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From dynamics to thermodynamics: Linear response and statistical mechanics

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We illustrate a dynamic approach to statistical mechanics based on a procedure which reverses the standard approach to the Fokker-Planck equation (FPE). Rather than using statistical mechanics, derived from thermodynamics along the lines pioneered by Boltzmann [L. Boltzmann, Wiss. Ber. **58**, 517 (1868)], we derive a FPE for a set of variables of interest interacting with a booster, i.e., a dynamical system mimicking the action of an ideal thermostat with no need of *ad hoc* statistical assumptions. We derive a mechanical expression for the temperature of the system of interest, which is proven to be a generalization of the one proposed by Boltzmann; in the case of boosters with a limited number of degrees of freedom, it is shown that our definition depends also on dynamic properties, which are not accounted for by the "standard" approach.

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I. INTRODUCTION

The purpose of this paper is to synthesize a number of separate results that have been obtained in the past few years and show how they provide a single coherent view of the mechanical basis of thermodynamics. This goal for statistical physics is shown to be a consequence of the existence of chaotic solutions to low-dimensional nonlinear dynamical equations and the linear response of ensembles of such systems to external perturbation.

The linear response theory (LRT) is a key ingredient of the view here illustrated; this establishes a connection between the proposed theoretical approach and an issue, the microscopic foundation of the LRT, which has been the subject of a revival of interest in the last few years [1–7]. The main result of this research work has been that the trajectory instability, responsible for the breakdown of the linear response of a single trajectory to a perturbation, turns out to be the physical source of a linear response at a statistical level. In the specific case of Hamiltonian systems in a continuous time representation, the linear response is shown [6,7] to take the form of Kubo-like theoretical predictions [8,9]. However, the work of Kubo [8] rests on the assumption that thermodynamics as well as ordinary statistical mechanics holds true, rather than using only dynamical properties of Hamiltonian systems. Since its formulation [8] the Kubo theory has been widely used in the field of condensed matter physics and it is thought that systems obeying ordinary statistical mechanics follow closely the theoretical predictions of this theory. The present paper confirms this close connection between LRT and ordinary statistical mechanics, by reversing, in a sense, the usual procedure, in that it proves that, if possible, a rigorously dynamical formulation of LRT [6,7] leads to a dynamical derivation of statistical mechanics, and thermodynamics as well.

As a further significant achievement of the approach illustrated in the present paper, not only do we derive the Boltzmann principle from dynamical arguments, but this principle is arrived at in a generalized form, which reduces to the ordinary version on increasing the number of degrees of freedom of the system. This means a definition of temperature which differs from the conventional one due to the dynamical corrections which tend to vanish when the number of degrees of freedom is increased.

To properly place our theoretical proposal within the context of the current literature on this subject, we refer the reader to the scheme of Fig. 1. With the help of this diagram, let us first illustrate the conventional approach of many textbooks on equilibrium statistical mechanics [10,11], corresponding to the left column of Fig. 1. It is assumed that the equilibrium distribution of a given Hamiltonian system is microcanonical. In textbooks on statistical mechanics written before chaotic dynamics was investigated [10], this connection is assumed with no dynamical derivation and for this reason is here indicated

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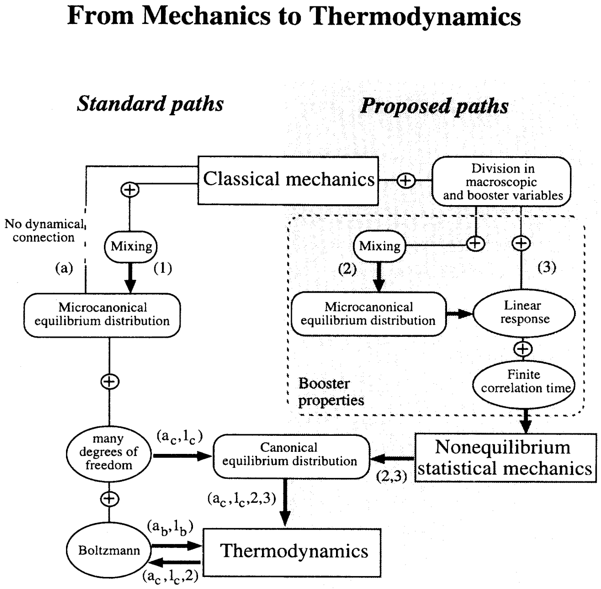

FIG. 1. Diagrammatic view of the standard approach to thermodynamics (left) and of the approach to thermodynamics presented here (right): for details, see text.

by the broken line (a). In more recent textbooks [11], reflecting the conceptual revolution provoked by the recognition of the importance of chaos, the microcanonical equilibrium distribution is given as a consequence of mixing [12]. In other words, classical mechanics and mixing imply a microcanonical equilibrium distribution, which, consequently, has a dynamical derivation. This approach is indicated by path (1) connecting classical mechanics to the microcanonical equilibrium distribution.

We have now two distinct ways to derive thermodynamics. The former refers to the pioneering proposal of Boltzmann [13], mentioned in the textbooks of the prechaos era [10]. This is the Boltzmann principle,

$$S = k_B \ln A(E), \tag{1}$$

which establishes a connection between the area $A(E)$ of the phase space explored by the system in a microcanonical state and its entropy S, and consequently with thermodynamics. This principle is usually supplemented by the assumption that the system has an extremely large number of degrees of freedom. This defines the path to thermodynamics shown in Fig. 1 as (a_b) or (1_b), according to whether the condition of microcanonical equilibrium is assumed or derived from dynamics.

The latter possibility to derive thermodynamics, illustrated by the paths (a_c) or (1_c), is again based on the assumption of an infinitely large number of degrees of freedom. Under this condition, the microcanonical equilibrium distribution is proved to be essentially indistinguishable from the canonical equilibrium. In other words, the microcanonical condition of equilibrium, supplemented by the condition that the system has a large number of degrees of freedom, implies the canonical equilibrium distribution, and this is enough to derive thermodynamics. On the issue of how to derive thermodynamics from the canonical equilibrium distribution, the reader can refer to a recent report by Mackey [14]. We thus arrive at the thermodynamical level through either the path (a_c) or (1_c), according to whether the microcanonical condition is assumed, or derived from dynamics. In conclusion, as originally pointed out by Khinchin [15], we can establish a connection between mechanics and thermodynamics without using the Boltzmann principle, and only using the canonical equilibrium distribution to derive thermodynamics. What about the Boltzmann principle? Without assuming the Boltzmann principle, after reaching the thermodynamical level by the joint use of the microcanonical distribution and of a large number of degrees of freedom, the Boltzmann principle is simply shown to be true [16]. This approach to thermodynamics is denoted by the paths (a_c) and (1_c) in Fig. 1.

We now illustrate the newer approach to thermodynamics proposed herein, and corresponding to the right part of the diagram shown in Fig. 1. Working from the bottom of the diagram, let us focus our attention on the box labeled *nonequilibrium statistical mechanics.* This indicates that we derive the canonical distribution necessary to found thermodynamics according to the indications of [14] as the equilibrium state of a Fokker-Planck equation (FPE). This FPE is derived from the top of the diagram by means of a deterministic derivation of Brownian motion along the lines established in earlier papers of Bianucci *et al.* [17–19], which are concisely reviewed here. The derivation of this FPE is carried out by using only dynamical properties and no *ad hoc* statistical assumptions on the existence of macroscopic thermodynamics. We proceed as follows. First of all we divide the set of variables of a given system into two groups, the former including the variables of interest, or macroscopic variables (*system of interest*), and the latter the *irrelevant*, or microscopic, variables (*booster*) [17–19]. The coupling between the variables of interest and the irrelevant ones is expressed by a Hamiltonian interaction, whose strength is kept under our control, to realize the conditions for a second-order perturbation treatment, necessary for our theoretical approach to work. In the numerical applications discussed in this paper the set of microscopic variables is a dynamical system in a condition of "full chaos" which we define subsequently. A booster exerts an influence on the system of interest which is indistinguishable from that of an ordinary thermostat. However, the adoption of the word thermostat might erroneously suggest that we are subtly adopting the same statistical assumptions used in the conventional approaches to the FPE [20–23] from microscopic dynamics. Since this is not the case, we prefer to adopt the more neutral term booster rather than thermostat.

Our approach follows two major avenues, indicated by the paths (2) and (3) of Fig. 1. In a sense, path (2) is a special case of the more general physical condition behind (3). Thus, let us illustrate path (3) first. A required property to proceed along this path is that the booster responds linearly to external perturbations, *linear re-*

sponse, and that its state relaxes to equilibrium in a finite time, *finite correlation time*. With these key properties we derive the FPE leading to both the equilibrium and nonequilibrium thermodynamics of the system of interest. The equilibrium distribution of the FPE is canonical, leading to a definition of temperature that is expressed in terms of the dynamical properties of the booster. This "mechanical" temperature can be regarded as referring either to the system of interest or to the booster. In the latter case, the system of interest is thought of as a sort of "thermometer," monitoring the temperature of the booster.

Let us describe now the basic aspects of path (2). This path is a special case of (3) corresponding to the assumption of mixing, a property which, in the case of the Hamiltonian booster used in this paper, is supported by the numerical simulations. The numerical simulations confirm what is argued in Ref. [6], i.e., that when the booster has more than a few degrees of freedom and its dynamics are so "chaotic" as to generate mixing and consequently ergodicity on the hypersurface at fixed energy, then the booster responds linearly to an external perturbation. The numerical results show also that for the booster we use the regression to equilibrium after an abrupt perturbation takes place in a finite time, satisfying the requirements of the theory. In this special case, the analytical expression for the "mechanical" temperature of the booster, in the limiting case of boosters with large numbers of degrees of freedom, is proved to coincide with the prediction of the Boltzmann principle, in full accord with the standard approach, path (1).

It must be pointed out that, at first sight, this theoretical approach to statistical mechanics, based on the deterministic derivation of the FPE along the lines established in Refs. [17–19], from a formal point of view does not have elements of significant novelty, since it is based on the derivation of an effective equation of motion for a set of relevant variables, a subject which has been the focus of the research work of many groups, and the source of very many papers, of which here we quote only a small number [20–23]. This lack of novelty depends on the fact that the properties of *linear response* and *finite correlation time* of the booster (see Fig. 1) necessary for us to derive the FPE for the system of interest, are shared by the standard thermostats of the cited literature, leading to reduced equations of motion for the systems of interest that can be traced back to those derived from the boosters. However, in the standard approach to the FPE the irrelevant part (the thermostat) is a linear system with an infinite number of degrees of freedom, placed in an initial state of canonical equilibrium (thermodynamical argument). Thus the regular "macroscopic" behavior of the system of interest is due to the regular microscopic dynamics of the thermostat. The irreversibility of the system of interest stems from taking an infinitely large number of degrees of freedom for the thermostat. In other words, dynamically this means that the single trajectories of the thermostat are "irreversible" by themselves. Finally, thermodynamics and temperature are introduced by hand through the choice of the canonical distribution for the bath initial condition. The novelty of our approach is that we do not use linear systems for the bath. This means that in our boosters single trajectories do not respond linearly to an external perturbation; it is only the average over many particle trajectories which responds linearly. The chaotic nature of our booster also implies a decay of the correlation functions in a finite time, even in the presence of very few degrees of freedom. The properties of *linear response* and *finite correlation time* of our booster, then, have a source and meaning very different from the one typically assumed for linear baths. Finally, we do not introduce any "thermodynamical" hypothesis about the initial conditions.

