculus. The main result used in our development concerns the stochastic differential system

$$\frac{dx_i}{dt} = h_i(\vec{x},t) + \sum_{j=1}^{\mathfrak{m}} g_{ij}(\vec{x},t) n_j(t) \qquad (\forall i = 1,\ldots,\mathfrak{n}) \quad (13)$$

(with $\mathfrak{n}$ equations and $\mathfrak{m}$ noise terms), which has a precise meaning only when we declare the adopted interpretation of the stochastic integrals. It means that we have to specify the parameter α, defining the position of the point at which we calculate any integrated function in the small intervals of the adopted Riemann sum ($0 < \alpha < 1$). Then, Eq.(13) is equivalent to the difference scheme (to the first order in Δt)

$$\begin{aligned} x_i(t+\Delta t) = x_i(t) &+ h_i(\vec{x}(t) + \alpha\Delta\vec{x}(t), t)\Delta t \\ &+ g_{ij}(\vec{x}(t) + \alpha\Delta\vec{x}(t), t)\Delta w_j(t), \end{aligned} \quad (14)$$

where $\Delta\vec{x}(t) = \vec{x}(t+\Delta t) - \vec{x}(t)$ and $\Delta w_j(t) = \int_t^{t+\Delta t} n_j(t)dt$ are the independent increments of the Wiener process. Moreover, the Gaussian noises $n_j(t)$ ($\forall j = 1,\ldots,\mathfrak{m}$) satisfy the properties $\mathbb{E}\{n_j(t)\} = 0$ and $\mathbb{E}\{n_i(t_1)n_j(t_2)\} = 2\delta_{ij}\delta(t_1 - t_2)$. From Eq.(14) we can obtain the following form of the difference scheme

$$\begin{aligned} x_i(t+\Delta t) = x_i(t) &+ h_i(\vec{x}(t),t)\Delta t + g_{ij}(\vec{x}(t),t)\Delta w_j(t) \\ &+ \alpha \frac{\partial g_{ij}(\vec{x}(t),t)}{\partial x_k} g_{kq}(\vec{x}(t),t)\Delta w_j(t)\Delta w_q(t), \end{aligned} \quad (15)$$

which shows the role of α in the case of multiplicative noise. The introduced stochastic differential equation corresponds to the following evolution equation for the probability density $W(\vec{x},t)$ (Fokker-Planck equation) [18]

$$\begin{aligned} \frac{\partial W(\vec{x},t)}{\partial t} = &-\sum_{i=1}^{\mathfrak{n}} \frac{\partial}{\partial x_i}[h_i W(\vec{x},t)] \\ &-\sum_{i=1}^{\mathfrak{n}} \frac{\partial}{\partial x_i}\left\{ 2\alpha \left[\sum_{k=1}^{\mathfrak{n}} \sum_{j=1}^{\mathfrak{m}} g_{kj} \frac{\partial g_{ij}}{\partial x_k} \right] W(\vec{x},t) \right\} \\ &+\sum_{i=1}^{\mathfrak{n}} \sum_{j=1}^{\mathfrak{m}} \frac{\partial^2}{\partial x_i \partial x_j}\left\{ \left[\sum_{k=1}^{\mathfrak{m}} g_{ik} g_{jk} \right] W(\vec{x},t) \right\}, \end{aligned} \quad (16)$$

where the first term represents the drift, the second one the noise induced drift (which depends on α) and the third one the diffusion (characterizing the noises effect). This theory includes the Itô ($\alpha = 0$) [77], the Stratonovich ($\alpha = 1/2$) [78] and the Hänggi-Klimontovich ($\alpha = 1$) [79, 80] particular cases (see also Ref.[81]). It is interesting to observe that the theory can be generalized to take into consideration the possible cross-correlation of the noises [82, 83].

Eventually, we can write the Fokker-Planck or Klein-Kramers equation associated with Eqs.(11) and (12) in this form

$$\begin{aligned} \frac{\partial W}{\partial t} = &\frac{1}{2}\frac{\partial W}{\partial p_k} p_i p_j \frac{\partial a^{ij}}{\partial q^k} - a^{kh}\frac{\partial W}{\partial q^k} p_h + n\beta W + \beta p_k \frac{\partial W}{\partial p_k} \\ &+ \frac{\partial V}{\partial q^k}\frac{\partial W}{\partial p_k} + D a_{ij}\frac{\partial^2 W}{\partial p_i \partial p_j}, \end{aligned} \quad (17)$$

where we adopted the Stratonovich interpretation and we introduced the effective potential energy $V = V_0 - \sum_{i=1}^{N} \vec{f}_i \cdot \vec{r}_i$. Interestingly, the noise induced drift term is exactly zero since $\sum_{k=1}^{\mathfrak{n}=2n} \sum_{j=1}^{\mathfrak{m}=3N} g_{kj} \frac{\partial g_{ij}}{\partial x_k} = 0$. It means that the Itô, Stratonovich and Hänggi-Klimontovich interpretations coincide for our Hamilton equations. It is a remarkable result that the stochastic differential equations of an arbitrary holonomic system in contact with a thermal bath have a time evolution independent of the adopted stochastic calculus.

A more interesting form of Eq.(17) can be found by introducing the Poisson brackets as follows

$$\frac{\partial W}{\partial t} = \{\mathcal{H}, W\} + \beta\left\{q^k, p_k W\right\} + D a_{ij}\left\{q^i, \left\{q^j, W\right\}\right\}, \quad (18)$$

where we defined the Hamiltonian function as $\mathcal{H} = \frac{1}{2}a^{kh}p_k p_h + V = \frac{1}{2}a^{kh}p_k p_h + V_0 - \sum_{i=1}^{N} \vec{f}_i \cdot \vec{r}_i$. Here, the three terms of drift (Liouville), friction and noise can be easily recognized. This equation can be simply obtained by recalling the definition of Poisson bracket $\{f,g\} = \frac{\partial f}{\partial q^i}\frac{\partial g}{\partial p_i} - \frac{\partial f}{\partial p_i}\frac{\partial g}{\partial q^i}$ [76]. In Eq.(17) or (18) we assume that $q \in \mathcal{A} \subset \mathbb{R}^n$ (configurational space) and $p \in \mathbb{R}^n$. It is worth noticing that a quantum version of Eq.(18) can be found in the literature [37–39].

The asymptotic behavior of Eq.(17) or (18) is characterized by the canonical or Gibbs distribution [84]. Indeed, if the forces $\vec{f}_i$ are constant in time and the integral defining the partition function

$$Z_{st} = \int_{\mathcal{A}} \int_{\mathbb{R}^n} e^{-\frac{\beta}{D}\mathcal{H}(q,p)} dq dp \quad (19)$$

is convergent, then the stationary solution of Eq.(17) or (18) is given by the Gibbs distribution in the phase space

$$W_{st}(q,p) = \frac{1}{Z_{st}} e^{-\frac{\beta}{D}\mathcal{H}(q,p)}. \quad (20)$$

This can be easily proved by substitution. This asymptotic solution allows the identification of the diffusion constant through the expression $D = K_B T\beta$, referred to as Einstein fluctuation-dissipation relation [4, 5]. This result can be further elaborated by considering the explicit expression of the partition function

$$Z_{st} = (2\pi K_B T)^{\frac{n}{2}} \int_{\mathcal{A}} \sqrt{\det(\mathbf{a})} e^{-\frac{V(q)}{K_B T}} dq, \quad (21)$$

leading to

$$W_{st}(q,p) = \frac{e^{-\frac{1}{2}\frac{1}{K_B T}p^T \mathbf{a} p} e^{-\frac{V(q)}{K_B T}}}{(2\pi K_B T)^{\frac{n}{2}} \int_{\mathcal{A}} \sqrt{\det(\mathbf{a})} e^{-\frac{V(q)}{K_B T}} dq}. \quad (22)$$

From the phase-space probability density given in Eq.(22), we can obtain the configurational probability density as $W_c(q) = \int_{\mathbb{R}^n} W_{st}(q,p)dp$. We get

$$W_c(q) = \frac{\sqrt{\det(\mathbf{a})}e^{-\frac{V(q)}{K_B T}}}{\int_{\mathcal{A}} \sqrt{\det(\mathbf{a})}e^{-\frac{V(q)}{K_B T}} dq}. \quad (23)$$

We remark that this reduced configurational density must be written with the essential term $\sqrt{\det(\mathbf{a})}$, which represents the measure element on the differential manifold defined by the metric tensor $\mathbf{a}$.

III. STOCHASTIC THERMODYNAMICS ON THE WHOLE PHASE SPACE

In this Section, we prove the coherence between the non-equilibrium evolution of the system described by the previously introduced Fokker-Planck (or Klein-Kramers) equation with the classical macroscopic thermodynamics. More specifically, we provide evidence that the first and the second principle of the thermodynamics can be directly derived from the previous formalism. As a result, we will obtain explicit expressions for the rate of heat flow and the entropy production. First of all, we define the internal energy $\mathcal{E}$ of the system as the average value of the sum of kinetic energy and potential energy

$$\begin{aligned}\mathcal{E} &= \mathbb{E}\left\{\frac{1}{2}a^{kh}(q)p_k p_h + V_0(q)\right\} \\ &= \int_{\mathbb{R}^n}\int_{\mathcal{A}}\left(\frac{1}{2}a^{kh}p_k p_h + V_0\right)W(q,p,t)dqdp, \quad (24)\end{aligned}$$

and we prove that this quantity is invariant to any change of generalized coordinates and momenta. To do this, we define a second set of generalized coordinates by the transformation $q^i = f^i(\tilde{q})$, which can be written in vector form as $q = f(\tilde{q})$. We define the Jacobian matrix $\mathbf{J}$ with elements $J^i_j = \frac{\partial q^i}{\partial \tilde{q}^j} = \frac{\partial f^i(\tilde{q})}{\partial \tilde{q}^j}$, satisfying the relation $dq = \mathbf{J}d\tilde{q}$ (matrix-vector product). It follows from Eq.(9) that the law of transformation of $\mathbf{a}$ is $\mathbf{a} = \mathbf{J}^{-T}\tilde{\mathbf{a}}\mathbf{J}^{-1}$. Moreover, we have that $\dot{q} = \mathbf{J}\dot{\tilde{q}}$ and, therefore, $p = \mathbf{J}^{-T}\tilde{p}$ (being $p = \mathbf{a}\dot{q}$). For the density W, the transformation is given by the general relation $W(q,p,t)\prod_i\left(dq^i dp_i\right) = \tilde{W}(\tilde{q},\tilde{p},t)\prod_i\left(d\tilde{q}^i d\tilde{p}_i\right)$. Since from previous conclusions we have that $\prod_i dq^i = \det(\mathbf{J})\prod_i d\tilde{q}^i$ and, similarly, $\prod_i dp_i = \det(\mathbf{J}^{-T})\prod_i d\tilde{p}_i$, we directly prove that $\prod_i\left(dq^i dp_i\right) = \prod_i\left(d\tilde{q}^i d\tilde{p}_i\right)$ and, finally, $\tilde{W}(\tilde{q},\tilde{p},t) = W(f(\tilde{q}),\mathbf{J}^{-T}\tilde{q},t)$. These results show that the quantities $K_0 = \frac{1}{2}a^{kh}(q)p_k p_h$ and $\mathcal{E} = \mathbb{E}\{K_0 + V_0\}$ are invariant to the change of coordinates, as expected.

