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Stochastic thermodynamics of systems with a continuous space of states

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We analyze the stochastic thermodynamics of systems with a continuous space of states. The evolution equation, the rate of entropy production, and other results are obtained by a continuous time limit of a discrete time formulation. We point out the role of time reversal and of the dissipation part of the probability current on the production of entropy. We show that the rate of entropy production is a bilinear form in the components of the dissipation probability current with coefficients being the components of the precision matrix related to the Gaussian noise. We have also analyzed a type of noise that makes the energy function to be strictly constant along the stochastic trajectory, being appropriate to describe an isolated system. This type of noise leads to nonzero entropy production and thus to an increase of entropy in the system. This result contrasts with the invariance of the entropy predicted by the Liouville equation, which also describes an isolated system.

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I. INTRODUCTION

The microscopic theory of systems in thermodynamic equilibrium as advanced by Gibbs is based on the following assumptions. An energy function is defined on the phase space, which is the space of the positions and velocities of the elementary constituents of the system. A probability distribution is assigned to the phase space that depends on the positions and velocity *only* through the energy function. The entropy is directly related to the probability distribution and is a generalization of the Boltzmann entropy. As a consequence of these assumptions, the entropy becomes a function of the mean energy from which it is possible to define temperature by the Clausius relation, and derive the laws of equilibrium thermodynamics.

The Gibbs probability distribution does not properly characterize the thermodynamic equilibrium in a dynamic sense but is a necessary condition for equilibrium. The appropriate dynamic characterization of thermodynamic equilibrium is provided by the stochastic thermodynamics [1–5]. Within this approach, thermodynamic equilibrium occurs when the probability of occurrence of any trajectory equals the probability of occurrence of its time-reversal trajectory. This condition is also known as microscopic reversibility or detailed balance condition and is translated as the absence of entropy production. As a consequence, the net current of any type, such as heat current, will be absent, a property that provides meaning to thermodynamic equilibrium in a dynamic sense.

The distinguishing feature of the stochastic approach to thermodynamics is the microscopic definition of the rate of entropy production. Based on the macroscopic bilinear relation between entropy production and thermodynamic forces and affinities, Schnakenberg [6] proposed a microscopic expression for the entropy production of systems described by a master equation. The time variation of the entropy of these systems was shown to have two parts, one of them being the production of entropy, given by the Schnakenberg expression, and the other being the entropy flux Φ [7–10]. The essential feature of the entropy production is its straight relationship with the irreversibility processes as expressed by the time-reversal symmetry [11]. The entropy production is also directly related to probability current so that in a nonequilibrium steady state these two quantities are nonvanishing [12–15]. The role of fluctuation theorems has also been addressed within the stochastic thermodynamics [16–18]. The entropy production was calculated for molecular motors [19], in chemical reaction networks [16,20], to determine the efficiency at maximum power [21], and in systems connected to multiple reservoirs [2,5]. It was also determined in irreversible interacting particle system where this quantity was shown to display a singular behavior at the transition point [10,22–24].

A formulation of stochastic thermodynamics for a continuous system has also been developed, in which case the stochastic evolution equation is the Fokker-Planck equation. It is assumed, usually in an implicit form, that the time-reversal trajectory is identified as the reverse trajectory, which is also the case of systems described by a master equation examined above. This approach is appropriate for overdamped continuous systems [25]. For one particle, the expression for the rate of entropy production is proportional to the square of the probability current. However, the application to a system that reaches a non-equilibrium steady state, an extension of this expression is needed and in fact, it has been advanced [26–29].

For underdamped continuous systems, the reverse trajectory is no longer identified with the time-reversal trajectory and an adequate formulation should be employed [25]. For a system described by a Fokker-Planck-Kramers equation, which is the stochastic equation appropriate for particles with inertia, it has been found that the rate of entropy production is related to just one part of the probability current [1,30,31], called, for this reason, the dissipation probability current.

The present approach describes underdamped systems, that is, system consisting of particles with inertia, with a continuous space of states. We focus on the production of entropy, understood as related to the probability of occurrence of a trajectory and its time reversal. When these two probabilities are equal we meet the condition for the thermodynamic equilibrium. Defining the production of entropy as the logarithm of the ratio of these two probabilities, it vanishes in thermodynamic equilibrium.

We consider systems consisting of interacting particles evolving according to the laws of classical mechanics. In addition to the deterministic forces, the system is also subject to random forces so that the representative point in the space of states describes a continuous stochastic trajectory. The deterministic force is a sum of a time-reversal force and a force that lacks this property and is identified as the dissipative force. The evolution equation is a continuity equation for the probability density whose current is split into two parts. One of them is the ordinary current related to the time-reversal force. The other is the dissipative probability current related to the dissipative force and the noise.

The evolution equation in the continuous space of states and other properties are obtained by starting from a discrete time formulation and then taking the continuous time limit. In this sense the present method is distinct from the previous similar methods [25,31]. Our main result is the expression for the rate of entropy production obtained from a discrete time expression of the production of entropy. The continuous time limit gives for the rate of entropy production a bilinear form in the components of the dissipative probability current which is positive definite. The vanishing of the dissipative probability current leads to no entropy production characterizing the thermodynamic equilibrium.

We analyze in detail two types of noises. One of them is the usual noise that describes the contact of a system with a heat reservoir. The other type makes the energy function to be strictly constant along a stochastic trajectory in phase space and thus describes an isolated system. There is no flux of entropy and the time variation of the entropy is entirely due to the generation of entropy inside the system. This result is distinct from that given by the Liouville equation which predicts an invariance of the entropy in time and no production of entropy, although this equation describes an isolated system.

It is convenient to regard the systems out of equilibrium as belonging in one of two classes. One of them includes the systems that are out of equilibrium because they have not yet relaxed to the equilibrium state. The other class includes those systems that are permanently out of equilibrium even when they have already relaxed to the stationary state. In this last case, entropy are permanently being produced by the system, a feature that characterizes an out of equilibrium state.

Differently from the energy, which is a conserved quantity, the entropy is not a conserved quantity but it cannot decrease, which is a brief statement of the second law of thermodynamics. Being a conserved quantity the increase of energy per unit time is given by

$$\frac{dU}{dt} = \Phi_u, \tag{1}$$

where Φ_u is the rate at which energy is being introduced into the system. The entropy increase per unit time, however, is given by

$$\frac{dS}{dt} = \Pi - \Phi, \tag{2}$$

where Φ is the rate at which entropy is being delivered to outside and Π is the entropy production and obeys the inequality $\Pi \geqslant 0$, a brief statement of the second law of thermodynamics.

The approach we use here starts with the discrete expression of the rate of the entropy production to reach the expression for continuous systems by taking the continuous time limit. Other approaches already consider the system to be continuous in time and start from the expression for the entropy flux defined as the heat flux divided by the temperature [28,32], or start by identifying the production of entropy as the relative entropy related to forward and backward processes [30].

II. EVOLUTION EQUATION

We consider a generic system whose state is defined as being the set of variables x_i understood as the components of a vector x belonging in a certain continuous space of states of a given dimension. As the system evolves in time, the point representing the vector x moves in the space of states, tracing a trajectory. Supposing that the system is in a certain state x at time t, the question arises as to which trajectory the system will follow starting at x. According to the stochastic assumption there is not just one trajectory starting from x but many possible trajectories, each one occurring with a certain probability.

To properly express the probability of occurrence of a certain trajectory during a given interval of time it is necessary to specify not only the initial and final points of the trajectory but also the intermediate points. These points are understood as a time sequence of random variables and the probability of the trajectory is a function of these variables. In addition, this probability could depend on previous states. However, according to the Markovian assumption adopted here, the probability of a trajectory will not depend conditionally on these other states. This assumption leads us to the conclusion that the probability of the whole trajectory can be set up by specifying the probabilities of small sections of the trajectory. The probability of these elementary trajectories dependent only on its initial and final points.