We want to point out that, although having the same motivation and the same philosophy as Refs. [17–19], the FPE derivation in the present paper is original with respect to that of these earlier papers in the following two ways.

(a) In these earlier papers [17–19] the coupling between the system of interest and booster was not Hamiltonian and the numerical treatment was restricted to the case of non-Hamiltonian boosters. In this paper we extend those results to the case of a Hamiltonian coupling between system of interest and booster, allowing us to deal with a fully Hamiltonian case, leading to the possibility to extend our theory to quantum mechanical systems [24–27].

(b) There was no defined time scale for the system of interest, which basically was a free particle. Here, we extend the results to the case when the system of interest has an internal time scale: the importance of this time scale, with respect to the booster time scale, will be clarified.

The fact that in the present approach the system of interest has a well defined time scale is not a minor detail. To derive the FPE, we need a dynamical mapping from the irregular and non-Gaussian dynamics of the chaotic booster onto an equivalent regular and Gaussian force driving the system of interest. To explain under which conditions this is possible, we introduce the following three time scales.

(i) In the case when the coupling between the booster and the system of interest is switched off, the only significant time scale is that of the equilibrium correlation functions of the booster variables. More specifically, since a key role is played by the booster variable through which the booster is coupled to the system of interest, the "doorway" variable ξ defined in Sec. II, we shall refer to the time scale of the equilibrium correlation function of the variable ξ as the unperturbed booster time scale (*unperturbed booster* TS).

(ii) The time scale of the unperturbed system of interest will be referred to as *unperturbed system* TS. This is the typical time scale over which the variables describing the system of interest (in the absence of coupling) evolve. For instance, for an integrable system this time will be the inverse of the typical frequency.

(iii) The third time scale comes into play when the coupling between the system of interest and the booster is switched on. In this condition, as we will prove, the unperturbed regular dynamics of the system is perturbed by a fluctuation-dissipation process, leading to a decay over a finite time scale. We shall refer to this relaxation time scale as *relaxation* TS. The relaxation TS will increase as the coupling strength between system of interest and booster becomes smaller.

The key ingredient necessary to realize the dynamical mapping mentioned above is the possibility of "filtering" the fast dynamics of the booster, thus realizing the Gaussianicity of the effective force via the central limit theorem. In the case of earlier papers [17,18], given that we had a free particle and the unperturbed system TS was not defined, we simply assumed that the relaxation TS ought to be much larger than the unperturbed booster TS. Within the present theoretical treatment we also have a defined unperturbed system TS. We still need the relaxation TS to be much larger than the unperturbed booster TS (that is, weak coupling constant Δ). However, contrary to intuition, it is now not required that in all cases the unperturbed system TS should be much larger than the unperturbed booster TS. It will become clear that in general we require this condition only if the number of degrees of freedom of the booster is small. In other words, we are now paving the way for the study of the joint action of chaotic dynamics and a large number of degrees of freedom. This fact leads us to establish a connection with the view of Khinchin [15], who shows equilibrium thermodynamics to be determined by the laws of large numbers applied to systems with an extremely large number of degrees of freedom. We stress that the condition of a large relaxation TS means a weak coupling between the system of interest and the booster. We conclude by recalling that, assuming always that the relaxation TS is much larger than the unperturbed booster TS, two conditions are possible.

(i) The unperturbed system TS is much larger than the relaxation TS; we recover a condition equivalent to that explored in some of our earlier papers [17,18], and we refer to this condition as the natural time scale separation (NTS) case.

(ii) The *unperturbed system* TS is arbitrary; the theory here developed leads to thermodynamics as a joint effect of fully developed chaos and the action of a large number of degrees of freedom, and we refer to this condition as the generalized time scale separation (GTS) case.

The paper is organized as follows. In Sec. II we define the formal structure of the systems we investigate. In Sec. III, using arguments valid in the NTS condition, we obtain a Langevin equation for the system of interest. In Sec. IV we derive the FPE using a formal approach, valid in both the NTS and the GTS cases. Section V is devoted to the numerical results and some general observations are made in Sec. VI. Finally, conclusions are drawn in Sec. VII.

II. FORMAL STRUCTURE OF THE DYNAMICAL SYSTEMS UNDER STUDY

According to the prescriptions illustrated in Sec. I, our theoretical approach refers to the dynamics of a general system of interest coupled to a booster. However, to make our treatment more transparent, we focus our attention on the special case of a two-dimensional system (x, v), where x is the displacement and v the velocity of a nonlinear oscillator. The booster is an n-dimensional deterministic system and the coupling between the system and the booster is characterized by the coupling strength Δ. The structure of the equations of motion of the system under study is

$$\begin{aligned} \dot{x} &= v, \\ \dot{v} &= -\frac{1}{m}\frac{\partial V(x)}{\partial x} - \frac{\Delta}{m}\xi, \\ \dot{\xi} &= F\left(\xi, \boldsymbol{\pi}, -\Delta x\right), \\ \dot{\boldsymbol{\pi}} &= \boldsymbol{G}\left(\xi, \boldsymbol{\pi}, -\Delta x\right), \end{aligned} \tag{2}$$

where the variables ξ and $\boldsymbol{\pi} \equiv (\pi_1, \ldots, \pi_{n-1})$ are those of the n-dimensional booster. We point out the special role of the variable ξ, the "doorway" variable, through which the booster exerts its influence on the system of interest.

The dynamics of the booster is defined by the following equations of motion:

$$\begin{aligned} \dot{\xi} &= F(\xi, \boldsymbol{\pi}, K(t)), \\ \dot{\boldsymbol{\pi}} &= \boldsymbol{G}(\xi, \boldsymbol{\pi}, K(t)), \end{aligned} \tag{3}$$

where $K(t)$ is a time dependent external perturbation. We term the booster perturbed when $K \neq 0$ and unperturbed when $K = 0$. Under the assumption that Δ is sufficiently weak, the dependence of the last two equations in (2) on $-\Delta x$, at least for a short time interval, can be regarded as independent of the motion of the booster, making it possible to interpret $-\Delta x$ as an external field, on equal footing with $K(t)$. The dynamical structure of Eq. (2) is a general form which applies, as widely illustrated in the next sections, to both Hamiltonian and non-Hamiltonian systems. In the former case the booster is Hamiltonian, the variable ξ is a spatial coordinate, and the vector $\boldsymbol{\pi}$ denotes the set of variables containing the momentum conjugate to ξ and all the additional pairs of canonically conjugate variables necessary for the booster dynamics to be given a complete representation. The latter case refers to a non-Hamiltonian booster, hence to a case where the booster variables ξ and $\boldsymbol{\pi}$ are connected to one another by the functions F and $\boldsymbol{G}$ of Eq. (3) without implying canonical conjugation.

In Sec. I we anticipated that we need the hypotheses of linear response and finite correlation time of the booster. We proceed to define these properties, starting first with the finite correlation time, (i), and then with the linear response of the booster, (ii).

(i) *Finite correlation time of the booster.* The regression to equilibrium of the booster, subsequent to the application of an external perturbation, takes place in a finite time. From a mathematical point of view, this property is expressed by the statement that all the correlation functions of the booster decay in time so quickly that they have finite time moments. A crucial role is played by the autocorrelation function $\varphi(t)$ of the doorway variable ξ, defined by

$$\varphi \equiv \frac{\langle \xi(t)\xi(0)\rangle_0}{\langle \xi^2 \rangle_0}, \tag{4}$$

where the symbol $\langle\ \rangle_0$ means an average over the unperturbed equilibrium distribution of the booster. The assumption of a finite correlation time of the booster means that

$$\tau \equiv \int_0^\infty \varphi(t)dt < \infty, \tag{5}$$

which is, at the same time, the definition of the booster correlation time τ.

Of some relevance for the theory illustrated in Sec. IV is also the first moment of the autocorrelation function $\varphi(t)$. This is

$$\eta^2 \equiv \int_0^\infty \varphi(u)udu, \tag{6}$$

and it will be useful to define the "macroscopic" transport properties of Sec. IV.

(ii) *Linear response of the booster.* Let us assume that the booster is placed in the equilibrium state in the absence of perturbations, and that the corresponding mean value of ξ vanishes. We apply at time $t = 0$ the perturbation $K(t)$. Then for linear response we mean that the average value of ξ at a given time $t > 0$, denoted by $\langle \xi(t)\rangle_K$, can be approximated by a linear function of the perturbation $K(t)$, through a time convolution with a response function $S(t)$:

$$\langle \xi(t)\rangle_K = \int_0^t S(u)K(t-u)du + O(K^2). \tag{7}$$

Another dynamical function relevant for our theory is the susceptibility $\chi(t)$ defined by

$$\chi(t) \equiv \int_0^t S(u)du. \tag{8}$$

In the special case when the external perturbation is abruptly applied to the booster at time $t = 0$, and is constant, i.e., when $K(t) = \theta(t)K$, Eq. (7) yields

$$\langle \xi(t)\rangle_K = K\chi(t) + O(K^2), \tag{9}$$

which makes evident why the function of Eq. (8) is called susceptibility. As a consequence of its own definition, see Eq. (8), the susceptibility must vanish at $t = 0$, and, due to the property (i), must reach in times of the order of the correlation time τ the stationary asymptotic value $\chi(\infty)$. To simplify the algebra, we shall adopt the definition $\chi \equiv \chi(\infty)$. These dynamical properties of the susceptibility make it natural to introduce another dynamical function $c(t)$ defined by

$$\chi(t) = [1 - c(t)]\ \chi. \tag{10}$$

It is evident that $c(0) = 1$ and $c(\infty) = 0$. From Eqs. (8) and (10) we have

$$S(t) = \frac{\partial}{\partial t}\chi(t) = -\chi\frac{\partial}{\partial t}c(t). \tag{11}$$

We define the following two moments:

$$\vartheta \equiv \int_0^\infty c(u)du \tag{12}$$

and

$$\beta^2 \equiv \int_0^\infty c(u)udu, \tag{13}$$

which turn out to be useful in defining the macroscopic "thermodynamical" properties of Sec. IV. Notice that the moments of Eqs. (6) and (13) are expressed as squared quantities to stress the fact that they have the dimension of a square time.

The problem of establishing if condition (ii) is satisfied by a Hamiltonian system is actually one of the most relevant and fundamental in statistical mechanics. On the basis of the results of Ref. [6], and of the numerical results of Sec. V as well, it is proved that this condition is fulfilled by boosters with a number of degrees of freedom large enough, although in general it is expressed in a form which does not coincide yet with the canonical version given by Kubo [8]; cf. Sec. IV. In Sec. V we shall see that eight degrees of freedom are enough to make the booster satisfy condition (ii).