We calculate now the rate of change of the internal energy with respect to the time

$$\frac{d\mathcal{E}}{dt} = \int_{\mathbb{R}^n}\int_{\mathcal{A}}\left(\frac{1}{2}a^{kh}p_k p_h + V_0\right)\frac{\partial W}{\partial t}dqdp. \quad (25)$$

To develop this expression we rewrite the Klein-Kramers equation in the form

$$\frac{\partial W}{\partial t} = -\mathcal{L} - \frac{\partial \mathcal{J}_k}{\partial p_k}, \quad (26)$$

which is equivalent to Eqs.(17) and (18) if we consider

$$\begin{aligned}\mathcal{L} &= \frac{\partial}{\partial q^k}\left(a^{kh}p_h W\right) \quad (27)\\ &\quad -\frac{\partial}{\partial p_k}\left(\frac{1}{2}\frac{\partial a^{ij}}{\partial q^k}p_i p_j W\right) - \frac{\partial}{\partial p_k}\left(\frac{\partial V}{\partial q^k}W\right), \\ \mathcal{J}_k &= -\beta p_k W - K_B T\beta a_{kh}\frac{\partial W}{\partial p_h}. \quad (28)\end{aligned}$$

While $\mathcal{L}$ represents the drift (Liouville) term, the divergence of $\mathcal{J}$ with respect to p represents the interaction with the thermal bath. In the present context, also the temperature T can be considered as an arbitrarily assigned function of time $T(t)$. This is useful to introduce an arbitrary thermodynamic evolution of the system. To begin the calculation, we firstly consider the term

$$\frac{d\mathbb{E}\{V_0\}}{dt} = -\int_{\mathbb{R}^n}\int_{\mathcal{A}} V_0\left(\mathcal{L} + \frac{\partial \mathcal{J}_k}{\partial p_k}\right)dqdp. \quad (29)$$

In order to simplify this kind of integrals we use repeatedly the following properties

$$\int_{\mathbb{R}^n}\int_{\mathcal{A}}\phi\frac{\partial\psi}{\partial p_k}dqdp = -\int_{\mathbb{R}^n}\int_{\mathcal{A}}\psi\frac{\partial\phi}{\partial p_k}dqdp, \quad (30)$$

$$\int_{\mathbb{R}^n}\int_{\mathcal{A}}\phi\frac{\partial\psi}{\partial q^k}dqdp = -\int_{\mathbb{R}^n}\int_{\mathcal{A}}\psi\frac{\partial\phi}{\partial q^k}dqdp. \quad (31)$$

Both expressions derive from the divergence theorem $\int_\Omega \frac{\partial f(x)}{\partial x_k}dx = \int_{\partial\Omega} f(x)\mathbf{n}_k dS$ applied to a product of function $f = \phi\psi$, leading to a sort of multi-dimensional integration by parts (here $\Omega = \mathbb{R}^n \times \mathcal{A}$, $x = (q,p)$, $dx = dqdp$ and $\mathbf{n}$ is the unit normal vector perpendicular to the boundary $\partial\Omega$ of Ω). In Eq.(30), the integral on the boundary is zero since we consider that p_k is defined over the whole real axis and the product $\phi\psi$ tends to zero sufficiently fast for $p_k \to \pm\infty$. In Eq.(31) we have to consider separately variables defined in $\mathbb{R}$ (for example translational variables) and variables defined in a given finite interval (for example rotational variables). For variables $q^k \in \mathbb{R}$, the integral on the boundary is zero since we suppose that $\phi\psi$ tends to zero sufficiently fast for $q^k \to \pm\infty$, as before. On the other hand, for variables q^k defined in a given finite interval, the matrix $a_{kh}(q)$, the density $W(q,p,t)$ and the product $\phi\psi$ are supposed periodic in q^k over its interval of definition (period) and, therefore, the integral on the boundary is zero since it is calculated on the end-points of this period. It is important to realize that these situations cover all the possibilities that we can found in the full description of a holonomic system with arbitrary generalized coordinates.

Anyway, the application of Eq.(30) to Eq.(29) immediately leads to

$$\frac{d\mathbb{E}\{V_0\}}{dt} = -\int_{\mathbb{R}^n}\int_{\mathcal{A}} V_0 \mathcal{L} dqdp. \quad (32)$$

Now, the same argument can be applied to the second and third term of $\mathcal{L}$ (see Eq.(27)), yielding

$$\frac{d\mathbb{E}\{V_0\}}{dt} = -\int_{\mathbb{R}^n}\int_{\mathcal{A}} V_0 \frac{\partial}{\partial q^k}\left(a^{kh}p_h W\right) dqdp. \quad (33)$$

A final application of the property in Eq.(31), leaves us with the first result

$$\frac{d\mathbb{E}\{V_0\}}{dt} = \mathbb{E}\left\{\frac{\partial V_0}{\partial q^k}a^{kh}p_h\right\}. \quad (34)$$

We apply now a similar procedure to the calculation of rate of change of the kinetic energy

$$\frac{d\mathbb{E}\{K_0\}}{dt} = -\int_{\mathbb{R}^n}\int_{\mathcal{A}} \frac{1}{2}a^{kh}p_k p_h \left(\mathcal{L} + \frac{\partial \mathcal{J}_k}{\partial p_k}\right) dqdp, \quad (35)$$

where we use repeatedly Eqs.(30) and (31) to obtain

$$\begin{aligned}\frac{d\mathbb{E}\{K_0\}}{dt} &= \int_{\mathbb{R}^n}\int_{\mathcal{A}}\left(\frac{1}{2}\frac{\partial a^{kh}}{\partial q^r}p_k p_h a^{rt}p_t W\right. \\ &\quad -a^{kr}p_k\frac{1}{2}\frac{\partial a^{ij}}{\partial q^r}p_i p_j W - a^{kr}p_k\frac{\partial V}{\partial q^r}W \\ &\quad \left.-\beta p_k a^{kr}p_r W - \beta K_B T a_{rt}a^{kr}p_k\frac{\partial W}{\partial p_t}\right) dqdp \\ &= \int_{\mathbb{R}^n}\int_{\mathcal{A}}\left(-a^{kr}p_k\frac{\partial V}{\partial q^r}W - \beta p_k a^{kr}p_r W\right. \\ &\quad \left.+\beta K_B T a_{rt}a^{tr}W\right) dqdp \\ &= -\mathbb{E}\left\{a^{kr}p_k\frac{\partial V}{\partial q^r}\right\} - 2\beta\mathbb{E}\{K_0\} + n\beta K_B T. \end{aligned} \quad (36)$$

By adding Eqs.(34) and (36) and by recalling that $V = V_0 - \sum_{i=1}^N \vec{f}_i\cdot\vec{r}_i$, we easily get

$$\frac{d\mathcal{E}}{dt} = \mathbb{E}\left\{a^{kr}p_k\sum_{i=1}^N \vec{f}_i\cdot\frac{\partial\vec{r}_i}{\partial q^r}\right\} - 2\beta\mathbb{E}\{K_0\} + n\beta K_B T. \quad (37)$$

Here, we can remember that $\vec{v}_i = \frac{\partial\vec{r}_i}{\partial q^s}\dot{q}^s = \frac{\partial\vec{r}_i}{\partial q^s}a^{st}p_t$ and the time derivative of the total energy assumes the simpler form

$$\begin{aligned}\frac{d\mathcal{E}}{dt} &= \sum_{i=1}^N \mathbb{E}\left\{\vec{f}_i\cdot\vec{v}_i\right\} + 2\beta\left(\frac{1}{2}nK_B T - \mathbb{E}\{K_0\}\right) \\ &= \frac{d\mathbb{E}\{L\}}{dt} + \frac{d\mathbb{E}\{Q\}}{dt}, \end{aligned} \quad (38)$$

where we can identify the rate of average work $\frac{d\mathbb{E}\{L\}}{dt}$ done on the system with the average power $\sum_{i=1}^N \mathbb{E}\left\{\vec{f}_i\cdot\vec{v}_i\right\}$ and the remaining term with the rate of average heat $\frac{d\mathbb{E}\{Q\}}{dt}$ entering the system. The explicit form of the latter can be easily interpreted as follows: if the average kinetic energy of the system $\mathbb{E}\{K_0\}$ is smaller than its equilibrium value $\frac{1}{2}nK_B T$ given by the equipartition theorem, then we observe a positive heat rate entering the system with a characteristic time $1/\beta$, being β the collision frequency. On the other hand, when $\mathbb{E}\{K_0\} > \frac{1}{2}nK_B T$, we have a negative heat rate leaving the system to thermalize it. This mechanism explains the convergence to the thermodynamic equilibrium through an exchange of heat with the environment, asymptotically leading to the equipartition with a relaxation time related to $1/\beta$. In conclusion, Eq.(38) represents the first principle of the thermodynamics, here obtained for an arbitrary out-of-equilibrium evolution and for an arbitrary holonomic system in contact with a thermal bath described by the Langevin or Fokker-Planck approach.

This energy balance can be also obtained through the following alternative procedure, which is interesting since offers another interpretation of the average heat rate. We consider the stochastic process corresponding to the total energy of the system $K_0 + V_0$. This is different from $\mathcal{E}$, which is its average value (being $\mathcal{E} = \mathbb{E}\{K_0 + V_0\}$). The time derivative of this quantity can be simply written as

$$\frac{d(K_0+V_0)}{dt} = \frac{1}{2}\frac{\partial a^{kh}}{\partial q^r}\dot{q}^r p_k p_h + a^{kh}\dot{p}_k p_h + \frac{\partial V_0}{\partial q^r}\dot{q}^r, \quad (39)$$

and it can be developed by inserting the stochastic Hamilton equations stated in Eqs.(11) and (12). We eventually obtain the expression

$$\begin{aligned}\frac{d(K_0+V_0)}{dt} &= \sum_{i=1}^N \vec{f}_i\cdot\frac{\partial\vec{r}_i}{\partial q^k}a^{kh}p_h - \beta a^{kh}p_k p_h \\ &\quad + \sum_{i=1}^N \sqrt{K_B T\beta m_i}\vec{n}_i\cdot\frac{\partial\vec{r}_i}{\partial q^k}\dot{q}^r, \end{aligned} \quad (40)$$

where, in turn, we can use the relations $a_{kh} = \sum_{i=1}^N m_i\frac{\partial\vec{r}_i}{\partial q^k}\cdot\frac{\partial\vec{r}_i}{\partial q^h}$ and $\vec{v}_i = \frac{\partial\vec{r}_i}{\partial q^s}\dot{q}^s = \frac{\partial\vec{r}_i}{\partial q^s}a^{st}p_t$, and we get

$$\begin{aligned}\frac{d(K_0+V_0)}{dt} &= \sum_{i=1}^N \vec{f}_i\cdot\vec{v}_i - \sum_{i=1}^N m_i\beta\vec{v}_i\cdot\vec{v}_i \\ &\quad + \sum_{i=1}^N \sqrt{K_B T\beta m_i}\vec{n}_i\cdot\vec{v}_i. \end{aligned} \quad (41)$$