The probability of occurrence of an elementary trajectory that starts within the elementary volume of the space of states dx around the state x and ends within dx' around x', after a small interval of time τ, is written as

$$P(x', x)dx'dx = K(x'|x)\rho(x)dx'dx, \tag{3}$$

where $\rho(x)dx$ is the probability of finding the system within dx around x at a given time t and $K(x'|x)dx'$ is the conditional probability of finding the system within dx' around x' at time $t + \tau$, given the occurrence of state x at time t.

The main assumption of the present approach is that x' is obtained from x by means of the following equation valid for small values of τ,

$$x_i' = x_i + F_i\tau + \xi_i\sqrt{\tau}, \tag{4}$$

where the forces $F_i(x)$ are given functions of x, and ξ_i are random variables with a Gaussian distribution $G(\xi|x)d\xi$, understood as a conditional probability, where ξ, the noise, denotes the vector with components ξ_i. The Gaussian distribution is such that the random variables ξ_i have zero means and covariances $\langle\xi_i\xi_j\rangle = \Gamma_{ij}$. The conditional probability distribution $K(x'|x)$ is obtained from $G(\xi|x)$ by performing the transformation $\xi \to x'$ dictated by Eq. (4). That is, the conditional probability $K(x'|x)$ of x at time $t+\tau$ given x at time t is

$$K(x'|x)dx' = G(\xi|x)d\xi, \tag{5}$$

where the random variable ξ is related to the random variable x' by Eq. (4).

To find the continuous time equation, we start by denoting by $\rho'(x')$ the probability distributions at time $t+\tau$, and by $\rho(x)$ the probability distribution at t. They are related to the conditional probability K through the equation

$$\rho'(x') = \int K(x'|x)\rho(x)dx, \tag{6}$$

understood as the evolution equation for the probability distribution in a discretized form. To find the evolution equation in the continuous form, one should take the limit $\tau \to 0$, which is carried out as follows. We start by multiplying both sides of Eq. (6) by an arbitrary state function $\mathcal{F}(x')$ and integrate in x',

$$\langle\mathcal{F}\rangle' = \int \mathcal{F}(x')K(x'|x)\rho(x)dxdx', \tag{7}$$

where the average on the left-hand side is over the distribution $\rho'(x')$. Changing the integration from x' to ξ the result is

$$\langle\mathcal{F}\rangle' = \int \mathcal{F}(x')G(\xi|x)\rho(x)dxd\xi, \tag{8}$$

where here x' is given by Eq. (4).

Next we need the expansion of $\mathcal{F}(x')$ up to linear terms in τ. The expansion is obtained in two stages. First we expand this function up to second powers of $\Delta x_i = x_i' - x_i$,

$$\Delta\mathcal{F} = \sum_i \frac{\partial\mathcal{F}}{\partial x_i}\Delta x_i + \frac{1}{2}\sum_{ij}\frac{\partial^2\mathcal{F}}{\partial x_i x_j}\Delta x_i\Delta x_j, \tag{9}$$

where $\Delta\mathcal{F} = \mathcal{F}(x') - \mathcal{F}(x)$. Replacing Eq. (4) into this equation we reach the desired expansion,

$$\Delta\mathcal{F} = \sum_i \frac{\partial\mathcal{F}}{\partial x_i}(F_i\tau + \xi_i\sqrt{\tau}) + \frac{1}{2}\sum_i \frac{\partial^2\mathcal{F}}{\partial x_i x_j}\xi_i\xi_j\tau, \tag{10}$$

valid up to terms of order τ.

Equation (10) is replaced in Eq. (8) and the integration in ξ is carried out. Taking into account that the average of ξ_i vanishes, and that the average of $\xi_i\xi_j$ is Γ_{ij}, the term proportional do $\sqrt{\tau}$ disappears and the whole right-hand side of the Eq. (8) turns out to be proportional to τ. After this procedure, we divide both sides of the equation by τ to reach the result

$$\frac{d}{dt}\langle\mathcal{F}\rangle = \langle\mathcal{K}^\dagger\mathcal{F}\rangle, \tag{11}$$

where we are considering that $\Delta\langle\mathcal{F}\rangle/\tau \to \partial\langle\mathcal{F}\rangle/\partial t$ when $\tau \to 0$, and $\mathcal{K}^\dagger$ is the differential operator given by

$$\mathcal{K}^\dagger\mathcal{F} = \sum_i F_i\frac{\partial\mathcal{F}}{\partial x_i} + \frac{1}{2}\sum_{ij}\Gamma_{ij}\frac{\partial^2\mathcal{F}}{\partial x_i x_j}, \tag{12}$$

and is the adjoint of the differential operator $\mathcal{K}$, defined by

$$\mathcal{K}\rho = -\sum_i \frac{\partial}{\partial x_i}(F_i\rho) + \frac{1}{2}\sum_{ij}\frac{\partial^2}{\partial x_i x_j}(\Gamma_{ij}\rho). \tag{13}$$

Writing Eq. (11) in the form

$$\int \mathcal{F}\frac{\partial\rho}{\partial t}dx = \int \mathcal{F}(\mathcal{K}\rho)dx, \tag{14}$$

obtained by appropriate integrations by parts and by taking into account that ρ vanishes rapidly in the limits of integration, we conclude that

$$\frac{\partial\rho}{\partial t} = \mathcal{K}\rho, \tag{15}$$

or in an explicit form,

$$\frac{\partial\rho}{\partial t} = -\sum_i \frac{\partial}{\partial x_i}(F_i\rho) + \frac{1}{2}\sum_{ij}\frac{\partial^2}{\partial x_i\partial x_j}(\Gamma_{ij}\rho), \tag{16}$$

which is the desired equation that gives the time evolution of the probability distribution $\rho(x,t)$ in a continuous form, and is a Fokker-Planck equation [33–36].

III. PRODUCTION OF ENTROPY

A. Time reversal and entropy production

Irreversible processes are characterized by the lack of time-reversal invariance which means that the probability of the occurrence of a certain process is different from the probability of its time reversal. In accordance with thermodynamics, a measure of irreversibility is how much entropy is being generated. Thus, the production of entropy is directly related to the lack of time reversibility.

Given a trajectory in the space of states, the time-reversal trajectory may not be, generally speaking, its reverse, as illustrated in Fig. 1. If a trajectory starts at the point x and ends at x', then the reverse starts at x' and ends at x, and may not coincide with the time-reversal trajectory which is understood as follows. Let $x \to \bar{x}$ be a mapping that associates to each state x a time-reversal state $\bar{x}$. If x and x' are the initial and final states of a trajectory, then the initial and final states of the time-reversal trajectory are, respectively, $\bar{x}'$ and $\bar{x}$. That is, the final state of the original trajectory maps onto the initial state of the time-reversal trajectory and vice-versa.

The type of time-reversal mapping that we consider is such that x_i either changes its sign or keep its sign in the transformation $x \to \bar{x}$. It is thus convenient to classify the variables x_i into two categories. If x_i keeps its sign, then it belongs in the first category or is of the even type. If x_i changes sign, then it belongs in the second category or is of the odd type. It is worth mentioning that if $\bar{x}_i\bar{x}_j = x_ix_j$, then x_i and x_j belong in the same category, otherwise they belong in distinct categories.