In addition to these conditions on the dynamics of the booster, we need also a condition of weak coupling between the oscillator and the booster. This means that the coupling parameter Δ must be sufficiently small. If ω_b is a typical frequency of a booster that responds linearly to external perturbations, and τ is defined by Eq. (5), a simple estimate for Δ such that the relaxation TS is much larger than the unperturbed booster TS, leads to

$$\Delta^2 \ll \omega_b^2/\tau^2. \tag{14}$$

For the practical purposes of this paper, we do not use this inequality, but the much more stringent condition of assessing numerically the linear response of the booster, and consequently the maximum allowed value of Δ is more directly obtained by studying the susceptibility of the booster.

III. THE LANGEVIN APPROACH

In this section we derive a Langevin equation equivalent to the FPE. The Langevin approach is not as complete as the FPE approach, and it is limited to the NTS condition. Nevertheless, the Langevin approach is attractive because it makes the physics underlying fluctuations and dissipation very clear, and for this reason we think it worthy of illustration.

Let us first focus our attention on diffusion. We can separate the action of diffusion from that of friction assuming that both the coupling constant Δ and the mass m go to zero keeping the ratio Δ/m constant. In this limit the booster is no longer perturbed by the system of interest. Assume also that the system of interest is a linear oscillator, with frequency ω, i.e., that

$V(x) = m\omega^2 x^2/2$. From Eq. (2) we have

$$\begin{pmatrix} x(t) \\ v(t) \end{pmatrix} = \begin{pmatrix} x_a(t) \\ v_a(t) \end{pmatrix} - \frac{\Delta}{m\omega}\int_0^t \xi(u) \begin{pmatrix} \sin[\omega(t-u)] \\ \omega\cos[\omega(t-u)] \end{pmatrix} du, \quad (15)$$

where the subscript "a" stands for the unperturbed time evolution of the oscillator of interest. For times $t \gg \tau$, $x(t)$ and $v(t)$ are determined by the "sum" of a very large number of unperturbed and uncorrelated fluctuations of $\xi(t)$. This shows why the central limit theorem can be used, in principle, even without the strong hypothesis that the oscillation frequency is small (NTS condition). In the limiting condition of times much larger than the correlation time τ the "force" $\xi(t)$ becomes indistinguishable from a Gaussian stochastic force with zero average and correlation time τ of Eq. (5). Let us now enforce the NTS condition, implying that the frequency ω is very small. In this case the diffusion coefficient of the velocity v turns out to be

$$D = \Delta^2 \langle \xi^2 \rangle_0 \tau / m^2. \quad (16)$$

Now we have to explain the origin of dissipation. The diffusion process can be slowed at will by decreasing the coupling strength Δ. Nevertheless, as slow as it is, under the action of the diffusion process, the space and velocity variables spread with no limit over the (x, v) phase space. This means that at a given time scale, depending on the coupling strength Δ, the value of the coordinate x can be so large as to make non-negligible the reaction term Δx, through which the system of interest perturbs the booster. Let us evaluate the effect of this reaction term on the booster. Under the assumption that the coupling constant Δ is weak, we can use the linear response property (ii), from which we obtain, using Eqs. (7) and (11),

$$\langle \xi \rangle_{-\Delta x} \approx \int_0^\infty \chi \frac{\partial c(u)}{\partial u} \Delta x(t-u) du. \quad (17)$$

Using the NTS condition we expand the backward time evolution of the variable x at the first order in time, using the approximation $x(t-u) \approx x - u\, v$. Then, integrating by parts, we obtain

$$\int_0^\infty \chi \frac{\partial c(u)}{\partial u} \Delta x(t-u) du \approx -\Delta\chi\, x + \left(\Delta\chi \int_0^\infty c(u) du \right) v. \quad (18)$$

The average of the "Gaussian" stochastic force ξ is no longer zero, but rather is given by Eq. (18). Defining the function $f(t) \equiv \xi - \langle \xi \rangle$, we can write the following two-dimensional Langevin equation:

$$\begin{aligned} \dot{x} &= v, \\ \dot{v} &= -\frac{1}{m}\frac{\partial V(x)}{\partial x} + \frac{\Delta^2}{m}\chi\, x - \frac{\Delta^2}{m}\chi\vartheta\, v + f(t), \end{aligned} \quad (19)$$

where $f(t)$ plays the role of an "effective" Gaussian stochastic force with *zero* average and correlation time τ, and the time ϑ of the response of the booster is defined in Eq. (12). The system of Eq. (19) is a Brownian oscillator, with renormalized potential $U(x)$

$$U(x) \equiv V(x) - \Delta^2 \chi \frac{x^2}{2} \quad (20)$$

and friction γ given by

$$\gamma = \frac{\Delta^2}{m}\chi\vartheta. \quad (21)$$

The fluctuation-dissipation theorem, according to which the temperature of the system of Eq. (19) is defined by the ratio of the diffusion coefficient D, given in Eq. (16), to the friction γ, given in Eq. (21), multiplied by the mass m, leads us to

$$k_B T \equiv m \langle v^2 \rangle_{\text{eq}} = m\frac{D}{\gamma} = \frac{\langle \xi^2 \rangle_0 \tau}{\chi\vartheta}. \quad (22)$$

Note that we have derived Eq. (19) under the assumption that the potential $V(x)$ is harmonic with frequency ω. However, using the weak-coupling assumption, the NTS condition, and the consequent condition of local linearity [28], according to which the slowly diffusing system only perceives the local frequency $\omega(x) = \sqrt{\partial^2 V(x)/\partial x^2/m}$, it is possible to extend the result of Eq. (19) to the nonlinear case. Under these conditions, Eq. (19) applies also to a generic potential, not necessarily harmonic.

IV. THE PROJECTION APPROACH TO THE FPE

The purpose of this section is to derive an equation of motion for the reduced probability distribution of the system of interest from the equation of motion of the whole system of Eq. (2). This equation is shown to be a two-dimensional FPE with the following structure:

$$\frac{\partial}{\partial t}\sigma(x,v;t) = \left\{ \mathcal{L}_a^{\text{eff}} + \frac{\partial}{\partial v} A(x,v) \left(\frac{\partial}{\partial v} + \frac{mv}{k_B T} \right) + \frac{\partial}{\partial v} B(x,v) \left(\frac{\partial}{\partial x} + \frac{U'(x)}{k_B T} \right) \right\} \sigma(x,v;t), \quad (23)$$

where

$$\mathcal{L}_a^{\text{eff}} \equiv \frac{U'(x)}{m}\frac{\partial}{\partial v} - v\frac{\partial}{\partial x} \quad (24)$$

is the effective unperturbed Liouvillian of the system of interest.

The theoretical tool used to derive this two-dimensional FPE is the projection method of Zwanzig [29] applied within the perturbation scheme of Refs. [30,31].

A. Linear response and finite correlation time of the booster

The derivation of the FPE (23) implies that the set of Eqs. (2) should be dealt with via a statistical treatment. This means that, rather than studying the single trajectories, we focus our attention on the equivalent time evolution of the probability distributions. Since the structure of Eq. (2) is general and applies to both the cases of Hamiltonian and non-Hamiltonian boosters, we refer to the representation in terms of the probability distributions as a *Liouville-like* picture, rather than a *Liouville* picture, as we would do in the strictly Hamiltonian case. The Liouville-like picture of the booster dynamics corresponding to Eq. (3) can be written as

$$\frac{\partial}{\partial t}\wp(\xi,\boldsymbol{\pi};t)=\Lambda(\xi,\boldsymbol{\pi},-K(t))\wp(\xi,\boldsymbol{\pi};t), \tag{25}$$

where $\wp(\xi,\boldsymbol{\pi};t)$ is the probability distribution of the booster variables and $\Lambda(\xi,\boldsymbol{\pi},-K(t))$ is the corresponding evolution operator determined according to the standard rules [14].

To proceed along these lines we enforce the hypotheses behind the paths (2) and (3) of Fig. 1, namely the finite correlation time (i) and the linear response (ii), conveniently adapted to the Liouville-like representation. First of all, the correlation function $\varphi(t)$, necessary to define property (i), can be written

$$\varphi(t)=\frac{\langle\xi e^{\mathcal{L}_b t}\xi\rangle_0}{\langle\xi^2\rangle_0}, \tag{26}$$

where $\mathcal{L}_b\equiv\Lambda(\xi,\boldsymbol{\pi},0)$ is the Liouville-like operator corresponding to the unperturbed booster ($K=0$).

The next step consists in enforcing the linear response assumption (ii) within the Liouville-like representation, and on the perturbed dynamics of the booster distribution, i.e., Eq. (25), with a weak perturbation $K\neq 0$. If assumption (ii) holds true, we can replace the Liouville-like operator $\Lambda(\xi,\boldsymbol{\pi},-K(t))$ with its first-order expansion in a power series of $K(t)$:

$$\frac{\partial}{\partial t}\wp(\xi,\boldsymbol{\pi};t)\approx\mathcal{L}_b\wp(\xi,\boldsymbol{\pi};t)-K(t)\Gamma_1\wp(\xi,\boldsymbol{\pi};t). \tag{27}$$

Thus the operator Γ_1 is the first-order contribution of this expansion. If assumption (ii) holds true, we are also allowed to expand the probability distribution of the booster around its unperturbed state, assumed to be the equilibrium state $\wp_0(\xi,\boldsymbol{\pi})$:

$$\wp(\xi,\boldsymbol{\pi};t)=\wp_0(\xi,\boldsymbol{\pi})+\wp_1(\xi,\boldsymbol{\pi};t)+O(K^2). \tag{28}$$

We assume now that the initial distribution of the system is given by the equilibrium state of the unperturbed booster, and hence that $\wp_1(\xi,\boldsymbol{\pi};0)=0$. Thus, inserting Eq. (28) into Eq. (27), we get

$$\wp_1(\xi,\boldsymbol{\pi};t)=-\int_0^t e^{\mathcal{L}_b u}K(t-u)\Gamma_1\wp_0(\xi,\boldsymbol{\pi})du. \tag{29}$$

Since, as in Sec. II, the mean value of ξ over the unperturbed equilibrium distribution is assumed to vanish, this first-order probability distribution can be used to determine the response of the variable ξ of the booster, yielding

$$\langle\xi(t)\rangle_K=-\int d\xi d\boldsymbol{\pi}\xi\int_0^t e^{\mathcal{L}_b u}K(t-u)\Gamma_1\wp_0(\xi,\boldsymbol{\pi})du. \tag{30}$$

Interchanging the order of integration between time and phase space we have

$$\langle\xi(t)\rangle_K=-\int_0^t\langle\xi e^{\mathcal{L}_b t}\Gamma_1\rangle_0 K(t-u)du. \tag{31}$$

Finally, comparing Eq. (31) with Eqs. (7) and (11) we have

$$S(t)=-\chi\frac{\partial}{\partial t}c(t)=-\langle\xi e^{\mathcal{L}_b t}\Gamma_1\rangle_0. \tag{32}$$

As in the LRT of Kubo [8], Eq. (32) relates the response function in the presence of an external perturbation to an unperturbed dynamical property of the booster with a correlationlike structure. In some cases, for instance the case of a Gaussian equilibrium distribution of the booster, this correlationlike structure can be converted into a real correlation function, making explicit the action of the operator Γ_1 on the booster distribution.