This is the stochastic energy balance, where we can easily identify the first term of the r.h.s. with the power of the external forces, or equivalently with dL/dt (not averaged). Moreover, the second and the third terms represent the power of the friction forces and of the noise forces, respectively [see also the last two terms of Eq.(10)]. Therefore, the sum of the second and third terms is equal to dQ/dt (again, not averaged). Furthermore, when we determine the expectation value of Eq.(41), we obtain one more time the first principle of

the thermodynamics where, however, the average heat rate assumes a new form given by

$$\frac{d\mathbb{E}\{Q\}}{dt} = \sum_{i=1}^{N} \mathbb{E}\left\{-m_i\beta\vec{v}_i\cdot\vec{v}_i + \sqrt{K_BT\beta m_i}\vec{n}_i\cdot\vec{v}_i\right\}, \quad (42)$$

which can be identified with the average power of friction and noise terms. Indeed, these terms represent the effect of the thermal bath on the mechanical system and, consequently, the energy exchanged through these mechanisms corresponds to the heat flow between system and environment. Of course, Eq.(42) represents the Sekimoto idea of the microscopic heat rate along a system trajectory [20, 21], here generalized for holonomic systems. While the averaged heat rate expression given in Eq.(42) is characterized by a microscopic interpretation of the Langevin bath, described by its specific friction and noise forces, the heat rate counterpart given in Eq.(38) explicitly describes the macroscopic effect of the interaction with the thermal bath obtained by the Fokker-Planck formalism. Interestingly enough, the comparison of the two heat rate forms immediately leads to the following expression

$$\sum_{i=1}^{N} \mathbb{E}\left\{\sqrt{K_BT\beta m_i}\,\vec{n}_i\cdot\vec{v}_i\right\} = nK_BT\beta, \quad (43)$$

which is an important properties giving the average power of the noise forces and being at the origin of the equipartition law stated in Eq.(38).

In order to substantiate the previous explicit expressions of the heat rate, we investigate now the mathematical form of the second principle of the thermodynamics by introducing the Gibbs entropy of the system as

$$\begin{aligned}\mathcal{S} &= -K_B\mathbb{E}\{\log W\}\\ &= -K_B\int_{\mathbb{R}^n}\int_{\mathcal{A}} W\log W\,dqdp. \end{aligned} \quad (44)$$

It means that the microscopic (non-averaged) entropy along a given system trajectory is defined as $-K_B\log W$, coherently with Refs.[22–24]. First of all, it is important to prove the invariance of the entropy to the changes of coordinates. If we consider a new set of variables $(\tilde{q},\tilde{p})$ with $q = f(\tilde{q})$, the entropy assumes the value $\tilde{\mathcal{S}} = -K_B\int_{\mathbb{R}^n}\int_{\tilde{\mathcal{A}}}\tilde{W}\log\tilde{W}d\tilde{q}d\tilde{p}$. The analysis of the invariance of the internal energy $\mathcal{E}$ delivered the relations $\prod_i\left(dq^idp_i\right) = \prod_i\left(d\tilde{q}^i d\tilde{p}_i\right)$ and $\tilde{W}(\tilde{q},\tilde{p},t) = W(f(\tilde{q}),\mathbf{J}^{-T}\tilde{q},t)$. These results also prove the invariant character of the entropy defined in the whole phase space, as in Eq.(44). This is an important point since we will see that the analysis of the entropy invariance in the reduced configurational space leads to a more complicated issue. Additional comments on this point can be found in Refs.[85–87].

The entropy rate can be elaborated as follows

$$\begin{aligned}\frac{d\mathcal{S}}{dt} &= -K_B\int_{\mathbb{R}^n}\int_{\mathcal{A}}\frac{\partial W}{\partial t}\log W\,dqdp\\ &= K_B\int_{\mathbb{R}^n}\int_{\mathcal{A}}\left(\mathcal{L}+\frac{\partial\mathcal{J}_k}{\partial p_k}\right)\log W\,dqdp. \end{aligned} \quad (45)$$

We firstly calculate $\int_{\mathbb{R}^n}\int_{\mathcal{A}}\mathcal{L}\log W dqdp = \mathcal{A}_1+\mathcal{A}_2+\mathcal{A}_3$ by considering the three terms of $\mathcal{L}$ given in Eq.(27). The first one leads to

$$\begin{aligned}\mathcal{A}_1 &= \int_{\mathbb{R}^n}\int_{\mathcal{A}}\frac{\partial}{\partial q^k}\left(a^{kh}p_hW\right)\log W\,dqdp\\ &= -\int_{\mathbb{R}^n}\int_{\mathcal{A}}a^{kh}p_h\frac{\partial W}{\partial q^k}dqdp\\ &= \int_{\mathbb{R}^n}\int_{\mathcal{A}}\frac{\partial a^{kh}}{\partial q^k}p_hW\,dqdp = \mathbb{E}\left\{\frac{\partial a^{kh}}{\partial q^k}p_h\right\}. \end{aligned} \quad (46)$$

The second one can be developed as follows

$$\begin{aligned}\mathcal{A}_2 &= -\int_{\mathbb{R}^n}\int_{\mathcal{A}}\frac{\partial}{\partial p_k}\left(\frac{1}{2}\frac{\partial a^{ij}}{\partial q^k}p_ip_jW\right)\log W\,dqdp\\ &= \int_{\mathbb{R}^n}\int_{\mathcal{A}}\frac{1}{2}\frac{\partial a^{ij}}{\partial q^k}p_ip_j\frac{\partial W}{\partial p_k}dqdp\\ &= -\int_{\mathbb{R}^n}\int_{\mathcal{A}}\frac{1}{2}\frac{\partial a^{ij}}{\partial q^k}\left(\delta_{ik}p_j+\delta_{jk}p_i\right)W\,dqdp\\ &= -\mathbb{E}\left\{\frac{\partial a^{kh}}{\partial q^k}p_h\right\}, \end{aligned} \quad (47)$$

and the third one gives

$$\begin{aligned}\mathcal{A}_3 &= -\int_{\mathbb{R}^n}\int_{\mathcal{A}}\frac{\partial}{\partial p_k}\left(\frac{\partial V}{\partial q^k}W\right)\log W\,dqdp\\ &= \int_{\mathbb{R}^n}\int_{\mathcal{A}}\frac{\partial V}{\partial q^k}\frac{\partial W}{\partial p_k}dqdp = 0. \end{aligned} \quad (48)$$

In these calculations, we have used several times the properties stated in Eqs.(30) and (31). Summing up, we proved that $\int_{\mathbb{R}^n}\int_{\mathcal{A}}\mathcal{L}\log W dqdp = 0$. We can therefore calculate the second part of Eq.(45) as

$$\begin{aligned}\frac{d\mathcal{S}}{dt} &= K_B\int_{\mathbb{R}^n}\int_{\mathcal{A}}\frac{\partial\mathcal{J}_k}{\partial p_k}\log W\,dqdp\\ &= -K_B\int_{\mathbb{R}^n}\int_{\mathcal{A}}\mathcal{J}_k\frac{1}{W}\frac{\partial W}{\partial p_k}dqdp. \end{aligned} \quad (49)$$

Now, from Eq.(28), we obtain the following expression

$$\frac{\partial W}{\partial p_k} = -\frac{1}{K_BT\beta}\left(a^{kh}\mathcal{J}_h+\beta a^{kh}p_hW\right), \quad (50)$$

which can be substituted in Eq.(49) to yield

$$\begin{aligned}\frac{d\mathcal{S}}{dt} &= \frac{1}{\beta T}\int_{\mathbb{R}^n}\int_{\mathcal{A}}\frac{a^{kh}\mathcal{J}_k\mathcal{J}_h}{W}dqdp\\ &\quad+\frac{1}{T}\int_{\mathbb{R}^n}\int_{\mathcal{A}}a^{kh}\mathcal{J}_kp_h\,dqdp. \end{aligned} \quad (51)$$

In order to give a physical interpretation of the two terms, we further develop the second one by introduc-

ing Eq.(28), as follows

$$\begin{aligned}&\int_{\mathbb{R}^n}\int_{\mathcal{A}} a^{kh}\mathcal{J}_k p_h dqdp\\ &= -\beta\int_{\mathbb{R}^n}\int_{\mathcal{A}} a^{kh}p_k p_h W dqdp\\ &\quad -\beta K_B T\int_{\mathbb{R}^n}\int_{\mathcal{A}} p_h\frac{\partial W}{\partial p_h}dqdp\\ &= 2\beta\left(\frac{1}{2}nK_BT - \mathbb{E}\left\{K_0\right\}\right) = \frac{d\mathbb{E}\left\{Q\right\}}{dt},\end{aligned} \tag{52}$$

where we have identified the rate of exchanged heat as in Eq.(38). Therefore, the entropy balance becomes

$$\frac{d\mathcal{S}}{dt} = \frac{1}{T}\frac{d\mathbb{E}\left\{Q\right\}}{dt} + \frac{1}{\beta T}\int_{\mathbb{R}^n}\int_{\mathcal{A}}\frac{a^{kh}\mathcal{J}_k\mathcal{J}_h}{W}dqdp. \tag{53}$$

First of all, we can observe that the second term (entropy production) is always non-negative since is constituted by a quadratic expression. The explicit expression of the entropy production represents a generalization of previous results [25–30] to the case of holonomic systems. Therefore, we obtain the second principle of the thermodynamics in the classical form

$$\frac{d\mathcal{S}}{dt} \geq \frac{1}{T}\frac{d\mathbb{E}\left\{Q\right\}}{dt}, \tag{54}$$

where the equality is satisfied only for quasi-static transformations, evolving not far from the thermodynamic equilibrium. This statement deserve a more detailed discussion. If we have a thermodynamic transformation that brings the system not far from the equilibrium (namely defined by $T(t) = T_0 + \epsilon\delta T(t)$ and $\vec{f}_i(t) = \vec{f}_{i0} + \eta_i\delta\vec{f}_i(t)$ with small parameters ϵ and $\eta_i, \forall i = 1...N$), the probability density will be a perturbation of the canonical distribution. It means that we can write $W(q,p,t) = W_{st}(q,p) + \epsilon\delta W_T(q,p,t) + \sum_i \eta_i\delta W_i(q,p,t)$ for suitable perturbations $\delta W_T(q,p,t)$ and $\delta W_i(q,p,t)$ (linear response theory). Now, it is not difficult to verify that $\mathcal{J}_k$ is zero when calculated for $W = W_{st}$. Therefore, the fluxes calculated for the perturbed probability density are quantities of the first order in ϵ and $\eta_i, \forall i = 1...N$. Consequently, since the term $\frac{d\mathbb{E}\{Q\}}{dt}$ is a linear function of the fluxes [see Eq.(52)], it will be a first order quantity in ϵ and η_i, as well. On the other hand, the entropy production term is of second order in ϵ and η_i, being a quadratic form of the fluxes. Finally, this proves that the entropy production is negligible with respect to the entropy flow, and we get the classical relation $\frac{d\mathcal{S}}{dt} = \frac{1}{T}\frac{d\mathbb{E}\{Q\}}{dt}$ for quasi-static transformations. In this regards, Eqs.(52) and (53) would be helpful to quantitatively establish if the entropy production is negligible or not depending on the extent of the perturbation.