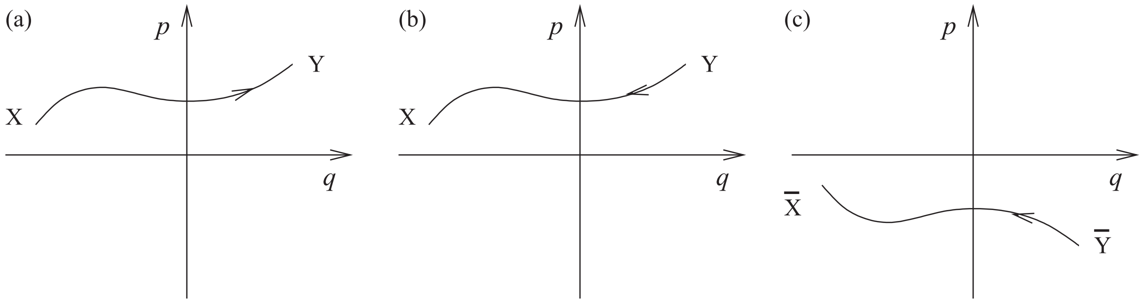

FIG. 1. Trajectories in the space of states, where q is an even variable and p is an odd variable. (a) The original trajectory, starting at X and ending at Y. (b) The backward trajectory (but not time-reversed), that starts at Y and ends at X. (c) The time-reversal trajectory, that starts at $\bar{\text{Y}}$ and ends at $\bar{\text{X}}$. The points $\bar{\text{X}}$ and $\bar{\text{Y}}$ are the time-reversal mappings of the points X and Y, respectively.

The time reversal of a vector state function such as the force F is defined in terms of its components. The time reversal of F_i is denoted $\bar{F}_i$ and equals F_i or $-F_i$ according to whether x_i is of the even or odd type, respectively.

In general, the probability of occurrence of a certain trajectory $x \to x'$, during a small interval of time τ, which is

$$P(x', x) = K(x'|x)\rho(x), \tag{17}$$

is different from the probability of occurrence of the time-reversal trajectory $\bar{x}' \to \bar{x}$, which is

$$P(\bar{x}, \bar{x}') = K(\bar{x}|\bar{x}')\rho(\bar{x}'). \tag{18}$$

A very special situation occurs when the probability of a trajectory and its time reversal is equal. Thermodynamic equilibrium corresponds to the case when this equality occurs for all trajectories. A measure of the departure from equilibrium may be given by the logarithm of the ratio of these two probabilities,

$$\ln \frac{P(x', x)}{P(\bar{x}, \bar{x}')}, \tag{19}$$

a quantity that vanishes when the two probabilities are equal. We must integrate over all possible trajectories occurring during the interval of time τ, leading us to the following expression for the production of entropy during the interval of time τ,

$$\int P(x', x) \ln \frac{P(x', x)}{P(\bar{x}, \bar{x}')} dx dx'. \tag{20}$$

The rate of production of entropy Π is defined by dividing Eq. (20) by τ and by multiplying by the Boltzmann constant k,

$$\Pi = \frac{k}{\tau} \int P(x', x) \ln \frac{P(x', x)}{P\bar{x}, \bar{x}')} dx' dx, \tag{21}$$

and it is understood that we should take the limit $\tau \to 0$. Writing this equation in the equivalent form

$$\Pi = \frac{k}{2\tau} \int \{P(x', x) - P(\bar{x}, \bar{x}')\} \ln \frac{P(x', x)}{P(\bar{x}, \bar{x}')} dx' dx, \tag{22}$$

it becomes clear that $\Pi \geqslant 0$ because the integrand is never negative. In terms of the conditional probability, the rate of entropy production reads

$$\Pi = \frac{k}{2\tau} \int \{K(x'|x)\rho(x) - K(\bar{x}|\bar{x}')\rho(\bar{x}')\} \times \ln \frac{K(x'|x)\rho(x)}{K(\bar{x}|\bar{x}')\rho(\bar{x}')} dx' dx. \tag{23}$$

For the discrete space of states, the integral is replaced by a summation, in which case this expression becomes the expression proposed by Schnakenberg for the production of entropy related to a master equation [6].

Equation (23) is not the entropy S of the system, which is defined by

$$S = -k \int \rho(x) \ln \rho(x) dx, \tag{24}$$

and, in general, it is not either the variation of the entropy with time dS/dt, which is

$$\frac{dS}{dt} = \frac{k}{2\tau} \int \{K(x'|x)\rho(x) - K(\bar{x}|\bar{x}')\rho(\bar{x}')\} \ln \frac{\rho(x)}{\rho(\bar{x}')} dx' dx, \tag{25}$$

where we assumed that $\rho(\bar{x}) = \rho(x)$. The difference $\Phi = \Pi - dS/dt$ is given by

$$\Phi = \frac{k}{2\tau} \int \{K(x'|x)\rho(x) - K(\bar{x}|\bar{x}')\rho(\bar{x}')\} \ln \frac{K(x'|x)}{K(\bar{x}|\bar{x}')} dx' dx, \tag{26}$$

and is interpreted as the flux of entropy per unit time *from* the system *to* the outside.

B. Rate of entropy production

Next we wish to determine the rate of entropy production in the limit $\tau \to 0$. We recall that the conditional probability $K(x'|x)$ is related to the noise probability distribution by relation Eq. (5), where $G(\xi|x)$ is the probability distribution of the noise ξ, related to x' by

$$\xi_i = \frac{1}{\sqrt{\tau}}[x_i' - x_i - F_i(x)\tau], \tag{27}$$

where F_i are functions of x.

We assume that the noises ξ_i are distributed according to the Gaussian distribution $G(\xi|x)$ in several variables, with zero means and covariances $\langle \xi_i \xi_j \rangle = \Gamma_{ij}$ that may depend on x. Given the covariances, the Gaussian distribution is uniquely determined and is given by

$$G(\xi|x) = \frac{1}{Z}\exp\left\{-\frac{1}{2}\sum_{ij}\xi_i B_{ij}\xi_j\right\}, \tag{28}$$

where

$$Z = \int \exp\left\{-\frac{1}{2}\sum_{ij}\xi_i B_{ij}\xi_j\right\}d\xi, \tag{29}$$

and B, the matrix with elements B_{ij}, is the inverse of the covariance matrix Γ, and may depend on x. As $G(\xi|x)$ describes a probability distribution, the eigenvalues of the precision matrix B and of the covariant matrix Γ are greater or equal to zero.

To determine the rate of entropy production, we write Eq. (23) in terms of the Gaussian distribution by the use of Eq. (5) and by employing the conditional probability $K(\bar{x}|\bar{x}')$ related to the time-reversal trajectory,

$$K(\bar{x}|\bar{x}')d\bar{x} = G(\xi^*|\bar{x}')d\bar{\xi}', \tag{30}$$

where ξ^* is given by

$$\xi_i^* = \frac{1}{\sqrt{\tau}}[\bar{x}_i - \bar{x}_i' - F_i(\bar{x}')\tau]. \tag{31}$$

Notice that the right-hand side of Eq. (31) is not the time reversal of the right-hand side of Eq. (27). For this reason, we are using the notation ξ_i^* and not $\bar{\xi}_i$. In terms of the Gaussian distribution, the rate of entropy production reads

$$\Pi = \frac{k}{2\tau}\int\{G(\xi|x)\rho(x) - G(\xi^*|\bar{x}')\rho(\bar{x}')\} \times \ln\frac{G(\xi|x)\rho(x)}{G(\xi^*|\bar{x}')\rho(\bar{x}')}d\xi dx, \tag{32}$$

which is obtained by a change of variables from x' to ξ, given by Eq. (27) and we remark that ξ_i^* is related to both x' and x by Eq. (31) so that all terms in the integrand involve only the variables ξ and x.