In principle, this result, implying the use of a first-order expansion, might be affected by the criticism of van Kampen [32], who objected to the use of the perturbation calculation by remarking that the response of chaotic trajectories to the perturbation is linear over such a short time region as to make the predictions of a first-order treatment essentially useless. We could avoid this criticism by attributing a coarse grained rather than a fine grained character to the distribution $\wp(\xi,\boldsymbol{\pi};t)$, and consequently a "master equation" nature to the operators $\mathcal{L}_b$ and Γ_1. Indeed, we anticipate that the derivation of the FPE (23) will not require the explicit expression of these operators, and that, consequently, our result is independent of whether or not the van Kampen criticism holds true. However, we remark that, according to Refs. [6,7], the van Kampen distinction between microscopic linearity and macroscopic linearity is fictitious: if a system responds linearly in a macroscopic time-space scale, then we can evaluate the susceptibility using a microscopic Liouville-like approach, like that of Kubo's LRT. In other words, any "macroscopic" response theory would lead to the same result as the Kubo-like (usually noncanonical) LRT. It is convenient to keep this property in mind, since, as shown in Sec. IV D, the dynamical derivation of the Boltzmann principle rests on a Kubo-like treatment.

B. Zwanzig projection method

We use the Zwanzig projection method in the perturbation version of Refs. [30,31,33]. A crucial step of this approach is the definition of the interaction part of the dynamical operator $\mathcal{L}$, driving the motion of the total probability distribution of the system of Eqs. (2),

$$\frac{\partial}{\partial t}\rho(x,v,\xi,\boldsymbol{\pi};t)=\mathcal{L}\rho(x,v,\xi,\boldsymbol{\pi};t), \tag{33}$$

where the dynamical operator $\mathcal{L}$ is given by

$$\mathcal{L}\equiv\mathcal{L}_a+\mathcal{L}_b+\mathcal{L}_I. \tag{34}$$

According to the linear response arguments which led us to Eq. (22), we can write the interaction part as

$$\mathcal{L}_I\equiv\frac{\Delta}{m}\xi\frac{\partial}{\partial v}+\Delta x\Gamma_1. \tag{35}$$

The second term on the right-hand side (RHS) of Eq. (35) is the perturbation operator defined via the linear response arguments of the preceding subsection, whereas the first term gives the action of the booster variable ξ on the system of interest. $\mathcal{L}_a$ is the unperturbed dynamical operator of the system of interest and its explicit expression is

$$\mathcal{L}_a\equiv-v\frac{\partial}{\partial x}+\frac{V'(x)}{m}\frac{\partial}{\partial v}. \tag{36}$$

Note that we left unspecified the explicit form of the operator $\mathcal{L}_b$ which drives the unperturbed motion of the booster.

According to the prescriptions of Refs. [30,31], we write Eq. (33) in the interaction picture, and we project the resulting equation on the space of interest using the projection operator $\mathcal{P}$ defined by

$$\mathcal{P}\cdots=\wp_0(\xi,\boldsymbol{\pi})\int d\xi d\boldsymbol{\pi}\cdots. \tag{37}$$

The reduced probability distribution of the system of interest reads

$$\sigma(x,v;t)\equiv\frac{1}{\wp_0(\xi,\boldsymbol{\pi})}\mathcal{P}\rho(\xi,\boldsymbol{\pi};t)=\int d\xi d\boldsymbol{\pi}\rho(\xi,\boldsymbol{\pi};t), \tag{38}$$

and (see Refs. [30,31]) its time evolution, at the second order in $\mathcal{L}_I$, is given by

$$\begin{aligned}\frac{\partial}{\partial t}\sigma(x,v;t)=\mathcal{L}_a\sigma(x,v;t)&+\left\{\frac{1}{\wp_0(\xi,\boldsymbol{\pi})}\mathcal{P}\mathcal{L}_I\wp_0(\xi,\boldsymbol{\pi})+\frac{1}{\wp_0(\xi,\boldsymbol{\pi})}\mathcal{P}\mathcal{L}_I\int_0^t du(1-\mathcal{P})e^{\mathcal{L}_0u}\mathcal{L}_I\wp_0(\xi,\boldsymbol{\pi})e^{-\mathcal{L}_au}\right\}\sigma(x,v;t)\\&+\frac{1}{\wp_0(\xi,\boldsymbol{\pi})}\mathcal{P}\mathcal{L}_Ie^{\mathcal{L}_0t}(1-\mathcal{P})\rho(x,v,\xi,\boldsymbol{\pi};0)\\&+\frac{1}{\wp_0(\xi,\boldsymbol{\pi})}\mathcal{P}\mathcal{L}_I\int_0^t(1-\mathcal{P})e^{\mathcal{L}_0u}\mathcal{L}_Ie^{-\mathcal{L}_0u}du(1-\mathcal{P})e^{\mathcal{L}_0t}\rho(x,v,\xi,\boldsymbol{\pi};0).\end{aligned} \tag{39}$$

This expression is not yet tractable. We now make some additional assumptions (already discussed in Sec. I), based on the physics of the system. The first one is related to the "macroscopic" character of the variables of interest. The condition that the relaxation TS is much larger than the unperturbed booster TS implies that the booster dynamics is "observed" at times much larger than the booster time scale τ, and that the upper limit of time integration in Eq. (39), t, is replaced by infinity. We also use property (i) of the booster, which, together with the observation at macroscopic times, implies that we can neglect the inhomogeneous term [34,35], i.e., the last term on the RHS of Eq. (39). We finally use the property $\langle\xi\rangle_0=0$, which, taking into account the explicit expression of $\mathcal{L}_I$ of Eq. (35), leads us to

$$\frac{1}{\wp_0(\xi,\boldsymbol{\pi})}\mathcal{P}\mathcal{L}_I\mathcal{P}\cdots=0. \tag{40}$$

Carrying out the necessary algebra, we can rewrite Eq. (39) as

$$\frac{\partial}{\partial t}\sigma(x,v;t)=\mathcal{L}_a\sigma(x,v;t)+\left\{\frac{\partial}{\partial v}\Delta^2\langle\xi^2\rangle_0\int_0^\infty du\varphi(u)e^{\mathcal{L}_a^\times u}\left[\frac{\partial}{\partial v}\right]+\frac{\partial}{\partial v}\Delta^2\int_0^\infty du\langle\xi e^{\mathcal{L}_bu}\Gamma_1\rangle_0e^{\mathcal{L}_a^\times u}[x]\right\}\sigma(x,v;t), \tag{41}$$

where we have introduced the superoperator $A^\times[\;]$, associated with a given operator A, defined as

$$A^\times[B]C\equiv(AB-BA)C. \tag{42}$$

We also used the property

$$e^{A^\times}[B]C=e^ABe^{-A}C \tag{43}$$

with B and C expressing generic operators.

Following the approach illustrated in Refs. [31] and [34], reviewed in the Appendix, we have

$$e^{\mathcal{L}_a^{\times} u}\left[\frac{\partial}{\partial v}\right]\cdots = \left\{\left(\frac{\partial}{\partial x}x_a(t-u)\right)\frac{\partial}{\partial v} - \left(\frac{\partial}{\partial v}x_a(t-u)\right)\frac{\partial}{\partial x}\right\}\cdots, \tag{44}$$

having used

$$e^{\mathcal{L}_a^{\times} u}[h(x)]\cdots = (e^{\mathcal{L}_a u}h(x))\cdots = h(x_a(t-u))\cdots, \tag{45}$$

where $h(x)$ is a given analytic function of the variable x and the unperturbed backward evolution of the variable x, $x_a(t-u)$, is defined as

$$x_a(t-u) \equiv e^{\mathcal{L}_a u}x. \tag{46}$$

The backward evolution $x_a(t-u)$ can be thought of as the unperturbed time evolution of the variable x corresponding to the system of interest placed, at the initial time $u = 0$, in a state corresponding to the point $(x, -v)$ of the phase space. Therefore $x_a(t-u)$ is a function of the coordinate x and the velocity v of the system of interest, as well as of the time u. Thus, using Eqs. (44) and (45), inserting the formal expression of the response function of Eq. (32) into the last term of Eq. (41), and integrating this term by parts, we can rewrite Eq. (41) as

$$\begin{aligned}\frac{\partial}{\partial t}\sigma(x,v;t) = \Bigg\{ &-v\frac{\partial}{\partial x} + \frac{V'(x)}{m}\frac{\partial}{\partial v} - \frac{\Delta^2}{m}x\chi\frac{\partial}{\partial v} + \frac{\partial}{\partial v}\frac{\Delta^2}{m^2}\langle\xi^2\rangle_0\int_0^\infty du\varphi(u)\left(\frac{\partial}{\partial x}x_a(t-u)\right)\frac{\partial}{\partial v}\\ &-\frac{\partial}{\partial v}\frac{\Delta^2}{m^2}\langle\xi^2\rangle_0\int_0^\infty du\varphi(u)\left(\frac{\partial}{\partial v}x_a(t-u)\right)\frac{\partial}{\partial x} + \frac{\partial}{\partial v}\frac{\Delta^2}{m}\chi\int_0^\infty duc(u)v_a(t-u)\Bigg\}\sigma(x,v;t).\end{aligned} \tag{47}$$

Note that we have replaced $\mathcal{L}_a$ with its explicit expression from Eq. (36).

Now let us compare Eq. (47) with the FPE (23). Under which conditions are these two equations equivalent? It is evident that by inspection

$$\begin{aligned}A(x,v) &= \frac{\Delta^2}{m^2}\langle\xi^2\rangle_0\int_0^\infty du\varphi(u)\left(\frac{\partial}{\partial x}x_a(t-u)\right),\\ B(x,v) &= -\frac{\Delta^2}{m^2}\langle\xi^2\rangle_0\int_0^\infty du\varphi(u)\left(\frac{\partial}{\partial v}x_a(t-u)\right),\end{aligned} \tag{48}$$

and

$$\frac{U'(x)}{m} + A(x,v)\frac{mv}{k_BT} + B(x,v)\frac{U'(x)}{k_BT} = \frac{V'(x)}{m} - \frac{\Delta^2}{m}x\chi + \frac{\Delta^2}{m}\chi\int_0^\infty duc(u)v_a(t-u). \tag{49}$$

The transport coefficients of the FPE of (23) are defined by Eq. (48). The temperature k_BT and the renormalized potential $U(x)$, necessary to complete the definition of the FPE, are derived from Eq. (48) and Eq. (49). Inserting Eq. (48) into Eq. (49) and noticing that

$$v_a(t-u) = \frac{d}{dt}x_a(t-u) \equiv -\mathcal{L}_a x_a(t-u) = v\frac{\partial}{\partial x}x_a(t-u) - \frac{V'(x)}{m}\frac{\partial}{\partial v}x_a(t-u), \tag{50}$$

we obtain

$$\begin{aligned}&\frac{U'(x)}{m} + \frac{\Delta^2}{m}\langle\xi^2\rangle_0\left[\int_0^\infty du\varphi(u)\left(\frac{\partial}{\partial x}x_a(t-u)\right)\right]\frac{v}{k_BT} - \frac{\Delta^2}{m^2}\langle\xi^2\rangle_0\left[\int_0^\infty du\varphi(u)\left(\frac{\partial}{\partial v}x_a(t-u)\right)\right]\frac{U'(x)}{k_BT}\\ &\quad= \frac{V'(x)}{m} - \frac{\Delta^2}{m}x\chi + \frac{\Delta^2}{m}\chi\left[\int_0^\infty duc(u)\left(\frac{\partial}{\partial x}x_a(t-u)\right)\right]v - \frac{\Delta^2}{m^2}\chi\left[\int_0^\infty duc(u)\left(\frac{\partial}{\partial v}x_a(t-u)\right)\right]V'(x).\end{aligned} \tag{51}$$