To conclude, we remark that the results obtained in this Section can be generalized in order to take into consideration an arbitrary number of thermostats. This is useful, e. g., to investigate the thermal conduction in the out-of-equilibrium regime or in the stationary state regime. Two simple examples of constraints are considered below.

A. First example: the simple pendulum

The Hamilton-Langevin equations for a simple pendulum can be easily obtained from Eqs.(11) and (12) in the form

$$\begin{aligned}\dot{\omega} &= -\frac{g}{\ell}\sin\theta - \beta\omega + \sqrt{\frac{K_BT\beta}{m\ell^2}}(n_y\cos\theta - n_x\sin\theta),\\ \dot{\theta} &= \omega,\end{aligned} \tag{55}$$

where ℓ is the length of the pendulum, g is the gravitational acceleration, θ is the angular position measured from a vertical line ($\theta = 0$ at equilibrium) and n_x, n_y are the noise terms ($x = \ell\cos\theta$ is the vertical axis, in the direction of g, $y = \ell\sin\theta$ is the horizontal axis). The Klein-Kramers equation describing the dynamics of $W(\theta,\omega,t)$ for this system can be eventually derived as

$$\frac{\partial W}{\partial t} = \frac{g}{\ell}\sin\theta\frac{\partial W}{\partial\omega} + \beta\frac{\partial}{\partial\omega}(\omega W) - \omega\frac{\partial W}{\partial\theta} + \frac{K_BT\beta}{m\ell^2}\frac{\partial^2 W}{\partial\omega^2}. \tag{56}$$

This result is coherent with Eq.(17) or (18). Unfortunately, due to the nonlinear character of the system, previous equations can not be solved analytically. However, the asymptotic behavior of Eq.(56) is characterized by the canonical or Gibbs distribution given in Eq.(22). Eventually, we obtain

$$W_{st}(\theta,\omega) = \frac{\exp\left(\frac{mg\ell}{K_BT}\cos\theta\right)\exp\left(-\frac{m\ell^2\omega^2}{2K_BT}\right)}{2\pi\ell\sqrt{2\pi mK_BT}I_0\left(\frac{mg\ell}{K_BT}\right)}, \tag{57}$$

where I_n represents the modified Bessel functions of the first kind and of order n. We can also obtain the configurational probability density as in Eq.(23)

$$W_c(\theta) = \frac{\exp\left(\frac{mg\ell}{K_BT}\cos\theta\right)}{2\pi I_0\left(\frac{mg\ell}{K_BT}\right)}. \tag{58}$$

This result can be used to obtain the average value of the vertical position x of the pendulum (average height) as

$$\mathbb{E}\left\{x\right\} = \ell\frac{I_1\left(\frac{mg\ell}{K_BT}\right)}{I_0\left(\frac{mg\ell}{K_BT}\right)}. \tag{59}$$

Of course, we can also prove that the average value of the horizontal position y of the pendulum is always zero: $\mathbb{E}\left\{y\right\} = 0$. To conclude, without external forces applied to the system, the first and second principles can be explicitly written as

$$\frac{d\mathcal{E}}{dt} = 2\beta\left(\frac{1}{2}K_BT - \frac{1}{2}m\ell^2\mathbb{E}\left\{\omega^2\right\}\right), \tag{60}$$

$$\frac{d\mathcal{S}}{dt} \geq \frac{\beta}{T}\left(K_BT - m\ell^2\mathbb{E}\left\{\omega^2\right\}\right), \tag{61}$$

which can be interpreted by means of the equipartition theorem, as discussed above.

B. Second example: the spherical pendulum

We consider now a spherical pendulum described by the standard spherical coordinates θ and ϕ (the z-axis is oriented in the direction of -g). Since the conjugate momenta are $p_\theta = m\ell^2\dot{\theta}$ and $p_\phi = m\ell^2\dot{\phi}\sin^2\theta$, we consider the canonical variables $(\theta, \phi, \omega = \dot{\theta}, \xi = \dot{\phi}\sin^2\theta)$. Accordingly, the Hamilton-Langevin system can be written as follows

$$\begin{aligned}
\dot{\omega} &= -\beta\omega + \frac{g}{\ell}\sin\theta + \xi^2\frac{\cot\theta}{\sin^2\theta} \\
&\quad + \sqrt{\frac{K_BT\beta}{m\ell^2}}(\cos\phi\cos\theta n_x + \sin\phi\cos\theta n_y - \sin\theta n_z), \\
\dot{\theta} &= \omega, \\
\dot{\xi} &= -\beta\xi + \sqrt{\frac{K_BT\beta}{m\ell^2}}(\cos\phi\sin\theta n_y - \sin\phi\sin\theta n_x), \\
\dot{\phi} &= \frac{\xi}{\sin^2\theta}.
\end{aligned} \tag{62}$$

The Klein-Kramers equation describing the dynamics of $W(\theta, \phi, \omega, \xi, t)$ for this system can be eventually derived from Eq.(17) or (18)

$$\begin{aligned}
\frac{\partial W}{\partial t} &= -\left(\frac{g}{\ell}\sin\theta + \xi^2\frac{\cot\theta}{\sin^2\theta}\right)\frac{\partial W}{\partial\omega} + \beta\frac{\partial}{\partial\omega}(\omega W) \\
&\quad + \beta\frac{\partial}{\partial\xi}(\xi W) - \omega\frac{\partial W}{\partial\theta} - \frac{\xi}{\sin^2\theta}\frac{\partial W}{\partial\phi} \\
&\quad + \frac{K_BT\beta}{m\ell^2}\frac{\partial^2 W}{\partial\omega^2} + \frac{K_BT\beta}{m\ell^2}\sin^2\theta\frac{\partial^2 W}{\partial\xi^2}.
\end{aligned} \tag{63}$$

Also in this case the system is strongly nonlinear and general solutions can not be found. Nevertheless, the asymptotic behavior of Eq.(63) is characterized by the canonical distribution given in Eq.(22), which can be explicitly written as

$$\begin{aligned}
W_{st}(\theta, \phi, \omega, \xi) &= \exp\left(-\frac{m\ell^2\omega^2}{2K_BT}\right)\exp\left(-\frac{m\ell^2\xi^2}{2K_BT\sin^2\theta}\right) \\
&\quad \times \frac{m^2g\ell^3\exp\left(-\frac{mg\ell}{K_BT}\cos\theta\right)}{8\pi^2K_B^2T^2\sinh\left(\frac{mg\ell}{K_BT}\right)},
\end{aligned} \tag{64}$$

By using Eq.(23), we can also obtain the configurational probability density as

$$W_c(\theta, \phi) = \frac{mg\ell}{4\pi K_BT}\frac{\sin\theta}{\sinh\left(\frac{mg\ell}{K_BT}\right)}\exp\left(-\frac{mg\ell}{K_BT}\cos\theta\right). \tag{65}$$

For instance, this result can be used to obtain the average value of the vertical position z of the pendulum as

$$\mathbb{E}\{z\} = -\ell\left[\coth\left(\frac{mg\ell}{K_BT}\right) - \frac{K_BT}{mg\ell}\right] = -\ell\mathcal{L}\left(\frac{mg\ell}{K_BT}\right), \tag{66}$$

where $\mathcal{L}(z)$ is the so-called Langevin function. Of course, we can also prove that $\mathbb{E}\{x\} = 0$ and $\mathbb{E}\{y\} = 0$. These results find applications to the physics of polymers [46, 47] and to the micromagnetism [67]. To conclude, without external forces applied to the system, the first and second principles can be explicitly written as

$$\frac{d\mathcal{E}}{dt} = \beta\left(2K_BT - m\ell^2\mathbb{E}\{\omega^2\} - m\ell^2\mathbb{E}\left\{\frac{\xi^2}{\sin^2\theta}\right\}\right), \tag{67}$$

$$\frac{d\mathcal{S}}{dt} \geq \frac{\beta}{T}\left(2K_BT - m\ell^2\mathbb{E}\{\omega^2\} - m\ell^2\mathbb{E}\left\{\frac{\xi^2}{\sin^2\theta}\right\}\right), \tag{68}$$

which, again, can be interpreted by means of the equipartition theorem, as discussed above.

IV. COVARIANT LANGEVIN AND SMOLUCHOVSKI EQUATIONS IN THE CONFIGURATIONAL SPACE OF A HOLONOMIC SYSTEM

In this Section, we will develop the theory for an overdamped system, where the inertial terms are negligible with respect to the friction ones (high friction limit). To begin, we have to reformulate some previous results in a covariant setting. In Eq.(11) and (12) we introduced $3N$ noise terms to drive a holonomic system with n degrees of freedom. In order to elaborate a covariant stochastic thermodynamics for the holonomic systems, it is interesting to write an equivalent Langevin equation with only $n < 3N$ noise terms. To this aim, we propose the system

$$\dot{q}^k = a^{kh}p_h, \tag{69}$$

$$\begin{aligned}
\dot{p}_k &= -\frac{1}{2}\frac{\partial a^{ij}}{\partial q^k}p_ip_j - \frac{\partial V_0}{\partial q^k} + \sum_{i=1}^{N}\vec{f}_i(t)\cdot\frac{\partial\vec{r}_i}{\partial q^k} \\
&\quad -\beta p_k + \sqrt{D}f_{kj}n^j,
\end{aligned} \tag{70}$$

where $f_{kj} = f_{kj}(q)$ are unknown functions and n^j are noise terms defined for $j = 1, ..., n$. To investigate the equivalence between the Langevin equation with $3N$ noise terms and the one with n noise terms, we look at the Fokker-Planck equation associated to Eqs.(69) and (70)

$$\begin{aligned}
\frac{\partial W}{\partial t} &= \{\mathcal{H}, W\} + \beta\{q^k, p_kW\} \\
&\quad + Df_{ik}f_{jh}\delta^{kh}\{q^i, \{q^j, W\}\}.
\end{aligned} \tag{71}$$

In order to have the statistical equivalence we impose the identity between Eqs.(18) and (71) and we get $f_{ik}f_{jh}\delta^{kh} = a_{ij}$, which is equivalent to $\mathbf{f}\mathbf{f}^T = \mathbf{a}$. It means that, given $\mathbf{a}$, the relation $\mathbf{f} = \sqrt{\mathbf{a}}\mathbf{R}$ (for any orthogonal matrix $\mathbf{R}$) fulfills the statistical equivalence. We remark that the square root of any symmetric and positive definite matrix is always well defined. Finally, the Langevin system

$$\dot{q}^k = a^{kh}p_h, \tag{72}$$

$$\begin{aligned}
\dot{p}_k &= -\frac{1}{2}\frac{\partial a^{ij}}{\partial q^k}p_ip_j - \frac{\partial V_0}{\partial q^k} + \sum_{i=1}^{N}\vec{f}_i(t)\cdot\frac{\partial\vec{r}_i}{\partial q^k} \\
&\quad -\beta p_k + \sqrt{D}\left(\sqrt{a}\right)_{kr}R^r_jn^j,
\end{aligned} \tag{73}$$

is statistically equivalent to Eqs.(11) and (12) for any orthogonal matrix $\mathbf{R}$. However, the rotation of noises is irrelevant and later on we will use the simplification $\mathbf{R} = \mathbf{I}_n$.