Before we start the calculation, we assume two properties of the covariances, the denial of which would lead to an artificial production of entropy. The first property is

$$\Gamma_{ij}(\bar{x}) = \Gamma_{ij}(x), \tag{33}$$

and is valid also for $B_{ij}(x)$, $Z(x)$ and $\rho(x)$. The second property is that $\Gamma_{ij}(x)$ vanishes whenever x_i and x_j belong in distinct categories, that is, if one is even and the other is odd, and is also valid for $B_{ij}(x)$. This property is conveniently written as

$$\Gamma_{ij}\bar{x}_i\bar{x}_j = \Gamma_{ij}x_i x_j. \tag{34}$$

C. Additive noise

We consider here the case in where the covariant matrix Γ does not depend on x, and the same is valid for the precision matrix B. We start by expanding the expression

$$\ln\frac{G(\xi|x)\rho(x)}{G(\xi^*|\bar{x}')\rho(\bar{x}')}, \tag{35}$$

up to terms of order $\sqrt{\tau}$. Using the definition of the Gaussian distribution, this expression may be written as

$$\frac{1}{2}\sum_{ij}B_{ij}(\xi_i^*\xi_j^* - \xi_i\xi_j) - \ln\frac{\rho(x')}{\rho(x)}, \tag{36}$$

where we used the property Eq. (33) for B_{ij} and ρ.

To determine the first term of Eq. (36), we observe that in accordance with the property Eq. (34), valid for B_{ij},

$$B_{ij}\xi_i^*\xi_j^* = B_{ij}\bar{\xi}_i^*\bar{\xi}_j^*, \tag{37}$$

where $\bar{\xi}_i^*$ is the time reversal of ξ_i^*,

$$\bar{\xi}_i^* = \frac{1}{\sqrt{\tau}}[x_i - x_i' - \bar{F}_i(\bar{x}')\tau], \tag{38}$$

so that, up to terms of order $\sqrt{\tau}$,

$$\bar{\xi}_i^* = -\xi_i - 2D_i(x)\sqrt{\tau}, \tag{39}$$

where

$$D_i(x) = \tfrac{1}{2}[\bar{F}_i(\bar{x}) + F_i(x)]. \tag{40}$$

The first term of Eq. (36), up to terms of order $\sqrt{\tau}$, becomes

$$\sum_{ij}B_{ij}[\xi_i D_j(x) + \xi_j D_i(x)]\sqrt{\tau}. \tag{41}$$

Considering that up to terms of order $\sqrt{\tau}$, $x_i' = x_i + \xi_i\sqrt{\tau}$, and using the property Eq. (33) for ρ, the second term of Eq. (36) becomes

$$-\sum_k\frac{\partial\ln\rho}{\partial x_k}\xi_k\sqrt{\tau}. \tag{42}$$

Collecting these results, we may write

$$\ln\frac{G(\xi|x)\rho(x)}{G(\xi^*|\bar{x}')\rho(\bar{x}')} = \mathcal{A}(\xi, x)\sqrt{\tau}, \tag{43}$$

where

$$\mathcal{A} = \sum_i\mathcal{A}_i\xi_i, \tag{44}$$

and

$$\mathcal{A}_i = 2\sum_j B_{ij}D_j - \frac{\partial\ln\rho}{\partial x_i}. \tag{45}$$

In a similar fashion we find

$$G(\xi|x)\rho(x) - G(\xi^*|\bar{x}')\rho(\bar{x}') = G(\xi|x)\rho(x)\mathcal{A}(\xi, x)\sqrt{\tau}, \tag{46}$$

and the rate of entropy production becomes

$$\Pi = \frac{k}{2}\int G(\xi|x)\rho(x)[\mathcal{A}(\xi, x)]^2 d\xi dx. \tag{47}$$

Replacing the result Eq. (44) for $\mathcal{A}$ in Eq. (47), performing the integral in ξ, and bearing in mind that $\langle\xi_i\xi_j\rangle = \Gamma_{ij}$, we reach the following desired result for the rate of entropy production:

$$\Pi = \frac{k}{2}\sum_{ij}\int\mathcal{A}_i\,\Gamma_{ij}\mathcal{A}_j\,\rho\,dx, \tag{48}$$

which is clearly nonnegative because the eigenvalues of Γ_{ij} are nonnegative.

Comparing Eqs. (23) and (25), we observe that they differ from the last factor in the integrand of both equations. An expression for dS/dt can thus be obtained by using the same reasoning that led us from Eq. (23) to Eq. (48). The result is

$$\frac{dS}{dt} = -\frac{k}{2}\sum_{ij}\int \mathcal{A}_i \Gamma_{ij}\frac{\partial \rho}{\partial x_j}\,dx. \tag{49}$$

To find an expression for the flux of entropy Φ, we recall that $\Phi = \Pi - dS/dt$. Subtracting Eqs. (48) and (49), we get

$$\Phi = k\sum_i \int \mathcal{A}_i D_i\,\rho\,dx, \tag{50}$$

where we used the relation $B\Gamma = I$.

IV. PROBABILITY CURRENT

A. Dissipation probability current

The evolution Eq. (16) can be written in the following form:

$$\frac{\partial \rho}{\partial t} = -\sum_i \frac{\partial J_i^c}{\partial x_i}, \tag{51}$$

where

$$J_i^c = F_i\rho - \frac{1}{2}\sum_j \frac{\partial}{\partial x_j}(\Gamma_{ij}\rho). \tag{52}$$

In this form, the evolution equation is a continuity equation and J_i^c is the probability current. Next, we wish to split the probability currents into two parts, one of them being invariant under time reversal. To this end, we consider first the splitting of the force F_i.

Any force $F_i(x)$ can always be split into two parts, one of them being

$$D_i(x) = \tfrac{1}{2}[F_i(x) + \bar{F}(\bar{x})], \tag{53}$$

and the other being

$$F_i^r(x) = \tfrac{1}{2}[F_i(x) - \bar{F}(\bar{x})]. \tag{54}$$

That is,

$$F_i(x) = F_i^r(x) + D_i(x). \tag{55}$$

The first part F_i^r is invariant under time reversal, holding the time-reversal property

$$\bar{F}_i^r(x) = -F_i^r(\bar{x}). \tag{56}$$

In an explicit form, if F_i^r is an odd type of force, which is identified as an ordinary force, then the time-reversal property reads $F_i^r(x) = F_i^r(\bar{x})$. If F_i is an even type of force, then the time-reversal property reads $F_i^r(x) = -F_i^r(\bar{x})$. From Eq. (56), it follows that $A_i = \partial F_i^r/\partial x_i$ holds the property

$$A_i(\bar{x}) = -A_i(x). \tag{57}$$

The second part D_i is the dissipative part, which holds the property

$$\bar{D}_i(x) = D_i(\bar{x}). \tag{58}$$

If D_i is an odd type of force, then this property reads, $D_i(x) = -D_i(\bar{x})$, and D_i is identified with a dissipative force, an example of which is the ordinary dissipation proportional to the velocity. If D_i is an even type of force, then this property reads $D_i(x) = D_i(\bar{x})$. Only the second part, D_i, that lacks the time-reversal property, contributes to the production of entropy as can be observed by looking at Eqs. (45) and (47).

In an analogous manner, the probability current is split into two parts,

$$J_i^c = J_i^r + J_i, \tag{59}$$

where the first part is the reversible probability current, and

$$J_i^r = F_i^r\rho, \tag{60}$$

which is invariant under time reversal, holding the property Eq. (56) because $\rho(\bar{x}) = \rho(x)$, and the second part is the irreversible probability current,

$$J_i = D_i\rho - \frac{1}{2}\sum_j \frac{\partial \rho\Gamma_{ij}}{\partial x_j}, \tag{61}$$

which holds the property Eq. (58) because $\Gamma_{ij}(\bar{x}) = \Gamma_{ij}(x)$.