In principle, the equality in Eq. (51) should take into account the implicit dependence of $x_a(t-u)$ on the coordinate x and the velocity v, the detailed nature of which is strongly dependent on the dynamics of the system under study. However, in addition to making the problem intractable, this would make the results dependent on the system of interest, whereas we are looking for a generally valid solution. For this reason we assume now that we can disregard the implicit dependence of $x_a(t-u)$ on the position x and the velocity v, and we derive from Eq. (51) the following expressions:

$$k_BT \equiv \frac{\langle\xi^2\rangle_0}{\chi}\frac{\int_0^\infty du\varphi(u)\left[\frac{\partial}{\partial x}x_a(t-u)\right]}{\int_0^\infty duc(u)\left[\frac{\partial}{\partial x}x_a(t-u)\right]}, \tag{52}$$

and

$$\begin{aligned} U'(x) &= \left[V'(x) - \Delta^2\chi x - \frac{\Delta^2}{m}\chi V'(x)\int_0^\infty duc(u)\left(\frac{\partial}{\partial v}x_a(t-u)\right)\right] \\ &\quad\times\left[1-\frac{\Delta^2}{m}\chi\int_0^\infty du\varphi(u)\left(\frac{\partial}{\partial v}x_a(t-u)\right)\frac{\int_0^\infty duc(u)\left[\frac{\partial}{\partial x}x_a(t-u)\right]}{\int_0^\infty du\varphi(u)\left[\frac{\partial}{\partial x}x_a(t-u)\right]}\right]^{-1} \\ &= V'(x) - \Delta^2 x\chi - \frac{\Delta^2}{m}\chi V'(x)\left[\int_0^\infty duc(u)\left(\frac{\partial}{\partial v}x_a(t-u)\right) - \int_0^\infty du\varphi(u)\left(\frac{\partial}{\partial v}x_a(t-u)\right)\right. \\ &\quad\left.\times\frac{\int_0^\infty duc(u)\left[\frac{\partial}{\partial x}x_a(t-u)\right]}{\int_0^\infty du\varphi(u)\left[\frac{\partial}{\partial x}x_a(t-u)\right]}\right] + O(\Delta^3). \end{aligned} \tag{53}$$

In the next subsection we discuss under which physical conditions the assumption which led us to Eqs. (52) and (53) is correct.

C. Mechanical expressions for the temperature of the system

We show here that the implicit dependence of the mechanical temperature of Eq. (52) and of the renormalized potential of Eq. (53) on the variables x and v can be disregarded if any of the following three conditions is realized.

(a) *The system of interest is a linear oscillator.* We recover in this case the results of a previous paper [19].

(b) *The property $c(t) = \varphi(t)$ is fulfilled.* As we shall see later, this is a condition realized by a booster in canonical equilibrium or, alternatively, in a microcanonical equilibrium in the limiting case of an infinite number of degrees of freedom.

(c) *The NTS condition is fulfilled.* This is the conventional condition of time scale separation which implies that the oscillator of interest has only low frequencies. We now discuss separately these three conditions.

(a) *The system of interest is a linear oscillator.* We assume $V(x) = m\omega^2x^2/2$. In this case we have

$$x_a(t-u) = x\cos(\omega u) - \frac{v}{\omega}\sin(\omega u), \tag{54}$$

from which

$$\left(\frac{\partial}{\partial x}x_a(t-u)\right) = \cos(\omega u) \tag{55}$$

and

$$\left(\frac{\partial}{\partial v}x_a(t-u)\right) = -\frac{\sin(\omega u)}{\omega}. \tag{56}$$

Thus we see that the dependence on x and v is lost. Furthermore, substituting Eqs. (55) and (56) into Eqs. (48), (52), and (53), we obtain

$$A = \frac{\Delta^2}{m^2}\langle\xi^2\rangle_0\mathrm{Re}\left[\hat\varphi(\omega)\right], \tag{57}$$

$$B = \frac{\Delta^2}{m^2}\langle\xi^2\rangle_0\frac{\mathrm{Im}\left[\hat\varphi(\omega)\right]}{\omega}, \tag{58}$$

$$k_BT = \frac{\langle\xi^2\rangle_0}{\chi}\frac{\mathrm{Re}\left[\hat\varphi(\omega)\right]}{\mathrm{Re}\left[\hat c(\omega)\right]}, \tag{59}$$

$$\begin{aligned} \Omega^2 &= \frac{\omega^2 - \frac{\Delta^2}{m}\chi + \frac{\Delta^2}{m}\chi\omega\mathrm{Im}[\hat c(\omega)]}{1+\frac{\Delta^2\chi}{m\omega}\frac{\mathrm{Im}[\hat\varphi(\omega)]\mathrm{Re}[\hat c(\omega)]}{\mathrm{Re}[\hat\varphi(\omega)]}} \\ &\approx \omega^2\left(1-\frac{\Delta^2\chi}{m\omega}\frac{\mathrm{Im}[\hat\varphi(\omega)]\mathrm{Re}[\hat c(\omega)]}{\mathrm{Re}[\hat\varphi(\omega)]}\right) \\ &\quad -\frac{\Delta^2}{m}\chi + \frac{\Delta^2}{m}\chi\omega\mathrm{Im}\left[\hat c(\omega)\right]. \end{aligned} \tag{60}$$

Note that the renormalized frequency Ω is defined through the renormalized potential $U(x)$, which turns out to be harmonic, $U(x) = m\Omega^2x^2/2$, and where the symbols Im[ ] and Re[ ] stand for the imaginary and the real parts of [ ], respectively; the carets over the functions c and φ mean the Fourier transform of these functions, having assumed $c(t) = \varphi(t) = 0$ for $t < 0$.

Using Eq. (11) we have that Eqs. (57), (58), (59), and (60) become identical to the corresponding equations derived in [19]. Thus we recover the properties pointed out in Ref. [19], i.e., the transport coefficients of Eqs. (57) and (58) depend on the frequency ω of the oscillator of interest. This agrees with the remark [33] that the influence of perturbations with frequencies comparable to those of the bath makes the transport parameters strongly depend on the frequency of the perturbation. At first sight, this seems to violate the condition of a time scale separation between microscopic and macroscopic dynamics, on which the "thermodynamics" of the system of interest should rest. However, this does not conflict with the GTS condition. The friction and diffusion coefficients are macroscopic parameters, and the "probing" of the resulting transport process has to be carried out in the region of macroscopic times, where the derivation of the FPE is valid in spite of the high value of the oscillator frequency used. The fact that the transport coefficients are strongly dependent on the "microscopic" frequency ω means that a transmission of information from the microscopic to the macroscopic dynamics is possible, without violating the Gaussian statistics and the standard "thermodynamical" condition within which the observation is carried out [19].

(b) *The property* $c(t) = \varphi(t)$ *is fulfilled.* In this case the temperature of Eq. (52) and the renormalized force of Eq. (53) become

$$k_B T = \frac{\langle \xi^2 \rangle_0}{\chi}, \tag{61}$$

$$U'(x) = V'(x) - \Delta^2 \chi x, \tag{62}$$

i.e.,

$$U(x) = V(x) - \Delta^2 \chi \frac{x^2}{2}. \tag{63}$$

Notice that in this case the "mechanical" temperature T and the effective potential $U(x)$ depend only on the stationary properties of the booster, namely, the susceptibility χ and the mean square value of the doorway variable ξ, whereas in cases (a) and (c) these "macroscopic" properties also depend on the relaxation dynamics of the booster.

It is worth mentioning that condition (b) allows us to prove that our approach recovers the same properties, temperature, transport coefficients, and renormalized potential of a system interacting with an ordinary thermal bath in a canonical equilibrium [31]. To prove this, let us assume that this ordinary thermal bath is given the temperature T_b. This is the standard case to which the conventional LRT by Kubo [8] refers, leading to

$$\chi_{\text{can}}^{\text{Kubo}}(t) = [1 - \varphi(t)]\, \chi_{\text{can}}^{\text{Kubo}}, \tag{64}$$

where

$$\chi_{\text{can}}^{\text{Kubo}} = \frac{\langle \xi^2 \rangle_0}{k_B T_b}. \tag{65}$$

Comparing (64) to (10) we see that $c(t) = \varphi(t)$, i.e., condition (b) is fulfilled. This makes it possible for us to use Eq. (61) and, thus, by replacing Eq. (65) into (61), to show that at equilibrium the system of interest, as prescribed by ordinary thermodynamics, has the same temperature as the thermal bath. As far as the transport coefficients are concerned, we recover the same result of Ref. [31], inserting Eq. (65) into Eq. (48). The renormalized potential of Ref. [31] is recovered by replacing Eqs. (64) and (65) into (63).

It is also worth mentioning that, as discussed in [6], Hamiltonian boosters with a large number of degrees of freedom can also fulfill condition (b). In [6] it is shown that if the booster is deterministic, Hamiltonian, and "mixing," and it has a sufficiently large number of degrees of freedom, then the standard Kubo LRT is expected to hold and, consequently, condition (b) is also realized.

(c) *The NTS condition is fulfilled.* Under this condition the unperturbed dynamics of the system of interest must also be regarded as "macroscopic" and we can think of the system of interest as a tool to determine the thermodynamic properties of the booster. If condition (c) holds, the susceptibility and the correlation functions of the booster decay over times much shorter than the typical evolution time of the unperturbed system of interest. Thus in Eqs. (52) and (53) we can expand the unperturbed backward evolution $x_a(t-u)$ in a power series of time u, yielding

$$\left(\frac{\partial}{\partial x} x_a(t-u) \right) = 1 - \frac{V''(x)}{m} \frac{u^2}{2} + O(u^3), \tag{66}$$

$$\left(\frac{\partial}{\partial v} x_a(t-u) \right) = -u + \frac{V''(x)}{m} \frac{u^3}{6} + O(u^4). \tag{67}$$

It is safe to neglect the terms $O(u^2)$ in these equations. By inspection, we have then recovered the expression for the temperature given by Eq. (22). Furthermore, from Eq. (48) we derive the following expressions for the transport coefficients A and B:

$$A = \frac{\Delta^2}{m^2} \langle \xi^2 \rangle_0 \tau,$$
$$B = \frac{\Delta^2}{m^2} \langle \xi^2 \rangle_0 \eta^2, \tag{68}$$

where η^2 is defined in Eq. (6). From Eqs. (68) and (22) we recover, for the friction of the system $\gamma \equiv A/k_B T$, the same expression obtained using the Langevin approach of Sec. III, Eq. (21).