We write now the final Langevin system in form of a second order differential equation. To do this, we simply determine $\ddot{q}^k$ from Eqs.(72) and we combine it with Eq.(73). We eventually obtain

$$\ddot{q}^k + \left\{ \begin{array}{c} k \\ nm \end{array} \right\} \dot{q}^n \dot{q}^m = -a^{kh} \frac{\partial V_0}{\partial q^h} + a^{kh} \sum_{i=1}^{N} \vec{f}_i(t) \cdot \frac{\partial \vec{r}_i}{\partial q^h} - \beta \dot{q}^k + \sqrt{D} (\sqrt{a^{-1}})^k_r R^r_s n^s. \quad (74)$$

Here, we introduced the identity $a^{kh} \left(\sqrt{a}\right)_{hr} = (\sqrt{a^{-1}})^k_r$, which means that the element (k, r) of $\sqrt{\mathbf{a}^{-1}}$ is given by $(\sqrt{a^{-1}})^k_r$. Moreover, we used the relation $\frac{\partial a^{kh}}{\partial q^i} = -a^{ks} \frac{\partial a_{st}}{\partial q^i} a^{th}$ and the definition of the Christoffel symbol of the second kind [88, 89]

$$\left\{ \begin{array}{c} k \\ nm \end{array} \right\} = \frac{1}{2} a^{kh} \left[\frac{\partial a_{hn}}{\partial q^m} + \frac{\partial a_{hm}}{\partial q^n} - \frac{\partial a_{nm}}{\partial q^h} \right]. \quad (75)$$

We underline that Eq.(74) is a stochastic differential equation fully living on the Riemannian manifold defined by the metric tensor a_{kh}. Without friction ($\beta = 0$), drift ($V_0 = 0$ and $\vec{f}_i = 0 \, \forall i$) and noise ($D = 0$) the equation represents the geodesic curves on the manifold [88, 89]. A wider discussion about Eq.(74) can be found in Ref.[72]. Similar results have been developed to deal with the covariant diffusion processes [87], and the dynamics in spaces with curvature [90–92] and torsion [93].

We are interested here in discussing the overdamped version of Eq.(74). For a non-constrained particle in motion within the three-dimensional space, the dynamic equation is $m \frac{d^2 \vec{r}}{dt^2} = -\frac{\partial V}{\partial \vec{r}} - m\beta \frac{d\vec{r}}{dt} + \sqrt{Dm} \vec{n}$, and for large values of β we can write $m \frac{d\vec{r}}{dt} = -\frac{1}{\beta} \frac{\partial V}{\partial \vec{r}} + \frac{\sqrt{Dm}}{\beta} \vec{n}$, being the inertial term negligible. The same idea can be applied to Eq.(74). However, for holonomic system it is difficult to directly identify the negligible terms for high values of β. Consequently, a more refined procedure allows to obtain a modified version of Eq.(74), which is able to correctly describe an overdamped system with generalized coordinates [72]. The result is

$$\dot{q}^k = -\frac{a^{kh}}{\beta} \frac{\partial V_0}{\partial q^h} + \frac{a^{kh}}{\beta} \sum_{i=1}^{N} \vec{f}_i(t) \cdot \frac{\partial \vec{r}_i}{\partial q^h} - \frac{K_B T}{\beta} a^{st} \left\{ \begin{array}{c} k \\ st \end{array} \right\} - \frac{\partial \chi^k_m}{\partial q^h} \chi^h_n \delta^{nm} + \chi^k_s n^s, \quad (76)$$

where the coefficients $\chi^k_s = \sqrt{\frac{K_B T}{\beta}} (\sqrt{a^{-1}})^k_s$ must be taken into consideration (as above said, we assumed $\mathbf{R} = \mathbf{I}_n$). This equation represents the covariant stochastic thermodynamics of an arbitrary holonomic overdamped system and we will prove its coherence with the principles of the macroscopic thermodynamics. As before, Eq.(76) is written by considering the Stratonovich interpretation. However, it is interesting to observe that its form is simpler if we adopt the Itô formalism. Indeed, we simply have

$$\dot{q}^k \overset{(\text{Itô})}{=} -\frac{a^{kh}}{\beta} \frac{\partial V_0}{\partial q^h} + \frac{a^{kh}}{\beta} \sum_{i=1}^{N} \vec{f}_i(t) \cdot \frac{\partial \vec{r}_i}{\partial q^h} - \frac{K_B T}{\beta} a^{st} \left\{ \begin{array}{c} k \\ st \end{array} \right\} + \sqrt{\frac{K_B T}{\beta}} (\sqrt{a^{-1}})^k_s n^s. \quad (77)$$

Here, to transform Eq.(76) into Eq.(77), we used the transformation rule between the Itô and the Stratonovich formalisms [18, 19, 94, 95]. In particular, if we have the stochastic equation given in Eq.(13), interpreted with the Stratonovich formalism, we can obtain the equivalent equation under the Itô interpretation as follows

$$\frac{dx_i}{dt} \overset{(\text{Itô})}{=} \hat{h}_i(\vec{x}, t) + \sum_{j=1}^{\mathfrak{m}} g_{ij}(\vec{x}, t) n_j(t), \quad (78)$$

where

$$\hat{h}_i(\vec{x}, t) = h_i(\vec{x}, t) + \sum_{k=1}^{\mathfrak{n}} \sum_{j=1}^{\mathfrak{m}} \frac{\partial g_{ij}(\vec{x}, t)}{\partial x_k} g_{kj}(\vec{x}, t) \quad (79)$$

represents the new drift coefficient of the Itô equation (the term added to h to get $\hat{h}$ is sometimes called Wong-Zakai correction, as described in Chapter 3 of Ref.[95]).

In particular, in the context of the Itô formalism, the free motion over the manifold ($V_0 = 0$ and $\vec{f}_i = 0 \, \forall i$) is governed by the simpler equation

$$\dot{q}^k \overset{(\text{Itô})}{=} -\frac{K_B T}{\beta} a^{st} \left\{ \begin{array}{c} k \\ st \end{array} \right\} + \sqrt{\frac{K_B T}{\beta}} (\sqrt{a^{-1}})^k_s n^s, \quad (80)$$

which is the equation defining the Brownian motion on a Riemannian manifold within the mathematical literature [96–99]. Thus, importantly, the classical mathematical definition of the Brownian motion on a manifold exactly corresponds to the overdamped version of the non-equilibrium evolution of a holonomic mechanical system. Probably, for this reason, the Itô interpretation of the stochastic calculus is the more appropriate choice for dealing with the overdamped dynamics of holonomic systems.

We can also analyze the Fokker-Planck equation associated with Eq.(76), which is the so-called Smoluchowski equation for the system. To do this, instead of analysing the dynamics of the actual probability density $W(q, t)$, it is preferable to consider the associated function [100–102]

$$P(q, t) = \frac{1}{\sqrt{\det(\mathbf{a})}} W(q, t). \quad (81)$$

Since $\int_{\mathcal{A}} W dq = 1$, we have $\int_{\mathcal{A}} P \sqrt{\det(\mathbf{a})} dq = 1$, which is more coherent with a covariant setting since we have introduced the measure element $d\mu = \sqrt{\det(\mathbf{a})} dq$, leading to $\int_{\mathcal{A}} P d\mu = 1$. A long but straightforward calculation

based on Eqs.(13) and (16) delivers the covariant Smoluchowski equation

$$\frac{\partial P}{\partial t} = \frac{1}{\beta}\frac{1}{\sqrt{\det(\mathbf{a})}}\frac{\partial}{\partial q^k}\left(a^{kh}\frac{\partial V}{\partial q^h}\sqrt{\det(\mathbf{a})}P\right) + \frac{K_B T}{\beta}\nabla^2 P, \tag{82}$$

where, as before, we introduced the effective potential energy $V = V_0 - \sum_{i=1}^{N} \vec{f}_i \cdot \vec{r}_i$. Moreover, ∇^2 represents the Laplace-Beltrami operator (the equivalent of the standard Laplace operator on a differential manifold), defined as [89]

$$\nabla^2 P = \frac{1}{\sqrt{\det(\mathbf{a})}}\frac{\partial}{\partial q^k}\left(\sqrt{\det(\mathbf{a})}a^{kh}\frac{\partial P}{\partial q^h}\right). \tag{83}$$

If we assume to have time-independent forces $\vec{f}_i$, the covariant Smoluchowski equation exhibits an asymptotic behavior represented by Eq.(23) or, considering Eq.(81), by

$$\begin{aligned} P_c(q) &= \frac{W_c(q)}{\sqrt{\det(\mathbf{a})}} = \frac{e^{-\frac{V(q)}{K_B T}}}{\int_{\mathcal{A}} e^{-\frac{V(q)}{K_B T}}\sqrt{\det(\mathbf{a})}dq} \\ &= \frac{e^{-\frac{V(q)}{K_B T}}}{\int_{\mathcal{A}} e^{-\frac{V(q)}{K_B T}} d\mu}. \end{aligned} \tag{84}$$

This can be easily proved by substitution and further justifies the definition of the quantity P in Eq.(81).

To conclude, if we consider the evolution of a free system ($V = 0$), the Smoluchowski equation collapses into the standard heat equation on a manifold

$$\frac{\partial P}{\partial t} = \frac{K_B T}{\beta}\nabla^2 P. \tag{85}$$

In this particular case, the asymptotic solution is given by the simple expression

$$P_c(q) = \frac{1}{\int_{\mathcal{A}}\sqrt{\det(\mathbf{a})}dq} = \frac{1}{\int_{\mathcal{A}} d\mu}, \tag{86}$$

representing the uniform distribution on the differential manifold ($q \in \mathcal{A}$).