B. Time variation of the entropy

The variation of the entropy

$$S = -k\int \rho\ln\rho dx, \tag{62}$$

with time is

$$\frac{dS}{dt} = -k\int \frac{\partial \rho}{\partial t}\ln\rho dx. \tag{63}$$

Using the evolution equation in the form Eq. (51), it can be written as

$$\frac{dS}{dt} = k\sum_i \int \frac{\partial J_i^c}{\partial x_i}\ln\rho\,dx. \tag{64}$$

Replacing J_i^c by $J_i^r + J_i$, the right-hand side will be a sum of two terms, one of which involves the integral

$$\sum_i \int \frac{\partial J_i^r}{\partial x_i}\ln\rho\,dx = \sum_i \int \frac{\partial F_i^r}{\partial x_i}\rho\,dx, \tag{65}$$

where the equality was obtained by two integrations by parts. But this expression vanishes in view of the property Eq. (57) and we are left only with the second part,

$$\frac{dS}{dt} = -k\sum_i \int J_i\frac{\partial \ln\rho}{\partial x_i}dx, \tag{66}$$

where an integration by parts has been performed.

If we define $F_i^{\text{ir}} = J_i/\rho$, then we may write, after an integration by parts,

$$\frac{dS}{dt} = k\sum_i \int \frac{\partial F_i^{\text{ir}}}{\partial x_i}\rho\,dx, \tag{67}$$

In this form we see that the time variation of the entropy is related to the change in the volume of phase space, measured by the divergence of F^{ir}.

C. Rate of entropy production

The comparison of Eqs. (49) and (66) indicates that J_i is related to $\mathcal{A}_i$ by

$$J_i = \frac{\rho}{2}\sum_j \mathcal{A}_j \Gamma_{ij}. \tag{68}$$

Inverting this relation, we find

$$\mathcal{A}_i = \frac{2}{\rho}\sum_j B_{ij}J_j, \tag{69}$$

where we used $B\Gamma = I$, which leads us to the following expression

$$\mathcal{A}_i = 2\sum_j B_{ij}D_j - \frac{\partial \ln \rho}{\partial x_i} - \sum_{jk} B_{ij}\frac{\partial \Gamma_{jk}}{\partial x_k}, \tag{70}$$

obtained by using Eq. (61), where again we used $B\Gamma = I$.

We have seen above that the rate of entropy production is given by Eq. (48), which was demonstrated to be the rate of entropy for the case in which Γ_{ij} does not depend on x, in which case Eq. (70) for $\mathcal{A}_i$ does not have the last term on the right-hand. Although we did not show that Eq. (48) is also valid for the case in which Γ_{ij} depends on x, we assume that it expresses the rate of entropy production in this case, with $\mathcal{A}_i$ given by Eq. (70).

Using the relation between $\mathcal{A}_i$ and J_i, the rate of entropy production can be written in terms of the dissipation probability current as

$$\Pi = k\sum_i \int J_i\mathcal{A}_i dx, \tag{71}$$

or as

$$\Pi = 2k\sum_{ij}\int \frac{1}{\rho}J_iB_{ij}J_j dx. \tag{72}$$

This expression is clearly nonnegative because the eigenvalues of B are nonnegative and we notice that it is related only to the dissipation part of the probability current. When B is diagonal, this formula was considered by Tomé and de Oliveira [1] and derived by Spinney and Ford [31] by a method which has similarities with the present approach. Equation (72) was derived by Chetrite and Gawędzki [30] by identifiying the production of entropy as a relative entropy related to forward and backward processes.

The flux of entropy Φ is obtained by recalling that $\Phi = \Pi - dS/dt$. Subtracting the Eqs. (64) and (72), we get

$$\Phi = 2k\sum_{ij}\int J_iB_{ij}L_j dx, \tag{73}$$

where

$$L_j = D_j - \frac{1}{2}\sum_k \frac{\partial \Gamma_{jk}}{\partial x_k}, \tag{74}$$

which can also be written as

$$\Phi = k\sum_i \int \mathcal{A}_iL_i\rho\, dx. \tag{75}$$

V. ENERGY, HEAT, AND WORK

From now on, we wish to describe a system that may be acted by internal as well as by external forces. The internal forces are considered to be conservative forces in the sense that they are derived from an energy function $E(x)$ associated to the system. Let x_i and x_j be a pair of even and odd variables, respectively. Then the even conservative force F_i^c and the odd conservative force F_j^c are obtained from the energy function $E(x)$ by

$$F_i^c = \frac{\partial E}{\partial x_j}, \quad F_j^c = -\frac{\partial E}{\partial x_i}. \tag{76}$$

The energy function holds the time-reversal property, $E(\bar{x}) = E(x)$, guaranteeing the time-reversal property Eq. (56) of the conservative forces.

In addition to the internal forces F_i^c, the system, if it is not isolated, may be acted by external forces F_i^e which are also considered to be time reversal. The force F_i^r becomes a sum of these two forces,

$$F_i^r = F_i^c + F_i^e, \tag{77}$$

and the evolution Eq. (16) becomes

$$\frac{\partial \rho}{\partial t} = -\sum_i \frac{\partial F_i^c\rho}{\partial x_i} - \sum_i \frac{\partial F_i^e\rho}{\partial x_i} - \sum_i \frac{\partial J_i}{\partial x_i}. \tag{78}$$

From the property Eq. (76), it follows at once the following result:

$$\sum_i \frac{\partial F_i^c}{\partial x_i} = 0. \tag{79}$$

Using this property, we find

$$\sum_i \frac{\partial F_i^c\rho}{\partial x_i} = \sum_i F_i^c\frac{\partial \rho}{\partial x_i}, \tag{80}$$

which can be written as

$$-\sum_i F_i^c\frac{\partial \rho}{\partial x_i} = \sum_{(ij)}\left(\frac{\partial E}{\partial x_i}\frac{\partial \rho}{\partial x_j} - \frac{\partial E}{\partial x_j}\frac{\partial \rho}{\partial x_i}\right) = \{E, \rho\}, \tag{81}$$

where the summation extends over all pairs (i, j) such that x_i and x_j consist of a pair of conjugate variables such that the x_i is even and x_j is odd, and this summation is recognized as the Poisson brackets between E and ρ.

The evolution Eq. (78) then becomes

$$\frac{\partial \rho}{\partial t} = \{E, \rho\} - \sum_i \frac{\partial F_i^e\rho}{\partial x_i} - \sum_i \frac{\partial J_i}{\partial x_i}. \tag{82}$$

The time evolution of the average of the energy $\langle E(x)\rangle$, understood as the thermodynamic internal energy U of the system, is obtained by multiplying Eq. (82) by $E(x)$ and integrating in x. The result is

$$\frac{dU}{dt} = \sum_i \int J_i\frac{\partial E}{\partial x_i}dx + \sum_i \int F_i^e\rho\frac{\partial E}{\partial x_i}dx, \tag{83}$$

obtained after appropriate integrations by parts. The first summation on the right hand-side is identified as the total heat flux introduced into the system,

$$\Phi_q = \sum_i \int J_i \frac{\partial E}{\partial x_i} dx, \tag{84}$$

and the second as minus the work performed by the system per unit time, or power generated by the system,

$$\Phi_w = -\sum_i \int F_i^e \rho \frac{\partial E}{\partial x_i} dx. \tag{85}$$

Equation (83) acquires the form

$$\frac{dU}{dt} = \Phi_q - \Phi_w, \tag{86}$$

which is understood as the global conservation of energy, and Φ_u in Eq. (1) is $\Phi_u = \Phi_q - \Phi_w$.