As far as the renormalized potential $U(x)$ is concerned, from Eqs. (66), (67), and (53), we have

$$U(x) \approx V(x) - \Delta^2 \chi \frac{x^2}{2} + \frac{\Delta^2}{m} \chi V(x) \left(\beta^2 - \eta^2 \frac{\vartheta}{\tau} \right), \tag{69}$$

where the constant β^2 is defined by Eq. (13). In the case when the correlation function and the susceptibility of the booster decay exponentially with the same decay time, the potential of Eq. (69) becomes equal to the renormalized potential of Eqs. (21) and (63).

D. A comparison with the Boltzmann principle

We now illustrate the relation between the present results and the ordinary approaches to thermodynamics [paths (a) and (1) of Fig. 1]. We derived the mechanical expression for the temperature of Eq. (52) via a FPE approach, where the system of interest would become some kind of instrument monitoring the thermodynamic properties of the booster. For this reason the most natural condition to adopt would seem to be condition (c) (NTS condition). However, we make the comparison between the mechanical expression for the temperature arrived at in this paper and the Boltzmann principle in each of the three conditions.

To begin with, we note that to make a fair comparison with the Boltzmann principle, we must make the same hypotheses used in the classical derivation of thermodynamics, and consequently we must assume that our booster is a Hamiltonian system with mixing dynamics (see Fig. 1), which implies a microcanonical equilibrium distribution for it. In this case, using a Kubo-like approach, the susceptibility $\chi(t)$ is proved to be [6]

$$\chi(t) = \frac{1}{A(E)}\frac{\partial}{\partial E}\left\{A(E)\langle\xi^2\rangle_0\left[1-\varphi(t)\right]\right\}, \tag{70}$$

where $A(E)$ is the area of the hypersurface of the phase space occupied by the unperturbed booster with energy E. From Eqs. (70) and (10) we have

$$\begin{aligned}\chi c(t) &= \frac{1}{A(E)}\frac{\partial}{\partial E}\left[A(E)\langle\xi^2\rangle_0\varphi(t)\right]\\ &= \langle\xi^2\rangle_0\varphi(t)\frac{\partial}{\partial E}\ln A(E) + \frac{\partial}{\partial E}\left[\langle\xi^2\rangle_0\varphi(t)\right].\end{aligned} \tag{71}$$

The last term of Eq. (71) rules out condition (b), which would imply $c(t) = \varphi(t)$. It is clear, then, that we are carrying out a comparison between the mechanical expression for the temperature of Eq. (52) and the temperature given by the Boltzmann principle, applied to the booster,

$$k_B T_{\mathrm{Boltz}} \equiv \left[\frac{\partial}{\partial E}\ln A(E)\right]^{-1}, \tag{72}$$

when either condition (a) or condition (c) applies.

Let us examine condition (a) first. In this case the theory of this paper results in Eq. (59). Thus, taking the Fourier transform of Eq. (71), we have, at a given frequency ω',

$$\begin{aligned}\chi \mathrm{Re}\left[\hat{c}(\omega')\right] &= \langle\xi^2\rangle_0 \mathrm{Re}\left[\hat{\varphi}(\omega')\right]\frac{\partial}{\partial E}\ln A(E)\\ &\quad + \frac{\partial}{\partial E}\left\{\langle\xi^2\rangle_0 \mathrm{Re}\left[\hat{\varphi}(\omega')\right]\right\}.\end{aligned} \tag{73}$$

Under condition (a), this frequency must be identified with ω. Replacing the resulting expression in Eq. (59) we obtain

$$\begin{aligned}k_B T &= \frac{\langle\xi^2\rangle_0 \mathrm{Re}\left[\hat{\varphi}(\omega)\right]}{\langle\xi^2\rangle_0 \mathrm{Re}\left[\hat{\varphi}(\omega)\right]\frac{\partial}{\partial E}\ln A(E) + \frac{\partial}{\partial E}\left\{\langle\xi^2\rangle_0 \mathrm{Re}\left[\hat{\varphi}(\omega)\right]\right\}}\\ &= \left[\frac{\partial}{\partial E}\ln A(E) + \frac{\partial}{\partial E}\ln\left\{\langle\xi^2\rangle_0 \mathrm{Re}\left[\hat{\varphi}(\omega)\right]\right\}\right]^{-1}.\end{aligned} \tag{74}$$

Let us now consider condition (c). In this case the theory of this paper results in the mechanical expression for the temperature of Eq. (22). The definition (12), in turn, implies that the denominator of Eq. (22) is derived from Eq. (73) with $\omega' = 0$, and the definition of correlation time of Eq. (5) implies that $\mathrm{Re}\left[\hat{\varphi}(0)\right]$ coincides with τ. Thus from Eq. (22) we get

$$\begin{aligned}k_B T &= \frac{A(E)\langle\xi^2\rangle_0\tau}{\frac{\partial}{\partial E}\left[A(E)\langle\xi^2\rangle_0\tau\right]}\\ &= \left[\frac{\partial}{\partial E}\ln A(E) + \frac{\partial}{\partial E}\ln\left(\langle\xi^2\rangle_0\tau\right)\right]^{-1}.\end{aligned} \tag{75}$$

In conclusion, we see that both condition (a) and condition (c) lead to an expression for the mechanical temperature which differs from the Boltzmann prediction by a "dynamical" correction, i.e., a correction involving the correlation function $\varphi(t)$. Only if

$$\frac{\partial}{\partial E}\ln A(E) \gg \frac{\partial}{\partial E}\ln\left\{\langle\xi^2\rangle_0 \mathrm{Re}\left[\hat{\varphi}(\omega')\right]\right\} \tag{76}$$

does the "mechanical" temperature of Eqs. (74) and (75) coincide with the Boltzmann prediction of Eq. (72).

What is the physical significance of Eq. (76)? We are inclined to interpret Eq. (76) as the missing connection between the equilibrium statistical properties and their dynamical realization. The dynamical realization of statistical mechanics results, in principle, in a departure from the standard prediction, through the term involving the correlation function $\varphi(t)$. The effect of this dynamic correction to the temperature is shown using the numerical simulations in Sec. V.

Notice that this interesting discovery does not conflict with the standard view, since it is straightforward to show that the standard Boltzmann prediction is recovered by increasing the number of degrees of freedom of the booster. To prove this, let us introduce the energy density $\epsilon \equiv E/n$ where E is the total energy of the system and n the number of degrees of freedom. Increasing n while keeping ϵ constant we have that the area $A(E)$ grows like E^n, leading to

$$\lim_{n\to\infty}\frac{\partial}{\partial E}\ln A(E) \approx \epsilon = \mathrm{const.} \tag{77}$$

On the other hand, we expect $\langle\xi^2\rangle_0$ and $\varphi(t)$ to become independent of n for large n, i.e.,

$$\lim_{n\to\infty}\frac{1}{n}\frac{\partial}{\partial\epsilon}\langle\xi^2\rangle_0 = 0, \tag{78}$$

$$\lim_{n\to\infty}\frac{1}{n}\frac{\partial}{\partial\epsilon}\varphi(t) = 0. \tag{79}$$

Clearly, these equations imply that Eq. (76) is satisfied.

We also note that the hypothesis of a large number of degrees of freedom, leading to Eq. (79) and thus making the last term of Eq. (71) vanish, implies that the booster satisfies also condition (b). Moreover, in this limit, using Eq. (78), the stationary susceptibility $\chi = \frac{1}{A(E)}\frac{\partial}{\partial E}\langle\xi^2\rangle_0 A(E)$ converges toward the standard Kubo one of Eq. (65). As a by-product, we have now also proven that in the limit of a large number of degrees of freedom the expression for the microcanonical susceptibility in Eq. (70) coincides with the expression for the canonical susceptibility obtained using Kubo LRT, Eq. (64).

In summary, our derivation of thermodynamics from classical mechanics has a range of validity more extended than that of the ordinary procedures, since the resulting "mechanical" temperature also depends on the microscopic *dynamical* properties. In addition to that, our approach also establishes an attractive connection between ordinary statistical mechanics and Kubo's LRT. This is so because the same limiting condition of a very large number of degrees of freedom, which makes the "mechanical" temperature become independent of microscopic dynamics as prescribed by the Boltzmann principle, also leads to the realization of the linear response in the specific form prescribed by Kubo, suggesting that statistical mechanics has the same underpinning as Kubo's LRT. In other words, we have found that it is possible to derive ordinary thermodynamics with the joint action of chaos and of a large number of degrees of freedom. We shall come back to this important issue in Sec. VI.

V. NUMERICAL RESULTS

The numerical results refer to two different kinds of composite systems. The first composite system is Hamiltonian and consists of a slow linear oscillator of interest interacting, via a harmonic coupling, with a Hamiltonian booster given by a Fermi-Pasta-Ulam (FPU) system, with a quartic interaction: according to the nomenclature of the related literature [37–39], a β-FPU system. The booster has eight degrees of freedom, i.e., it consists of a chain of eight nonlinear oscillators, and it is in a physical configuration which, according to the results of numerical calculations [37,38] and theoretical arguments [39], corresponds to a state of "fully developed chaos." In this condition, we argue that the dynamics of the booster is virtually mixing. The second composite system is a "slow" nonlinear oscillator, with a quartic potential, interacting with a non-Hamiltonian booster, the dynamics of which is determined by a one-dimensional map. The latter system is not Hamiltonian, but this is the price we pay to have a rigorous theoretical proof [1–3] of the mixing dynamics of the booster. As we shall see, the boosters are so quick and the unperturbed dynamics of the system so slow that they fulfill condition (c) of Sec. IV, i.e., the NTS condition. We note that the former system fulfills also condition (a) of Sec. IV, since in this case the system of interest is a linear oscillator.

A. Hamiltonian case

The Hamiltonian of the former composite system is

$$H = \frac{v^2}{2} + \frac{\omega^2 x^2}{2} + \Delta x \zeta_1 + \sum_{i=1}^{8} \frac{\dot{\zeta}_i^{\,2}}{2} + W(\zeta_8) + \sum_{i=2}^{8} W(\zeta_i - \zeta_{i-1}), \tag{80}$$

where

$$\xi \equiv \zeta_1, \qquad W(\zeta) \equiv \frac{\zeta^4}{4} + \frac{\zeta^2}{2}. \tag{81}$$

We integrate this system using a fourth-order symplectic Runge-Kutta algorithm [36]. The integration time step was chosen so that the total energy was always conserved with at least eight significant figures at the end of each run.

Let us discuss first the booster dynamics, in both the unperturbed and perturbed cases. The energy ϵ per oscillator given to the booster for $\Delta = 0$ is $\epsilon = 10$, and according to Refs. [37–39] this should be a convenient choice to produce a regime of fully developed chaos: the unperturbed dynamics of the booster corresponding to this energy density, within the accuracy of a numerical treatment [37,38], is expected to be mixing and then ergodic. It is worth remarking that, when the coupling with the system of interest is switched on, part of the booster energy is transferred to the system of interest, decreasing the booster energy by approximately 10%. This change is expected to be weak enough to leave the dynamical properties of the booster virtually unchanged.