V. STOCHASTIC THERMODYNAMICS ON THE REDUCED CONFIGURATIONAL SPACE

Now, we study the balance equations for energy and entropy under the assumption of overdamped dynamics. Because of this hypothesis, we can identify the internal energy of the system with the potential energy V_0. Indeed, the kinetic energy is not considered here because of the negligible effects of the inertial terms, as discussed in previous Section. As a conclusion, we state that

$$\begin{aligned} \mathcal{E} = \mathbb{E}\{V_0(q)\} &= \int_{\mathcal{A}} V_0(q) W(q,t) dq \\ &= \int_{\mathcal{A}} V_0(q) P(q,t)\sqrt{\det(\mathbf{a})}dq. \end{aligned} \tag{87}$$

It is not difficult to prove that this quantity is invariant to any coordinates transformation. The rate of change of the internal energy is therefore given by

$$\frac{d\mathcal{E}}{dt} = \int_{\mathcal{A}} V_0(q)\frac{\partial P(q,t)}{\partial t}\sqrt{\det(\mathbf{a})}dq. \tag{88}$$

Here, we can use Eq.(82) written in the form of a covariant continuity equation

$$\frac{\partial P}{\partial t} + \mathcal{J}^k_{\|k} = 0, \tag{89}$$

where the symbol $\mathcal{J}^k_{\|k}$ represents the covariant divergence of the flux $\mathcal{J}^k$. More explicitly, we have

$$\frac{\partial P}{\partial t} + \frac{1}{\sqrt{\det(\mathbf{a})}}\frac{\partial}{\partial q^k}\left(\sqrt{\det(\mathbf{a})}\mathcal{J}^k\right) = 0, \tag{90}$$

with a flux

$$\mathcal{J}^k = -\frac{1}{\beta}a^{kh}\frac{\partial V}{\partial q^h}P - \frac{K_B T}{\beta}a^{kh}\frac{\partial P}{\partial q^h}. \tag{91}$$

As before, in order to consider an arbitrary thermodynamic transformation of the overdamped system, we introduce an assigned time-dependent temperature $T(t)$. For an arbitrary function $f(q)$ of the generalized coordinates we have the property

$$\begin{aligned} \frac{d\mathbb{E}\{f(q)\}}{dt} &= \frac{d}{dt}\int_{\mathcal{A}} f(q)W(q,t)dq \\ &= \int_{\mathcal{A}} f(q)\frac{\partial P(q,t)}{\partial t}\sqrt{\det(\mathbf{a})}dq \\ &= -\int_{\mathcal{A}} f(q)\frac{\partial}{\partial q^k}\left(\sqrt{\det(\mathbf{a})}\mathcal{J}^k\right)dq \\ &= \int_{\mathcal{A}} \frac{\partial f(q)}{\partial q^k}\mathcal{J}^k\sqrt{\det(\mathbf{a})}dq. \end{aligned} \tag{92}$$

Therefore, we can write

$$\frac{d\mathcal{E}}{dt} = \int_{\mathcal{A}} \frac{\partial V_0}{\partial q^k}\mathcal{J}^k\sqrt{\det(\mathbf{a})}dq, \tag{93}$$

where we can remember that $V = V_0 - \sum_{i=1}^{N}\vec{f}_i\cdot\vec{r}_i$, or equivalently, $\frac{\partial V_0}{\partial q^k} = \frac{\partial V}{\partial q^k} + \sum_{i=1}^{N}\vec{f}_i\cdot\frac{\partial \vec{r}_i}{\partial q^k} = \frac{\partial V}{\partial q^k} + \tilde{\mathcal{Q}}_k$, being $\tilde{\mathcal{Q}}_k$ the generalized forces $\tilde{\mathcal{Q}}_k = \sum_{i=1}^{N}\vec{f}_i\cdot\frac{\partial\vec{r}_i}{\partial q^k}$, related to the externally applied forces $\vec{f}_i$. We directly obtain that

$$\begin{aligned} \frac{d\mathcal{E}}{dt} &= \int_{\mathcal{A}}\frac{\partial V}{\partial q^k}\mathcal{J}^k\sqrt{\det(\mathbf{a})}dq \\ &\quad + \int_{\mathcal{A}}\tilde{\mathcal{Q}}_k\mathcal{J}^k\sqrt{\det(\mathbf{a})}dq. \end{aligned} \tag{94}$$

We can elaborate the second term as follows

$$\begin{aligned} &\int_{\mathcal{A}}\tilde{\mathcal{Q}}_k\mathcal{J}^k\sqrt{\det(\mathbf{a})}dq \\ &= \sum_{i=1}^{N}\vec{f}_i\cdot\int_{\mathcal{A}}\frac{\partial\vec{r}_i}{\partial q^k}\mathcal{J}^k\sqrt{\det(\mathbf{a})}dq \\ &= \sum_{i=1}^{N}\vec{f}_i\cdot\frac{d\mathbb{E}\{\vec{r}_i\}}{dt} = \frac{d\mathbb{E}\{L\}}{dt}, \end{aligned} \tag{95}$$

where we used the property stated in Eq.(92) once again. So, the energy balance assumes the form of the first principle of the thermodynamics

$$\frac{d\mathcal{E}}{dt} = \sum_{i=1}^{N} \vec{f}_i \cdot \frac{d\mathbb{E}\{\vec{r}_i\}}{dt} + \int_{\mathcal{A}} \frac{\partial V}{\partial q^k} \mathcal{J}^k \sqrt{\det(\mathbf{a})} dq = \frac{d\mathbb{E}\{L\}}{dt} + \frac{d\mathbb{E}\{Q\}}{dt} \tag{96}$$

provided that we identify the rate of heat flux as

$$\frac{d\mathbb{E}\{Q\}}{dt} = \int_{\mathcal{A}} \frac{\partial V}{\partial q^k} \mathcal{J}^k \sqrt{\det(\mathbf{a})} dq. \tag{97}$$

In this case, it is difficult to give a direct physical interpretation of the mathematical form of the heat rate. However, we will give a better explanation of this term by means of a specific example.

As already done in Section III, the energy rate $d\mathcal{E}/dt$ can be also obtained by an alternative procedure. We consider the stochastic process corresponding to the total energy of the system, namely the quantity V_0 (K_0 is negligible because of the overdamped motion assumption). This variable is different from $\mathcal{E}$, which is indeed its average value (being $\mathcal{E} = \mathbb{E}\{V_0\}$). The time derivative of V_0 can be simply written as

$$\frac{dV_0}{dt} = \frac{\partial V_0}{\partial q^i} \dot{q}^i, \tag{98}$$

and it can be developed by inserting the term $\frac{\partial V_0}{\partial q^k}$ taken from the overdamped stochastic equation given in Eq.(76). It means that we can substitute the quantity

$$\frac{\partial V_0}{\partial q^i} = -\beta a_{ik} \dot{q}^k + \sum_{j=1}^{N} \vec{f}_j \cdot \frac{\partial \vec{r}_j}{\partial q^i} - K_B T a_{ik} a^{st} \left\{ \begin{array}{c} k \\ st \end{array} \right\} - \beta a_{ik} \frac{\partial \chi_m^k}{\partial q^h} \chi_n^h \delta^{nm} + \beta a_{ik} \chi_s^k n^s \tag{99}$$

in Eq.(98), eventually obtaining

$$\frac{dV_0}{dt} = -\beta \sum_{j=1}^{N} m_j \vec{v}_j \cdot \vec{v}_j + \sum_{j=1}^{N} \vec{f}_j \cdot \vec{v}_j - K_B T \dot{q}^i a_{ik} a^{st} \left\{ \begin{array}{c} k \\ st \end{array} \right\} - \beta \dot{q}^i a_{ik} \frac{\partial \chi_m^k}{\partial q^h} \chi_n^h \delta^{nm} + \sqrt{K_B T \beta} \dot{q}^i \left(\sqrt{a}\right)_{is} n^s, \tag{100}$$

where we remember that $\chi_s^k = \sqrt{\frac{K_B T}{\beta}} (\sqrt{a^{-1}})_s^k$. Here, it is not difficult to identify the term $\sum_{j=1}^{N} \vec{f}_j \cdot \vec{v}_j$ with the power of the external forces dL/dt (not averaged). Moreover, the other terms must be considered as the microscopic interpretation of the heat rate dQ/dt (again, not averaged). Therefore, if we take into consideration the expected value of Eq.(100), i.e. $d\mathcal{E}/dt$, we obtain a new form for the average heat rate, as follows

$$\frac{d\mathbb{E}\{Q\}}{dt} = \mathbb{E}\left\{ -\beta \sum_{j=1}^{N} m_j \vec{v}_j \cdot \vec{v}_j - \beta \dot{q}^i a_{ik} \frac{\partial \chi_m^k}{\partial q^h} \chi_n^h \delta^{nm} - K_B T \dot{q}^i a_{ik} a^{st} \left\{ \begin{array}{c} k \\ st \end{array} \right\} + \sqrt{K_B T \beta} \dot{q}^i \left(\sqrt{a}\right)_{is} n^s \right\}, \tag{101}$$

where we can identify the first term with the power of the friction and the others with the power of the noise. In particular, the second term is characteristic of the Stratonovich interpretation and the third one represents the curvature of the space induced by the holonomic constraints. This term is important since it makes the theory fully covariant on the differential manifold defined by a_{kh}. Moreover, the last term in Eq.(101) is the specific force×velocity product corresponding to the noises applied to the system. It is interesting to observe that if we adopt the Itô formalism, the previous expression assumes the simpler form

$$\frac{d\mathbb{E}\{Q\}}{dt} \overset{(\text{Itô})}{=} \mathbb{E}\left\{ -\beta \sum_{j=1}^{N} m_j \vec{v}_j \cdot \vec{v}_j - K_B T \dot{q}^i a_{ik} a^{st} \left\{ \begin{array}{c} k \\ st \end{array} \right\} + \sqrt{K_B T \beta} \dot{q}^i \left(\sqrt{a}\right)_{is} n^s \right\}, \tag{102}$$

coherently with Eq.(77) (here we have applied the Wong-Zakai correction [95]). We remark that Eqs.(101) and (102) represent the overdamped counterpart of Eq.(42), obtained for an arbitrary underdamped system. It means that Eq.(102) represents the generalization of the Sekimoto idea [20, 21] in a fully covariant setting.

The time derivative of V_0 in Eq.(98) can be also developed by directly inserting the overdamped stochastic equation given in Eq.(76). The result follows

$$\frac{dV_0}{dt} = -\frac{\partial V_0}{\partial q^k} \frac{a^{kh}}{\beta} \frac{\partial V_0}{\partial q^h} + \frac{a^{kh}}{\beta} \frac{\partial V_0}{\partial q^k} \sum_{i=1}^{N} \vec{f}_i \cdot \frac{\partial \vec{r}_i}{\partial q^h} - \frac{K_B T}{\beta} a^{st} \left\{ \begin{array}{c} k \\ st \end{array} \right\} \frac{\partial V_0}{\partial q^k} - \frac{\partial V_0}{\partial q^k} \frac{\partial \chi_m^k}{\partial q^h} \chi_n^h \delta^{nm} + \frac{\partial V_0}{\partial q^k} \chi_s^k n^s. \tag{103}$$

We can now compare this expression with the development of Eq.(93) with Eq.(91)

$$\frac{d\mathcal{E}}{dt} = -\mathbb{E}\left\{ \frac{\partial V_0}{\partial q^k} \frac{a^{kh}}{\beta} \frac{\partial V_0}{\partial q^h} \right\} + \mathbb{E}\left\{ \frac{a^{kh}}{\beta} \frac{\partial V_0}{\partial q^k} \sum_{i=1}^{N} \vec{f}_i \cdot \frac{\partial \vec{r}_i}{\partial q^h} \right\} - \frac{K_B T}{\beta} \int_{\mathcal{A}} \frac{\partial V_0}{\partial q^k} a^{kh} \frac{\partial P}{\partial q^h} \sqrt{\det(\mathbf{a})} dq. \tag{104}$$