VI. A SPECIAL TYPE OF NOISE

The noise, which is represented by the covariances matrix Γ is not yet fully specified. Some of their essential properties have already been presented in Eqs. (33) and (34), and are: $\Gamma_{ij}(\bar{x}) = \Gamma_{ij}(x)$; and $\Gamma_{ij}(x)$ vanishes whenever x_i and x_j consists of a pair of even and odd types. There are many choices of noise depending on the physical situation one wants to describe. Here we take a look at the type of noise that leaves a certain quantity $E(x)$ invariant along the trajectory determined by this noise. The quantity E is strictly constant in every possible stochastic trajectory, and not only on the average. If two states x and x' are related by

$$x_i' = x_i + F_i\tau + \xi_i\sqrt{\tau}, \tag{87}$$

then the expansion of $E(x') - E(x)$ up to terms of order τ is

$$E(x') - E(x) = \sum_i \frac{\partial E}{\partial x_i}(F_i\tau + \xi_i\sqrt{\tau}) + \frac{1}{2}\sum_{ij} \frac{\partial^2 E}{\partial x_i \partial x_j}\Gamma_{ij}\tau, \tag{88}$$

where as before Γ_{ij} denotes the covariance of the random variables ξ_i.

If $E(x') = E(x)$ along the trajectory, then the following constraint should be obeyed:

$$\sum_j \xi_j f_j = 0, \tag{89}$$

where

$$f_j = \frac{\partial E}{\partial x_j} \tag{90}$$

and

$$\sum_i f_i F_i + \frac{1}{2}\sum_{ij}\Gamma_{ij}\frac{\partial f_i}{\partial x_j} = 0. \tag{91}$$

The first condition means that the random variables are not independent variables but are connected by Eq. (89). Multiplying Eq. (89) by ξ_i and taking the average over the random variable ξ, we find

$$\sum_j \Gamma_{ij} f_j = 0, \tag{92}$$

which relates the covariances and f_i. Owing to the relation Eq. (92), the condition Eq. (91) is equivalently expressed by

$$F_i = \frac{1}{2}\sum_j \frac{\partial \Gamma_{ij}}{\partial x_j}. \tag{93}$$

If a certain quantity remains constant along a stochastic trajectory, then the random variables ξ_i should be connected by Eq. (89), and F_i should be related to the covariances by Eq. (93).

Replacing the condition Eq. (93) in Eq. (74), we see that the quantity L_i vanishes and so does the flux of entropy, given by Eq. (73). In other terms, the flux of entropy vanishes for the conservative noise that we are considering here and one concludes from this property that the variation of the entropy of the system dS/dt equals the rate of the entropy production Π.

A noise that meet the condition Eq. (89) is set up as follows. For $i \neq j$, let ξ_{ij} be random variables with zero means, each one with variance $\lambda_{ij} = \lambda_{ji} \geqslant 0$, that is, $\langle \xi_{ij}^2 \rangle = \lambda_{ij}$. These are independent random variables, except ξ_{ij} and ξ_{ji} which are related by

$$\xi_{ji} = -\xi_{ij}. \tag{94}$$

The random variable ξ_i is defined in terms of these new random variables by

$$\xi_i = \sum_{j(\neq i)} \xi_{ij} f_j. \tag{95}$$

Using property Eq. (94), the condition Eq. (91) follows immediately. We recall that $f_i = \partial E/\partial x_i$ and may depend on x, where $E(x)$ is the conserved quantity.

From Eq. (95) we may determine the covariances $\Gamma_{ij} = \langle \xi_i \xi_j \rangle$. Using the property Eq. (94) we find

$$\Gamma_{ij} = -\lambda_{ij} f_i f_j, \tag{96}$$

for $i \neq j$, and

$$\Gamma_{ii} = \sum_{j(\neq i)} \lambda_{ij} f_j^2. \tag{97}$$

From these results, we see that Eq. (92) is verified.

VII. THERMODYNAMIC EQUILIBRIUM

A. Noise-dissipation relation

From now on we consider only the situations such that the external forces are not present, in which case the evolution equation is

$$\frac{\partial \rho}{\partial t} = \{E, \rho\} - \sum_i \frac{\partial J_i}{\partial x_i}. \tag{98}$$

It remains to choose which type of noise to use. The choice of noise, represented by the covariances Γ_{ij}, and of the dissipative forces D_i is guided by the type of situation one wants to describe. If we wish to describe an equilibrium situation, then the noise represented by the covariances Γ_{ij} and the dissipation represented by D_i cannot be arbitrary but must hold a relationship between them, a noise-dissipation relation.

For long times, the density ρ will reach a stationary density ρ_s, which makes the right-hand side of Eq. (98) vanish.

If $J_i(\rho_s)$ is nonzero for some i, then Π is nonzero and the stationary state will be a state in which entropy is continuously been produced, and this is not an equilibrium state. The thermodynamic equilibrium is characterized by the vanishing of the entropy production which implies that J_i should vanish for all i. Denoting by ρ_e the equilibrium probability distribution then the condition for thermodynamic equilibrium is

$$J_i(\rho_e) = 0, \tag{99}$$

for all i. Recalling the definition of J_i, given by Eq. (61), this condition is equivalent to

$$D_j - \frac{1}{2}\sum_k \frac{\partial \Gamma_{jk}}{\partial x_k} = \frac{1}{2}\sum_k \Gamma_{jk}\frac{\partial \ln \rho_e}{\partial x_k}, \tag{100}$$

for all i.

Let us analyze the types of covariances Γ_{ij} and the dissipative force D_i that may lead the system to the thermodynamic equilibrium. As the quantity $J_i(\rho_e)$ vanishes for each i, the second summation on the right-hand side of Eq. (98) disappears and the first summation must vanish as well, that is,

$$\{E, \rho_e\} = 0. \tag{101}$$

This equation is fulfilled if ρ_e is a function of E, that is if $\rho_e(x) = \rho[E(x)]$ depends on x through the energy function $E(x)$. In other words, in the thermodynamic equilibrium, the probability density is a function of the energy function, which is the main property of the equilibrium Gibbs distributions. The general condition for thermodynamic equilibrium is reduced to the condition represented by Eq. (100) where ρ_e is understood as a function of the energy function $E(x)$. With this understanding, the Eq. (100) is the noise-dissipation relation.

The Eqs. (99) and (101) are the two conditions that gives the equilibrium probability distribution. The first condition represents the detailed balance condition or microscopic reversibility and the second is related to the conservation of energy. These two conditions are the ones used implicitly by Maxwell in his second derivation of the velocity distribution that bears his name [37].

B. Canonical setting

Let us consider two relevant cases. The first is the one in which ρ_e is proportional to $e^{-\beta E}$, which corresponds to the Gibbs canonical distribution. In this case Eq. (100) reduces to

$$D_j - \frac{1}{2}\sum_k \frac{\partial \Gamma_{jk}}{\partial x_k} = -\frac{\beta}{2}\sum_k \Gamma_{jk}\frac{\partial E}{\partial x_k}, \tag{102}$$

which is the noise-dissipation relation for the present case.

Using relation Eq. (100), the flux of entropy Eq. (73) reduces to the following simple form:

$$\Phi = k\sum_i \int J_i \frac{\partial \ln \rho_e}{\partial x_i} dx = -\frac{1}{T}\sum_i \int J_i \frac{\partial E}{\partial x_i} dx. \tag{103}$$

The comparison of Eqs. (84) and (103) leads us to the relation

$$\Phi = -\frac{\Phi_q}{T}, \tag{104}$$

which connects the flux of entropy and the heat flux. Since $dU/dt = \Phi_q$ and $dS/dt = \Pi - \Phi$, we reach the relation

$$\frac{dS}{dt} = \Pi + \frac{1}{T}\frac{dU}{dt}. \tag{105}$$

Near equilibrium, the rate of entropy production vanishes and we are left with the relation $dU = TdS$, which confirms that the noises and dissipation satisfying the noise-dissipation relation Eq. (102) describe a system in contact with a reservoir at a temperature T.