Notice that due to the particular choice of the system of interest, a linear oscillator, condition (a) is satisfied. This would be enough to make our theory applicable to the whole system booster plus oscillator of interest. However, if condition (c) were also satisfied, we would have a further simplification in our theoretical expression for the temperature. As we shall see, in the numerical simulations we eventually use a frequency ω for the system of interest small enough to be far from the resonances of the correlation function $\varphi(t)$.

Clearly, to apply the theory of this paper we need first to characterize the dynamics of the booster, beginning with its correlation function $\varphi(t)$. According to the general discussion of Sec. I, this unperturbed dynamical property must be characterized by a finite correlation time. The result of a direct simulation of this correlation function is shown as a full line in Fig. 2. The fit with the analytical expression (for large times, $t > 100$)

$$\varphi(t)_{\text{fit}} = \exp(-\alpha t)\cos(\delta t + \phi) \tag{82}$$

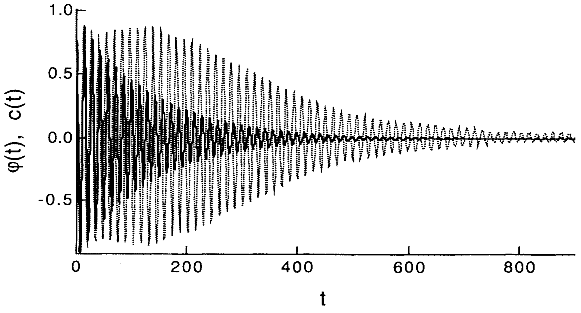

FIG. 2. Comparison between the correlation function $\varphi(t)$ (solid line) and the normalized susceptibility $c(t)$ (dashed line) obtained from numerical simulations in the β-FPU model with eight oscillators [Eq. (80)]. The total energy of the chain is $E = 80$.

turns out to be extremely good since for times $t > 100$ the difference between the best fit and the numerical correlation function would be a horizontal straight line virtually coinciding, in the scale of the figure, with the abscissa axis. The best fit yields $\alpha = 0.0076$, $\delta = 0.44$, and $\phi = 0.038$ rads. The agreement between this fitting function and the numerical results suggests that in the limit of large times this correlation function decays exponentially; this confirms that this system satisfies condition (i) (finiteness of the relaxation time), on which our approach to the FPE is based. We add that, as it should, the short-time behavior of the numerical results departs from the exponential-like structure of the fitting function. This is a well known problem stalking the representation of a decay process via an exponential-like expression [40]. However, it must be stressed that the good agreement at large times does not rule out the possibility that long and weak tails with an inverse power law falloff might be present and masked by the numerical fluctuations. In this unlucky case, the error fluctuations would play the same role as the environmental fluctuations which prevent the long tails from having a significant influence on the macroscopic time evolution of the system of interest. In Sec. VI we shall come back to discussing this problem.

Having an estimate of the typical resonant frequency appearing in the correlation function, the parameter δ above, and of its typical width, the parameter α, it is easy to pick a value for ω such that condition (c) is realized. In the simulations we set $\omega = 0.2$ and we checked numerically that actually $\mathrm{Re}\,[\hat{\varphi}(\omega)] \approx \mathrm{Re}\,[\hat{\varphi}(0)] \equiv \tau$.

To apply Eq. (75), we need to know the value of τ, the area under the correlation function $\varphi(t)$, and of the derivative of τ with respect to the total energy E of the booster. In practice, the value of τ turns out to be rather small, whereas the correlation function $\varphi(t)$ is characterized by very fast oscillations, making a numerically accurate derivation of τ extremely difficult; a possibility would be to increase the number of sampling points of $\varphi(t)$, but the problem soon becomes intractable. We then followed a different procedure. We took the equations of the booster and introduced an auxiliary variable defined as $w = \dot{\xi}$. Then we examined the free diffusion of w. It is straightforward to see that, under the assumption of the finiteness of the area under the correlation function $\varphi(t)$, the second moment $\langle w^2(t)\rangle$ is

$$\begin{aligned}\langle w^2(t)\rangle &= \int_0^t \int_0^t \langle \xi(s)\xi(s')\rangle_0 ds ds' \\ &\approx 2\langle \xi^2\rangle_0 \tau t + \text{const}, \qquad t \to \infty. \end{aligned} \tag{83}$$

Knowing $\langle \xi^2\rangle_0$ and fitting a straight line to $\langle w^2(t)\rangle$ for large t, we derived τ for different values of $\epsilon = E/n$. To use Eq. (75) we must also evaluate numerically the dependence of $A(E)$ and $\langle \xi^2\rangle_0$ on E, which we derive explicitly by integrating the corresponding expressions on the appropriate energy surfaces.

Next, we check that the booster responds linearly to the external perturbation or, equivalently, as it is proved in [6], that Eq. (70) is satisfied by our booster: the comparison between the numerical $\chi(t)$ and Eq. (70) is shown in Fig. 3. To check the validity of Eq. (70), the calculation of $\chi(t)$ is carried out with a numerical "experiment": first, we determined a number of "unperturbed" initial conditions, obtained following the trajectory of the system in the absence of any external perturbation. Then an external (constant) perturbation K is switched on, the resulting trajectories are averaged, and the response is determined.

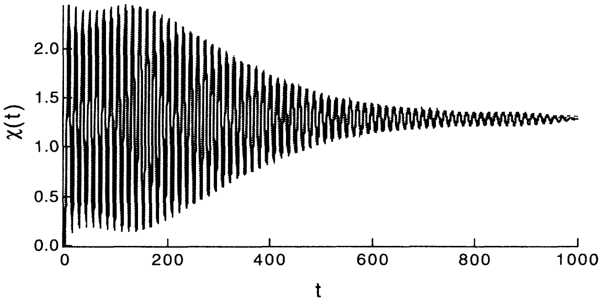

FIG. 3. Comparison between the numerical $\chi(t)$ (solid line) and the theoretical $\chi(t)$ (dashed line, barely visible under the solid line), obtained using the LRT approach in the microcanonical case, Eq. (70), as function of time. The simulations refer to a β-FPU model with eight oscillators [Eq. (80)]. The total energy of the chain is $E = 80$.

The evaluation of the theoretical susceptibility $\chi(t)$ of Eq. (70) from the numerical data poses a delicate numerical problem. In principle, we should determine a correlation function $\varphi(t)$ for a range of values of the energy of the booster around a given energy, and then we should proceed to a direct differentiation. However, in practice we found that, due to the finiteness of the number of trajectories used to build the correlation function, the statistical fluctuations would make the result for the derivative of $\varphi(t)$ with respect to E totally meaningless. Therefore we had to approach the problem differently. We decided to compute the correlation function for several values of E around the value of interest; then we interpolated, *for any given time t*, to find (via a linear least square fit) the bona fide value of the correlation function $\varphi(t)$ and its derivative with respect to E. This procedure turned out to be amazingly reliable, with results only very weakly dependent on the number of different correlation functions used for the fit and the range of energies considered. We see from Fig. 3 that the "true" $\chi(t)$ and Eq. (70) are in remarkable agreement; even the details of the oscillating behavior of $\chi(t)$ are well reproduced. This is a very satisfactory confirmation of the validity of Eq. (70) and of what is argued in Ref. [6].

According to Ref. [6], we conclude that the number of degrees of freedom in our system is large enough to guarantee condition (ii) (applicability of a linear response theory). But, as is evident from Fig. 2, it is *not* large enough to realize also condition (b) (coincidence between microcanonical and canonical susceptibility). Hence we should be able to observe a discrepancy between the observed temperature, the theoretical prediction of Eq. (75), and the "standard" Boltzmann temperature, given by Eq. (72).

From the simulations we find

$$\langle \xi^2 \rangle_0 \tau = 0.56, \tag{84}$$

$$\frac{\partial}{\partial E} \langle \xi^2 \rangle_0 \tau = 0.01, \tag{85}$$

$$\left[\frac{\partial}{\partial E} \ln A(E) \right]^{-1} = 14.95, \tag{86}$$

from which, using Eq. (75), we expect a temperature of

$$k_B T = 11.78 \tag{87}$$

that must be compared with the numerical results. Notice that the significant discrepancy between the Boltzmann prediction, Eq. (86), and our prediction, Eq. (87), as widely discussed in Sec. IV D, is due to the dynamical property (85). To complete the discussion of our theoretical approach to thermodynamics, we now couple the booster to the system of interest to check whether the temperature perceived by the system of interest is really that predicted by Eq. (87).

The coupling constant Δ must be chosen so that we are within the range of validity of the linear response theory. The critical value $K_{\max}$ below which the booster responds linearly is

$$K_{\max} \approx 1. \tag{88}$$

It follows that Δ must satisfy

$$\Delta \sqrt{\langle x^2 \rangle_{\mathrm{eq}}} \ll K_{\max}. \tag{89}$$

The mean quadratic value of x, in turn, is given by

$$\langle x^2 \rangle_{\mathrm{eq}} = \langle v^2 \rangle_{\mathrm{eq}} / \omega^2, \tag{90}$$

and the mean square value of the velocity is estimated by assuming that the thermodynamic prediction we want to prove [Eq. (75)] is indeed true. Thus, using for the temperature the value Eq. (87) and for the frequency of the system the earlier used value, $\omega = 0.2$, we find that Δ must satisfy the inequality

$$\Delta \ll \omega / \sqrt{k_B T} \approx 0.05. \tag{91}$$

From the structure of our FPE, we have immediately that the friction coefficient, in terms of the system parameters, reads

$$\gamma = \Delta^2 \langle \xi^2 \rangle_0 \tau / k_B T. \tag{92}$$

Using Eqs. (84), (87), and (91) we have

$$\gamma \ll 10^{-4}. \tag{93}$$

Comparing this damping coefficient to the frequency $\omega = 0.2$ of the system of interest, we have that the decay is strongly underdamped: from the FPE, we have then that the relaxation time is, to a good approximation, given simply by $1/\gamma$.

We show in Fig. 4 the result of the numerical integration of the equations of motion obtained coupling the system of interest and the booster. We plot in the figure the evolution of $\langle v^2(t) \rangle$ for a sample of 400 particles, starting from the initial condition

$$\rho(x, v, \zeta_i, \dot{\zeta}_i, t = 0) \propto \delta(v) \delta(x) \delta(H_{\mathrm{booster}} - E), \tag{94}$$

and for different values of the coupling constant Δ. It is clear that as far as the dynamics of the mean velocity square is concerned, the process seems to be a true brownian motion with exponential relaxation to an equilibrium value.

From the structure of the FPE, we know that, starting from the initial condition of Eq. (94), the relaxation of $\langle v^2(t) \rangle$ should be described by a function of the form (we are in a strongly underdamped regime)

$$f(t) = k_B T \left(1 - e^{-\gamma t} \right). \tag{95}$$

We used Eq. (95) to fit the results of the numerical simulations done for different Δ. The comparison between the theoretical prediction for γ and the result of the fit is summarized in Fig. 5. The numerical values for γ follow the theory very closely.

The temperature we expect, on the grounds of Eq. (87), is shown as a horizontal solid line in Fig. 4. It is clear that the simulations relax to a value close to this, which is markedly different from the value expected following the "standard" Boltzmann prescription, Eq. (86), shown as a dashed line.