The third term $\mathcal{T}$ of the r.h.s. of this relation can be

further elaborated as follows

$$\begin{aligned}\mathcal{T} &= -\frac{K_B T}{\beta}\int_{\mathcal{A}} \frac{\partial V_0}{\partial q^k} a^{kh} \frac{\partial P}{\partial q^h}\sqrt{\det(\mathbf{a})}dq \\ &= \frac{K_B T}{\beta}\int_{\mathcal{A}} \frac{\partial}{\partial q^h}\left(\frac{\partial V_0}{\partial q^k} a^{kh}\sqrt{\det(\mathbf{a})}\right) P dq \\ &= \frac{K_B T}{\beta}\mathbb{E}\left\{\frac{\partial^2 V_0}{\partial q^k \partial q^h} a^{kh}\right\} \\ &\quad + \frac{K_B T}{\beta}\mathbb{E}\left\{-\frac{\partial V_0}{\partial q^k} a^{ks}\frac{\partial a_{st}}{\partial q^h} a^{th} + \frac{1}{2}\frac{\partial V_0}{\partial q^k} a^{kh} a^{ij}\frac{\partial a_{ij}}{\partial q^h}\right\},\end{aligned} \tag{105}$$

where we used the properties giving the derivative of measure element $\partial\sqrt{\det(\mathbf{a})}/\partial q_h = (1/2)\sqrt{\det(\mathbf{a})}a^{ij}\partial a_{ij}/\partial q^h$ and the derivative of the inverse metric tensor $\partial a^{kh}/\partial q^i = -a^{ks}(\partial a_{st}/\partial q^i)a^{th}$. In the last term of Eq.(105), it is possible to recognize a Christoffel symbol, defined in Eq.(75), eventually obtaining

$$\begin{aligned}\mathcal{T} &= \frac{K_B T}{\beta}\mathbb{E}\left\{\frac{\partial^2 V_0}{\partial q^k \partial q^h} a^{kh}\right\} \\ &\quad - \frac{K_B T}{\beta}\mathbb{E}\left\{\frac{\partial V_0}{\partial q^k} a^{ij}\left\{\begin{array}{c} k \\ ij \end{array}\right\}\right\}.\end{aligned} \tag{106}$$

The comparison of Eq.(104) with the average value of Eq.(103) gives finally the relation

$$\begin{aligned}&\mathbb{E}\left\{\frac{\partial V_0}{\partial q^k}\chi_s^k n^s - \frac{\partial V_0}{\partial q^k}\frac{\partial \chi_m^k}{\partial q^h}\chi_n^h \delta^{nm}\right\} \\ &\quad = \frac{K_B T}{\beta}\mathbb{E}\left\{\frac{\partial^2 V_0}{\partial q^k \partial q^h} a^{kh}\right\},\end{aligned} \tag{107}$$

which can be written in the Itô formalism as follows

$$\mathbb{E}\left\{\frac{\partial V_0}{\partial q^k}(\sqrt{a^{-1}})_s^k n^s\right\} \overset{\text{(Itô)}}{=} \sqrt{\frac{K_B T}{\beta}}\mathbb{E}\left\{\frac{\partial^2 V_0}{\partial q^k \partial q^h} a^{kh}\right\}. \tag{108}$$

The properties stated in Eqs.(107) and (108) represent specific results holding for overdamped holonomic systems and can be viewed as particular virial theorems for the noise term, as we will discuss in a specific solvable model in the following Section.

Now, in order to give a more complete thermodynamic picture, and to further corroborate Eq.(97), we try to obtain the entropy balance for the system. At first glance, the natural generalization of Eq.(44) for overdamped systems, could be considered as

$$\begin{aligned}\mathcal{S}_0 &= -K_B \mathbb{E}\{\log W\} \\ &= -K_B \int_{\mathcal{A}} W \log W dq.\end{aligned} \tag{109}$$

We firstly verify if this proposal is invariant to any change of generalized coordinates. To do this, we recall that if $q = f(\tilde{q})$ we get $dq = \mathbf{J}d\tilde{q}$ (matrix-vector product), where $J_j^i = \frac{\partial q^i}{\partial \tilde{q}^j} = \frac{\partial f^i(\tilde{q})}{\partial \tilde{q}^j}$. For the density W, the transformation is given by the general relation $W(q,t)\prod_i (dq^i) = \tilde{W}(\tilde{q},t)\prod_i (d\tilde{q}^i)$. Since from previous results we have $\prod_i dq^i = \det(\mathbf{J})\prod_i d\tilde{q}^i$, we directly prove that $\tilde{W}(\tilde{q},t) = \det(\mathbf{J})W(f(\tilde{q}),t)$. We conclude that $\tilde{\mathcal{S}}_0 = \int_{\tilde{\mathcal{A}}}\tilde{W}\log\tilde{W}d\tilde{q} = \int_{\mathcal{A}} W\log[W\det(\mathbf{J})]\,dq$. And finally, we have the difference $\tilde{\mathcal{S}}_0 - \mathcal{S}_0 = \int_{\mathcal{A}} W\log[\det(\mathbf{J})]\,dq$, which proves that the proposed entropy definition is not invariant to the change of generalized coordinates. This point is also discussed in Refs.[85–87]. A more convenient definition in a covariant setting is the following

$$\begin{aligned}\mathcal{S} &= -K_B \mathbb{E}\{\log P\} \\ &= -K_B \int_{\mathcal{A}} P\log P\sqrt{\det(\mathbf{a})}dq \\ &= -K_B \int_{\mathcal{A}} P\log P d\mu.\end{aligned} \tag{110}$$

We can prove its invariance to the change of generalized coordinates as follows. We previously obtained the law of transformation of $\mathbf{a}$ as $\mathbf{a} = \mathbf{J}^{-T}\tilde{\mathbf{a}}\mathbf{J}^{-1}$. Then, we easily get $\sqrt{\det(\tilde{\mathbf{a}})} = \det(\mathbf{J})\sqrt{\det(\mathbf{a})}$, or equivalently, the invariance of the measure elements $\sqrt{\det(\tilde{\mathbf{a}})}d\tilde{q} = \sqrt{\det(\mathbf{a})}dq$. In addition, from $\tilde{W}(\tilde{q},t) = \det(\mathbf{J})W(f(\tilde{q}),t)$ and the definition $W(q,t) = P(q,t)\sqrt{\det(\mathbf{a})}$, we deduce that also the density P is invariant under coordinates transformations: $\tilde{P}(\tilde{q},t) = P(f(\tilde{q}),t)$. The invariance of the density P and of the measure element finally proves the invariance of the entropy defined in Eq.(110). We have therefore proved that the configurational entropy for overdamped systems must be correctly defined as in Eq.(110) to preserve the covariant character of the theory.

We study the time evolution of $\mathcal{S}$ through the expression

$$\frac{d\mathcal{S}}{dt} = -K_B\int_{\mathcal{A}}\frac{\partial P}{\partial t}\log P\sqrt{\det(\mathbf{a})}dq, \tag{111}$$

which can be elaborated with Eqs.(90) and (91). Straightforward calculations yield

$$\begin{aligned}\frac{d\mathcal{S}}{dt} &= K_B\int_{\mathcal{A}}\frac{\partial}{\partial q^k}\left(\sqrt{\det(\mathbf{a})}\mathcal{J}^k\right)\log P dq \\ &= -K_B\int_{\mathcal{A}}\frac{1}{P}\frac{\partial P}{\partial q^k}\mathcal{J}^k\sqrt{\det(\mathbf{a})}dq,\end{aligned} \tag{112}$$

where we can substitute the derivative $\frac{\partial P}{\partial q^k}$ obtained from Eq.(91). This procedure delivers

$$\begin{aligned}\frac{d\mathcal{S}}{dt} &= \frac{1}{T}\int_{\mathcal{A}}\mathcal{J}^k\frac{\partial V}{\partial q^k}\sqrt{\det(\mathbf{a})}dq \\ &\quad + \frac{\beta}{T}\int_{\mathcal{A}} a_{kh}\mathcal{J}^k\mathcal{J}^h\frac{\sqrt{\det(\mathbf{a})}}{P}dq,\end{aligned} \tag{113}$$

where in the first term we can be easily identify the heat rate given in Eq.(97), by obtaining the final form of the entropy balance as

$$\frac{d\mathcal{S}}{dt} = \frac{1}{T}\frac{d\mathbb{E}\{Q\}}{dt} + \frac{\beta}{T}\int_{\mathcal{A}} a_{kh}\mathcal{J}^k\mathcal{J}^h\frac{\sqrt{\det(\mathbf{a})}}{P}dq. \tag{114}$$

As before, we can observe that the second term describing the entropy production is always non-negative and we obtain the second principle of the thermodynamics in the classical form

$$\frac{d\mathcal{S}}{dt} \geq \frac{1}{T}\frac{d\mathbb{E}\left\{Q\right\}}{dt}, \tag{115}$$

where the equality is satisfied only for quasi-static transformations (the proof of this property is similar to the one proposed for underdamped systems). Finally, we proved the principles of the thermodynamics also within the formalism adopted for overdamped holonomic systems. Interestingly enough, we remark that if we had considered the first (non-covariant) entropy definition given in Eq.(109), we would have found the following result

$$\frac{d\mathcal{S}_0}{dt} = \frac{1}{T}\frac{d\mathbb{E}\left\{Q\right\}}{dt} + \frac{\beta}{T}\int_{\mathcal{A}} a_{kh}\mathcal{J}^k\mathcal{J}^h\frac{\sqrt{\det(\mathbf{a})}}{P}dq - K_B\frac{d}{dt}\mathbb{E}\left\{\log\sqrt{\det(\mathbf{a})}\right\}, \tag{116}$$

where the third term has no physical interpretation and could be named geometric entropy rate. This is another confirmation of the validity of Eq.(110), which must be used in place of Eq.(109).

A. Analytically solvable model

We consider here a quite simple example of overdamped system, which can be solved analytically. It is useful to better understand the theoretical results of this Section. We considered a simple linear system since we can obtain the general solution through the classical Ornstein-Uhlenbeck process [103, 104]. Unfortunately more complex systems with constraints can not be solved analytically. Anyway, the aim of this example is to better explain the behavior of overdamped systems, even if not subjected to holonomic constraints. We analyze a one-dimensional harmonic oscillator with an externally applied force f, under the assumption of overdamped motion. Therefore, we define $V_0(x) = \frac{1}{2}m\omega^2x^2$ and the overdamped Langevin equation [see Eq.(76) or (77)] can be written as

$$\frac{dx}{dt} = -\frac{\omega^2}{\beta}x + \frac{f}{m\beta} + \sqrt{\frac{K_BT}{m\beta}}n. \tag{117}$$

As anticipated above, this model can be simply solved since it is described by a classical Ornstein-Uhlenbeck process [103, 104]. Accordingly, the average value $\bar{x}$ of x and its variance Σ follow the differential equations

$$\frac{d\bar{x}}{dt} = -\frac{\omega^2}{\beta}\bar{x} + \frac{f}{m\beta}, \tag{118}$$

$$\frac{d\Sigma}{dt} = -2\frac{\omega^2}{\beta}\Sigma + \frac{2K_BT}{m\beta}. \tag{119}$$

We solve these equations with the initial conditions $\bar{x}(0) = 0$ and $\Sigma(0) = 0$ (deterministic initial state) by assuming a constant applied force f, and we eventually find

$$\bar{x} = \frac{f}{m\omega^2}\left(1 - e^{-\frac{\omega^2}{\beta}t}\right), \tag{120}$$

$$\Sigma = \frac{K_BT}{m\omega^2}\left(1 - e^{-2\frac{\omega^2}{\beta}t}\right). \tag{121}$$

In this particular case, we have that the probability density W of x corresponds to a Gaussian function with average $\bar{x}$ and variance Σ (of course, we also have $P = W/\sqrt{m}$), i.e,

$$W(x) = \frac{1}{\sqrt{2\pi\Sigma}}\exp\left[-\frac{1}{2\Sigma}\left(x - \bar{x}\right)^2\right]. \tag{122}$$