If the temperature is kept constant, then the variation with time of the free energy $F = U - TS$ is related to the entropy production by $dF/dt = -T\Pi$, which follows from Eq. (105). Since $\Pi \geqslant 0$, then $dF/dt \leqslant 0$ and the free energy decreases monotonically in time towards its equilibrium value. It is satisfying to realize that this inequality can be regarded as the H theorem of Boltzmann. Indeed, if we define the H function of Boltzmann by

$$H = \int \rho \ln \frac{\rho}{\rho_e} dx, \tag{106}$$

and recalling that ρ_e is proportional do the exponent of $-\beta E$, we see that H equals $-\beta F$, except for an additive constant, a relation giving the result

$$\frac{dH}{dt} = -\beta\frac{dF}{dt} = k\Pi \geqslant 0, \tag{107}$$

which is understood as the H theorem of Boltzmann.

C. Microcanonical setting

The second relevant case is the one in which ρ_e vanish unless $E(x) = E_0$, which corresponds to the Gibbs microcanonical distribution. This condition is met if the left- and right-hand sides of the Eq. (100) vanish, which give the conditions

$$D_i = \frac{1}{2}\sum_j \frac{\partial \Gamma_{ij}}{\partial x_j} \tag{108}$$

and

$$\sum_j \Gamma_{ij}\frac{\partial E}{\partial x_j} = 0. \tag{109}$$

The covariances obeying this relation is obtained from the special type of noise that we have analyzed above.

Replacing result Eq. (108) into Eq. (74), we see that L_i vanishes identically and so does the flux of entropy, given by Eq. (50).

The heat flux also vanishes. To see this, it suffices to observe that the covariances and dissipative forces, characterized by Eqs. (108) and (109), yields

$$J_i = -\frac{1}{2}\sum_j \Gamma_{ij}\frac{\partial \rho}{\partial x_j}, \tag{110}$$

which replaced in Eq. (84) and making use of relation Eq. (109) gives the vanishing of Φ_q. Thus, not only the flux of entropy is absent but also the heat flux, confirming that the noise characterized by Eqs. (108) and (109) describe an isolated system.

The insertion of Eq. (110) into Eq. (98) gives the evolution in the form

$$\frac{\partial\rho}{\partial t}=\{E,\rho\}+\frac{1}{2}\sum_{ij}\frac{\partial}{\partial x_i}\Gamma_{ij}\frac{\partial\rho}{\partial x_j}, \tag{111}$$

and describes an isolated system as we have demonstrated. In this sense it is similar to the Liouville equation

$$\frac{\partial\rho}{\partial t}=\{E,\rho\}, \tag{112}$$

which describes a isolated system. However, in the case of the Liouville equation, the entropy is strictly constant in time, and there is no entropy production. This is in contrast with thermodynamic law of the increase of entropy in isolated systems, but in agreement with the Eq. (111), which will generate entropy. The variation of the entropy, which equals the rate of entropy production Π, is given by

$$\frac{dS}{dt}=\frac{k}{2}\sum_{ij}\int\frac{\Gamma_{ij}}{\rho}\frac{\partial\rho}{\partial x_j}\frac{\partial\rho}{\partial x_i}dx, \tag{113}$$

which is clear nonnegative because Γ_{ij} has nonnegative eigenvalues, and we conclude that $dS/dt\geqslant 0$.

VIII. MECHANICAL SYSTEM

A. General equations

Here we apply the results obtained previously to a mechanical system composed by a certain number of interacting particles with equal masses. The positions of the particles are denoted by x_i, understood as even variables, and the momenta of the particles by p_i, understood as odd variables. The discrete time equations of motion are

$$x_i'=x_i+\frac{p_i}{m}\tau, \tag{114}$$

$$p_i'=p_i+F_i\tau+D_i\tau+\xi_i\sqrt{\tau}, \tag{115}$$

where $F_i(x)$ is a conservative force that depends only on x, that is, $F_i=-dV/dx_i$, and D_i is the dissipative force. The conservative force F_i and p_i/m hold the property Eq. (56), as desired, and the dissipative force is assumed to hold the property Eq. (58), which reads $D_i(x,-p)=-D_i(x,p)$.

Equation (98) gives the time evolution of the probability density $\rho(x,p)$ reads

$$\frac{\partial\rho}{\partial t}=\{\mathcal{H},\rho\}-\sum_i\frac{\partial J_i}{\partial p_i}, \tag{116}$$

where $\mathcal{H}$ is the energy function

$$\mathcal{H}=\sum_i\frac{p_i^2}{2m}+V(x), \tag{117}$$

and we recall that $F_i=-\partial\mathcal{H}/\partial x_i$ and $p_i/m=\partial\mathcal{H}/\partial p_i$.

We analyze initially the ordinary case in which the dissipative force is proportional to the momentum, $D_i=-\gamma p_i$, and the covariances are diagonal and do not depend on x nor on p, and are given by $\Gamma_{ii}=2m\gamma/\beta_i$. In this case the quantity J_i is

$$J_i=-\gamma\left(p_i\rho+\frac{m}{\beta_i}\frac{\partial\rho}{\partial p_i}\right). \tag{118}$$

Replacing in Eq. (116), the evolution equation reads

$$\frac{\partial\rho}{\partial t}=\{\mathcal{H},\rho\}+\gamma\sum_i\frac{\partial p_i\rho}{\partial p_i}+\gamma m\sum_i\frac{1}{\beta_i}\frac{\partial^2\rho}{\partial p_i^2}, \tag{119}$$

which we recognize as the Fokker-Planck-Kramers equation for many particles.

If $\beta_i=\beta$ is the same for all i, then the noise-dissipation relation is obeyed for the Gibbs probability density ρ_e proportional to $e^{-\beta\mathcal{H}}$ and the Eq. (119) describes a system in contact with a reservoir at a temperature $T=1/k\beta$. For long times the system relax to the equilibrium state. If β_i are distinct, then for long times the system reaches a nonequilibrium stationary state because J_i cannot be zero for all i and $\Pi\neq 0$. In this case the equation can be understood as describing a system in contact with several heat reservoirs at temperatures $T_i=k\beta_i$.

Another situation is the one in which ρ_e vanishes unless $H(x,p)=E_0$, which we have discussed above, and understood as describing an isolated system. In equilibrium, it leads to the Gibbs microcanonical distribution. In the present case where the equation of motion is given by Eqs. (114) and (115), the covariances are related only to the momentum variable, so that the relation Eq. (109) gives

$$\sum_j\Gamma_{ij}p_j=0. \tag{120}$$

The solution for Γ_{ij} is

$$\Gamma_{ij}=-\lambda_{ij}p_ip_j,\quad i\neq j, \tag{121}$$

$$\Gamma_{ii}=\sum_{j\neq i}\lambda_{ij}p_j^2, \tag{122}$$

where $\lambda_{ij}=\lambda_{ji}\geqslant 0$, which replaced into Eq. (108) gives again the usual form of the dissipative force,

$$D_i=-\gamma_ip_i,\qquad\gamma_i=\frac{1}{2}\sum_{j(\neq i)}\lambda_{ij}. \tag{123}$$

The explicit form of J_i is

$$J_i=\frac{1}{2}\sum_{j(\neq i)}\lambda_{ij}p_j\left(p_i\frac{\partial\rho}{\partial p_j}-p_j\frac{\partial\rho}{\partial p_i}\right). \tag{124}$$

The flux of entropy Φ vanishes identically and the time variation of entropy dS/dt equals the rate of entropy Π. Using Eq. (113), we find

$$\frac{dS}{dt}=\frac{k}{2}\sum_{i<j}\lambda_{ij}\int\frac{1}{\rho}\left(p_j\frac{\partial\rho}{\partial p_i}-p_i\frac{\partial\rho}{\partial p_j}\right)^2dx, \tag{125}$$

and we may conclude that $dS/dt\geqslant 0$.

B. Weakly interacting particles

As an example of a system that evolves with strictly constant energy, we consider a system of weakly interacting particles in which case the energy function can be taken as being just the kinetic energy,

$$\mathcal{H}=\sum_i\frac{p_i^2}{2m}. \tag{126}$$

The evolution equation is

$$\frac{\partial \rho}{\partial t} = \{\mathcal{H}, \rho\} + \frac{1}{2}\sum_{ij} \frac{\partial}{\partial p_i}\Gamma_{ij}\frac{\partial \rho}{\partial p_j}, \tag{127}$$

where the covariances depend on p_i according to Eqs. (121) and (122).

As the energy function is strictly constant in time, the equilibrium probability density is $\rho_e(p)$ is proportional to $\delta(\mathcal{H}(p) - E_0)$, as we have already seen. To solve Eq. (127), we assume a probability distribution of the following form $\rho(p) = g(p)\delta[\mathcal{H}(p) - E_0]$, which we expect to be valid near equilibrium, where

$$g = \frac{1}{\zeta}\exp\left\{-\frac{1}{2}\sum_{i\neq j} b_{ij}p_i p_j\right\}, \tag{128}$$

and the quantities b_{ij} are time dependent. Replacing this form in the evolution equation we find the following equation for b_{ij}, for $i \neq j$,

$$\frac{db_{ij}}{dt} = -\alpha_{ij}b_{ij}, \tag{129}$$

where

$$\alpha_{ij} = \lambda_{ij} + \frac{1}{2}\sum_{k(\neq i)} \lambda_{ik} + \frac{1}{2}\sum_{k(\neq j)} \lambda_{jk}. \tag{130}$$

The solution for b_{ij} is

$$b_{ij} = c_{ij}e^{-\alpha_{ij}t}, \tag{131}$$

and we see that for long times the probability distribution decays exponentially with time to the equilibrium distribution.

Let us determined the variation of entropy dS/dt, which for the present case equals the rate of entropy production. Using Eq. (113), we find

$$\frac{dS}{dt} = \frac{k}{2}\sum_{i\neq j} b_{ij}^2\Big\{\lambda_{ij}\big[\langle p_j^4\rangle - \langle p_i^2\rangle\langle p_j^2\rangle\big] + \sum_{k(\neq i)} \lambda_{ik}\langle p_k^2\rangle\langle p_j^2\rangle\Big\}, \tag{132}$$

where the averages are determined by using the equilibrium probability distribution. We see that dS/dt is positive and decays exponentially to zero

I the probability density is only a function of the momenta, we see that the Poisson brackets in Eq. (127) vanishes but that is not the case of last term on the right-hand side of Eq. (127). The vanishing of the Poisson brackets means that the Liouville equation gives ρ constant in time and thus do not relax to the equilibrium solution, if it was out of equilibrium at the beginning. This is in contrast with the solution of Eq. (127) which predicts a relaxation to equilibrium and a nonzero production of entropy, and $dS/dt > 0$ out of equilibrium.

IX. CONCLUSION

We have developed an approach to stochastic thermodynamics of systems with a continuous space of states. The results were obtained by a continuous time limit of a discrete time formulation, which includes the evolution equation and the rate of entropy production. We have emphasized the role of the time reversal and of the dissipation probability current in the properties related to irreversible processes. When this part of the probability current vanishes, the rate of entropy production vanishes, and the equilibrium sets in. The rate of entropy production was shown to be a bilinear form in the components of the dissipation probability current and is positive definite.

We have also analyzed a type of noise that makes the energy function to be strictly constant along a stochastic trajectory and thus describing an isolated system. The increase in entropy is entirely due to the generation of entropy inside the system. This theoretical result is in agreement with thermodynamics in the sense that the entropy of an isolated system, in general, increases. This result contrasts with the prediction given by the Liouville equation that the entropy is constant in time, and there is not generation of entropy, although this equation describes an isolated system as the energy is strictly constant in time.

[1] T. Tomé and M. J. de Oliveira, Phys. Rev. E **82**, 021120 (2010).

[2] M. Esposito, Phys. Rev. E **85**, 041125 (2012).

[3] U. Seifert, Rep. Prog. Phys. **75**, 126001 (2012).

[4] C. Van de Broeck, C. Bechinger, F. Sciortino, and P. Ziherl (eds.), in *Proceedings of the International School of Physics "Enrico Fermi,"* Course 184 (IOS, Amsterdam, 2013), p. 155.

[5] T. Tomé and M. J. de Oliveira, Phys. Rev. E **91**, 042140 (2015).

[6] J. Schnakenberg, Rev. Mod. Phys. **48**, 571 (1976).

[7] L. Jiu-Li, C. Van den Broeck, and G. Nicolis, Z. Phys. B **56**, 165 (1984).

[8] C. Y. Mou, J.-L. Luo, and G. Nicolis, J. Chem. Phys. **84**, 7011 (1986).

[9] J. L. Lebowitz and H. Spohn, J. Stat. Phys. **95**, 333 (1999).

[10] L. Crochik and T. Tomé, Phys. Rev. E **72**, 057103 (2005).

[11] C. Maes and K. Netočný, J. Stat. Phys. **110**, 269 (2003).

[12] R. K. P. Zia and B. Schmittmann, J. Phys. A: Math. Gen. **39**, L407 (2006).

[13] R. K. P. Zia and B. Schmittmann, J. Stat. Mech.: Theory Expt. (2007) P07012.

[14] D. Andrieux and P. Gaspard, J. Stat. Phys. **127**, 107 (2007).

[15] B. Gaveau and L. S. Schulman, Phys. Rev. E **79**, 021112 (2009).

[16] T. Schmiedl and U. Seifert, J. Chem. Phys. **126**, 044101 (2007).

[17] R. J. Harris and G. M. Schütz, J. Stat. Mech.: Theory Expt. (2007) P07020.

[18] U. Seifert, Eur. Phys. J. B **64**, 423 (2008).

[19] D. Andrieux and P. Gaspard, Phys. Rev. E **74**, 011906 (2006).

[20] T. Tomé and M. J. de Oliveira, J. Chem. Phys. **148**, 224104 (2018).

[21] M. Esposito, K. Lindenberg, and C. Van den Broeck, Phys. Rev. Lett. **102**, 130602 (2009).

[22] T. Tomé and M. J. de Oliveira, Phys. Rev. Lett. **108**, 020601 (2012).

[23] D. Hartich, A. C. Barato, and U. Seifert, J. Stat. Mech.: Theory Expt. (2014) P02016.

[24] O. Barbosa and T. Tomé, J. Stat. Mech.: Theory Expt. (2018) P063202.

[25] D. Luposchainsky and H. Hinrichsen, J. Stat. Phys. **153**, 828 (2013).
[26] K. Sekimoto, Prog. Theor. Phys. Suppl. **130**, 17 (1998).
[27] T. Tomé, Braz. J. Phys. **36**, 1285 (2006).
[28] C. Maes, K. Netočný, and B. Wynants, Physica A **387**, 2675 (2008).
[29] C. Van den Broeck and M. Esposito, Phys. Rev. E **82**, 011144 (2010).
[30] R. Chetrite and K. Gawędzki, Commun. Math. Phys. **282**, 469 (2008).
[31] R. E. Spinney and I. J. Ford, Phys. Rev. E **85**, 051113 (2012).
[32] C. Maes, K. Netočný, and M. Verschuere, J. Stat. Phys. **111**, 1219 (2003).
[33] N. G. van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1981).
[34] C. W. Gardiner, *Handbook of Stochastic Methods for Physics, Chemistry and Natural Sciences* (Springer, Berlin, 1983).
[35] H. Risken, *The Fokker-Planck Equation, Methods of Solution and Applications* (Springer, Berlin, 1984).
[36] T. Tomé and M. J. de Oliveira, *Stochastic Dynamics and Irreversibility* (Springer, Heidelberg, 2015).
[37] M. J. de Oliveira, Phys. Rev. E **99**, 052138 (2019).