Concerning the energy balance we can easily determine $\frac{d\mathbb{E}\{Q\}}{dt}$ by means of Eq.(97). With the help of Eq.(91), this heat rate can be written as follows for our specific model

$$\frac{d\mathbb{E}\left\{Q\right\}}{dt} = -\frac{1}{m\beta}\left[m^2\omega^4(\Sigma + \bar{x}^2) - 2m\omega^2\bar{x}f + f^2\right] + \frac{K_BT\omega^2}{\beta}. \tag{123}$$

Therefore, by using the solutions obtained in Eqs.(120) and (121), we get

$$\frac{d\mathbb{E}\left\{Q\right\}}{dt} = \frac{2\omega^2}{\beta}\left(\frac{1}{2}K_BT - \frac{1}{2}\frac{f^2}{m\omega^2}\right)e^{-2\frac{\omega^2}{\beta}t}, \tag{124}$$

which allows us to obtain the total heat ΔQ entering the system during the process

$$\Delta Q = \int_0^{+\infty}\frac{d\mathbb{E}\left\{Q\right\}}{dt}dt = \frac{1}{2}K_BT - \frac{1}{2}\frac{f^2}{m\omega^2}, \tag{125}$$

This result can be interpreted as follows: the first term $\frac{1}{2}K_BT$ represents the heat entering the system in order to add the suitable thermal fluctuation to the potential energy of the harmonic oscillator (note indeed that the system has no thermal perturbations for $t = 0$). The second term $\frac{1}{2}\frac{f^2}{m\omega^2}$ represents the dissipation during the relaxation of the system towards the thermodynamic equilibrium. Indeed, this value exactly corresponds to the work done by the friction force $-m\beta\frac{dx}{dt}$ during the whole process, and appears as heat leaving the system. The total heat ΔQ is therefore positive or negative depending on the sign of $\frac{1}{2}K_BT - \frac{1}{2}\frac{f^2}{m\omega^2}$, which is fixed once all parameters are defined. The two terms describing thermal fluctuations and dissipation are however completely independent and there is no dynamic compensation between them, as described by Eq.(38) for the underdamped systems. In this overdamped case, the dynamic compensation is replaced by the exponential behavior described in Eq.(124). The rate of work done by f is easily determined as

$$\frac{d\mathbb{E}\left\{L\right\}}{dt} = \mathbb{E}\left\{f\frac{dx}{dt}\right\} = f\frac{d\bar{x}}{dt} = \frac{f^2}{m\beta}e^{-\frac{\omega^2}{\beta}t}, \tag{126}$$

and the total work ΔL done by f is therefore given by

$$\Delta L = \int_0^{+\infty} \frac{d\mathbb{E}\{L\}}{dt} dt = \frac{f^2}{m\omega^2}. \tag{127}$$

By adding the two contributions in Eqs.(124) and (126), we obtain the time derivative of the average total energy in the form

$$\frac{d\mathbb{E}\{\mathcal{E}\}}{dt} = \left[\frac{f^2}{m\beta} \left(1 - e^{-\frac{\omega^2}{\beta}t}\right) + \frac{\omega^2 K_B T}{\beta} e^{-\frac{\omega^2}{\beta}t} \right] e^{-\frac{\omega^2}{\beta}t}. \tag{128}$$

Since $\mathbb{E}\{\mathcal{E}\} = 0$ for $t = 0$, we can directly integrate Eq.(128), eventually obtaining

$$\mathbb{E}\{\mathcal{E}\} = \frac{f^2}{2m\omega^2} \left(1 - e^{-\frac{\omega^2}{\beta}t}\right)^2 + \frac{K_B T}{2} \left(1 - e^{-2\frac{\omega^2}{\beta}t}\right), \tag{129}$$

which, in turn, delivers the energy variation ΔE during the process, which also corresponds to the asymptotic energy as

$$\Delta E = \lim_{t\to\infty} \mathbb{E}\{\mathcal{E}\} = \frac{f^2}{2m\omega^2} + \frac{K_B T}{2} = V_0(x_{eq}) + \frac{K_B T}{2}, \tag{130}$$

where we defined $x_{eq} = \lim_{t\to\infty} \bar{x}(t)$ as the equilibrium position with the applied force f. This quantity describes the potential energy of the equilibrium point plus its thermal perturbation. It means that the term $\frac{K_B T}{2}$ in Eq.(130) represents the fluctuations of the potential energy (equipartition for one degree of freedom) and not the fluctuations of the kinetic energy, which are not considered in the overdamped scheme. We underline that in the underdamped case we would have $\Delta E = V_0(x_{eq}) + K_B T$ since the total energy contains also the fluctuations of the kinetic energy which are represented by another equipartition term $\frac{K_B T}{2}$. The thermodynamics coherence of the overdamped Langevin approach is therefore preserved provided that we remember to have neglected the inertial and kinetic effects. We also remark that the total work done on the system is split in two equal contributions, namely dissipation and stored energy. The results given in Eqs.(128) and (129) have been also validated by the direct integration stated in Eqs.(87) and (88), performed by using the Gaussian probability density of the present Ornstein-Uhlenbeck process [see Eq.(122)].

We analyze the meaning of Eqs.(101) and (102) in the context of the present application. If we multiply Eq.(117) by the velocity dx/dt, we easily get

$$-\beta m \left(\frac{dx}{dt}\right)^2 + \sqrt{K_B T m \beta} \frac{dx}{dt} n = \frac{m\omega^2}{2} \frac{d}{dt} x^2 - f \frac{dx}{dt}. \tag{131}$$

Now, we can average this relation by using the property $\mathbb{E}\left\{x^2\right\} = \Sigma - \bar{x}^2$ and Eqs.(120) and (121). We eventually obtain

$$\mathbb{E}\left\{ -\beta m \left(\frac{dx}{dt}\right)^2 + \sqrt{K_B T m \beta} \frac{dx}{dt} n \right\} = \frac{2\omega^2}{\beta} \left(\frac{1}{2} K_B T - \frac{1}{2} \frac{f^2}{m\omega^2} \right) e^{-2\frac{\omega^2}{\beta}t}, \tag{132}$$

where the r.h.s. can be identified with the heat rate $\frac{d\mathbb{E}\{Q\}}{dt}$ given in Eq.(124). Therefore, Eqs.(101) and (102) have been confirmed for this specific case and they represent the average heat rate as the average power of the friction and noise forces.

Also, we can better elucidate the meaning of Eqs.(107) and (108). To do this, we multiply Eq.(117) by x, and we easily get

$$\sqrt{K_B T m \beta} x n = \frac{m\beta}{2} \frac{d}{dt} x^2 + m\omega^2 x^2 - f x. \tag{133}$$

As before, averaging Eq.(133) and using the relation $\mathbb{E}\left\{x^2\right\} = \Sigma - \bar{x}^2$ and Eqs.(120) and (121), we get

$$\mathbb{E}\{xn\} = \sqrt{\frac{K_B T}{\beta m}}, \tag{134}$$

which is valid at any time t. This result exactly corresponds to Eqs.(107) and (108) with $V_0(x) = \frac{1}{2} m\omega^2 x^2$ and represents a sort of virial theorem for the stochastic force applied to the particle (dealing indeed with the force-position product).

Concerning the entropy balance, by using the Gaussian density in Eq.(122), we determine the entropy value $\frac{1}{2} K_B \log(2\pi e \Sigma)$ and its time derivative

$$\frac{d\mathcal{S}}{dt} = \frac{K_B \omega^2}{\beta} \frac{e^{-2\frac{\omega^2}{\beta}t}}{1 - e^{-2\frac{\omega^2}{\beta}t}}. \tag{135}$$

Since we know the rate of entropy flow

$$\frac{d\mathcal{S}_f}{dt} = \frac{1}{T} \frac{d\mathbb{E}\{Q\}}{dt} = \frac{2\omega^2}{\beta T} \left(\frac{1}{2} K_B T - \frac{1}{2} \frac{f^2}{m\omega^2} \right) e^{-2\frac{\omega^2}{\beta}t}, \tag{136}$$

calculated on the basis of Eq.(124), we can simply obtain the rate of entropy production as follows

$$\frac{d\mathcal{S}_p}{dt} = \frac{d\mathcal{S}}{dt} - \frac{d\mathcal{S}_f}{dt} = \frac{\omega^2}{\beta T} \left(\frac{f^2}{m\omega^2} + \frac{K_B T}{\beta} \frac{e^{-2\frac{\omega^2}{\beta}t}}{1 - e^{-2\frac{\omega^2}{\beta}t}} \right) e^{-2\frac{\omega^2}{\beta}t}, \tag{137}$$

which is always positive, as expected. The same result can be obtained by performing the integral appearing in Eq.(114). To conclude, in this Section, we have shown the behavior of the main quantities involved in the description of the stochastic thermodynamics within the reduced configurational space for a simple paradigmatic system. Through this example, the meaning of the different quantities should be clearer and their physical interpretation more precise.

VI. CONCLUSIONS

In this work we developed the concept of stochastic thermodynamics for holonomic systems. The main difficulty to overcome in approaching this issue is that the mechanical constraints describing an holonomic system generate a configurational phase space which has the natural character of a Riemannian manifold. Therefore, all evolution equations live in this differential manifold, defined by the metric tensor of the holonomic structure. By working in this mathematical environment, we described the main features of the stochastic thermodynamics in both the underdamped and overdamped hypotheses. In particular, we have shown the coherence between the Langevin approach, here applied to holonomic systems, with the two principles of thermodynamics giving the balance equations for energy and entropy. In the underdamped case, the Klein-Kramers equation, stated in Eq.(18), is written in terms of the Poisson brackets and exhibits the Gibbs distribution as asymptotic solution when the thermodynamic equilibrium can be reached. On the other hand, during the out-of-equilibrium regime, the first and the second principle are given in Eqs.(38) and (53). In the first one, the Sekimoto concept of heat along a trajectory is generalized to holonomic constraints, and in the second one, the entropy production is explicitly written in terms of the metric tensor of the system. Concerning the overdamped case, we obtained the covariant Langevin and Smoluchovski equations, stated in Eqs.(76) and (82), which rigorously represent a Brownian motion on a differential manifold. The Smoluchovski equation allowed us to obtain the energy and entropy balances for overdamped holonomic systems [see Eq.(96) and (114)]. Importantly, when working within the reduced configurational space, the entropy definition must be suitably modified to be covariant or, equivalently, to be invariant under coordinates transformations.

Coherently with the sentence by van Kampen [105] "The question of the existence and correct form of equations describing Brownian motion on a manifold cannot be answered by mathematics alone, but requires a study of the underlying physics", we developed the mathematical formalism for holonomic systems by combining the Lagrange and Hamilton equations with the Langevin approach. The formulation introduced in this paper will be used to further investigate the out-of-equilibrium (or the stationary state) regime and the fluctuation theorems in the context of holonomic systems, which are important mechanical configurations to model realistic physical structures ranging from soft matter and biophysics to condensed matter and nano-technology.

AUTHOR CONTRIBUTION STATEMENT

S.G. conceived and performed the research, and wrote the manuscript.

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