Finally, we need to check that the equilibrium condition of the system of interest is indeed described by a canonical distribution. This implies that all cumulants of the variable v of order higher than 2 should vanish identically. Furthermore, given that the system of interest is a harmonic oscillator, we also have that the cumulants of order higher than 2 should identically vanish *at all times.*

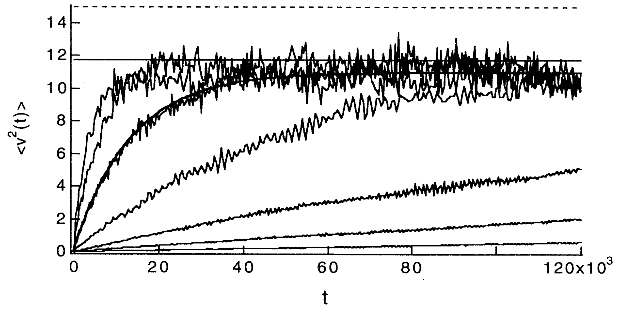

FIG. 4. Relaxation of $\langle v^2(t) \rangle$ for the system of Eq. (80), and total energy $E = 80$. The jagged lines are the result of numerical simulations, done averaging the motion of 400 particles, starting from the initial distribution of Eq. (94), for different values of Δ: from bottom right to top left we have $\Delta = 0.001$, 0.003, 0.006, 0.01, 0.02, 0.04, and 0.08. The dashed line is the Boltzmann temperature [Eq. (72)]. The horizontal solid line is the temperature obtained following our proposal [Eq. (75)]. The thick solid line superimposed on the relaxation of $\Delta = 0.02$ is the best fit done with Eq. (95).

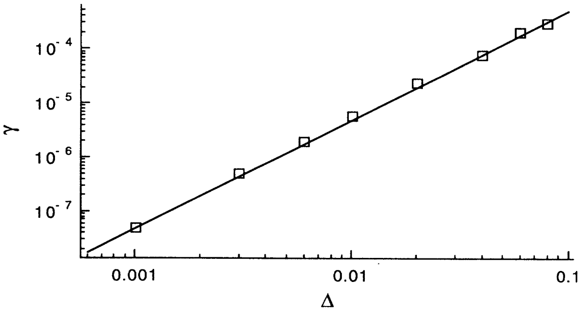

FIG. 5. Comparison between the theoretical damping from Eq. (92) (solid line) and the corresponding damping observed in the numerical simulations, as function of Δ (squares). The system simulated is the one of Eq. (80); total energy $E = 80$.

We checked this property, plotting in Fig. 6 the cumulant of order 4, for a given Δ, as a function of time: it is clear that indeed, apart from some statistical fluctuations, this cumulant is reasonably close to zero.

In conclusion, with the help of a numerical treatment we have shown that a Hamiltonian booster with only eight degrees of freedom is sufficiently large to give the oscillator of interest thermodynamical properties. The friction and the temperature of the oscillator of interest are proved to fit very satisfactorily the theoretical values.

B. Non-Hamiltonian case

We recall that the theory developed so far can be applied to a generic system, not necessarily a Hamiltonian one, like a chaotic map. The reason to use a chaotic map as a booster is that in this case conditions (i) and (ii) are *exactly* satisfied. We showed in the preceding section that for a system of interest given by a linear oscillator our theory is indeed applicable: here, given that we are much more confident about the correct behavior of the booster, we focus on using a system of interest which is nonlinear [hence condition (a) does not apply], and on relying only on condition (c) (NTS condition): in the simulations, the potential used has the form $V(x) = x^2 + x^4$. There is clearly an intrinsic problem: the nonlinear potential of the system of interest is harder than a harmonic one. In principle, if the energy of the system increased enough, the dynamics would involve higher and higher frequencies, violating the NTS condition. In practice, however, due to the choice of the parameters, the equilibrium distribution involves frequencies small enough to satisfy the NTS condition, apart from some negligible contributions coming from the distribution tails.

The theory developed in this paper refers to the situation when the time is a continuous variable, whereas the evolution in a mapping takes place at discrete times. We can cure this problem with an appropriate choice of the relaxation time in the booster (in the simulations, this time was taken to be 100 map iterations): the idea is that, if the relaxation time of the booster is fairly large compared to 1, then the evolution of the map, on the scale of its relaxation time, will become indistinguishable from a continuous one. As for the coupling between the map and the system of interest, it is obvious that the system of interest is integrated using a discrete numerical integrator (a fourth-order predictor-corrector, in practice): the unitary time of evolution in the map is assumed to be equal to the time step dt used in the integration of the system of interest.

The map used as the unperturbed booster is the unidimensional piecewise linear map studied by Grossmann in [41]. This map has a correlation function that is an exponential with a decay time τ that depends on the only parameter that enters in the equation defining the mapping [41]. As we said above, we choose this parameter so that $\tau = 100dt$. The system of interest perturbs this map by an additive term $\Delta x \delta f(\xi)$ where $\delta f(\xi)$ is a piecewise quadratic function (see [41]). Applying a constant perturbation K to the booster, we find that it responds linearly for $|K| < 10^{-3}$, thus characterizing the region of linear behavior. From [41], we know that, in the linear regime, the response function $S(t) \equiv \partial\chi(t)/\partial t$ is proportional to the correlation function $\varphi(t)$, which makes it easy to evaluate the function $c(t)$. From the results of Ref. [41], we can easily work out the booster parameters needed under condition (c); and finally we can evaluate the coefficients and the temperature of the FPE.

Figures 7 and 8 summarize the comparison between

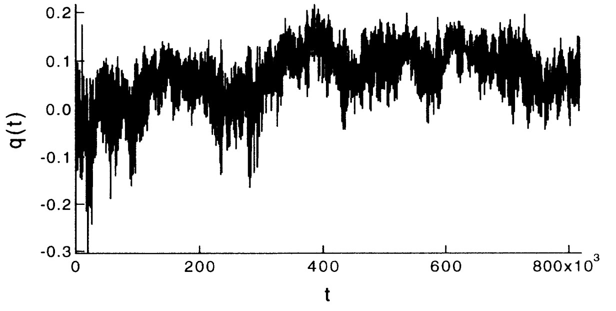

FIG. 6. Plot of the quantity $q(t) \equiv [1 - \langle v^4(t)\rangle]/[3\langle v^2(t)\rangle^2]$ vs t, for the system of Eq. (80), total energy $E = 80$, and $\Delta = 0.01$.

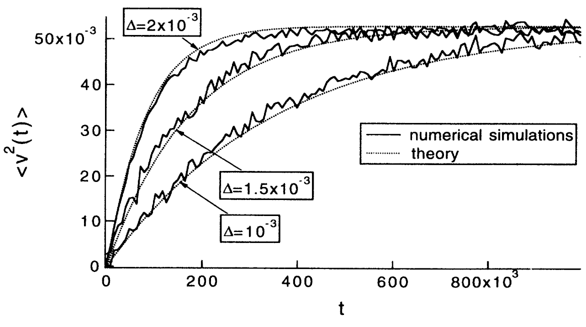

FIG. 7. Comparison between the theoretical relaxation of $\langle v^2(t)\rangle$ and the simulations for the non-Hamiltonian system of Sec. V B. The parameters used in the simulations are indicated on the graph.

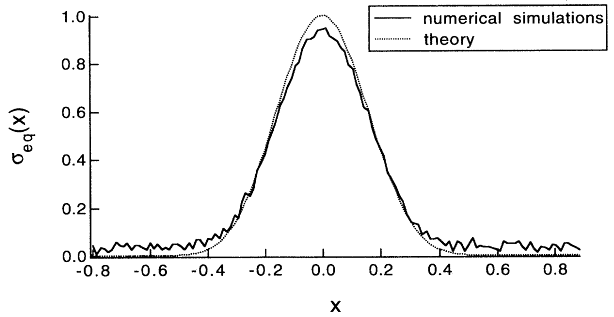

FIG. 8. Comparison between the theoretical equilibrium distribution of the variable x [$\exp -U(x)/k_BT$], and the simulations for the non-Hamiltonian system of Sec. V B. See the graph for a key to the curves.

numerical simulations and theoretical predictions. In Fig. 7 we compare the relaxation obtained in the numerical simulations with the theoretical prediction based on the FPE of Eq. (23), with A and B given by Eq. (68), and the temperature from Eq. (22) [condition (c)]: we stress that no adjustable parameter has been used in drawing the theoretical curves. Similarly, we show in Fig. 8 the equilibrium distribution of the variable x obtained from the numerical simulations, and the theoretical predictions. As expected, we find that the distribution is given by the exponential of the effective nonlinear potential [see Eq. (23)], divided by the appropriate temperature. Again, the theoretical curve has been drawn without any adjustable parameters.

This example shows that a non-Hamiltonian system with only one degree of freedom can "work" as a thermal bath for the system of interest. In this case the correct statistics of the system of interest is a pure consequence of the central limit theorem applied to the "chaotic" dynamics of the booster. For this reason, to obtain the right statistics we have to use a very small coupling constant Δ so that the process of relaxation of the system of interest is very slow compared to the fast dynamics of the booster. As a consequence we have that the numerical simulations take, for such a "small" system also, several days of CPU time.

VI. SOME GENERAL REMARKS

The most important result of our approach to thermodynamics, when compared to the standard one, is its dynamical derivation. The macroscopic dynamical properties of the system of interest are the consequence of an accumulation process of a large number of uncorrelated booster fluctuations, filtered by the dynamics of the unperturbed system of interest. It is a natural consequence, hence, that the time scale of the booster, compared to the time scale of the system, should explicitly appear in the coefficient of our FPE. This new approach, because it involves the dynamics of the booster directly, shows where the real problem of a realization of the thermodynamics lies.

We must admit that it is difficult to prove in general that the Hamiltonian boosters exactly fulfill the dynamical properties (i) and (ii) used as hypotheses in our approach. Only in some cases of non-Hamiltonian boosters is it possible to prove that these properties are exactly satisfied. However, comparing the numerical results of the Hamiltonian case of the preceding section, where there is no general theorem supporting these properties, with the non-Hamiltonian case, where these properties can be rigorously derived, we see that both result in "ordinary statistical mechanics" within the limits of the numerical accuracy. In other words, it seems that Hamiltonian systems can also satisfy properties (i) and (ii). But is this perhaps just an artifact of the finite precision of the numerical results? We are currently not able to answer. For example, an important problem still open is whether the *true* behavior of the correlation function $\varphi(t)$ in the long-time region is dominated by fluctuations due to numerical errors. Are these time regions characterized by an inverse power law or not? If there are long and weak tails, these may be hidden by the numerical fluctuations, which play the same role as the environmental fluctuations. In this case, the approach to thermodynamics illustrated in this paper would not be completely objective. Notable efforts to rid the approach to thermodynamics of subjective aspects are those by Prigogine and co-workers [42].

We do not address directly this very delicate issue, and we limit ourselves to remarking, on the basis of the general arguments used by Lee [43], that a rigorous exponential decay might be incompatible with the current physical paradigms. According to the main conclusions of this paper, the presence of slow tails would induce the breakdown of the linear response, and consequently the breakdown of ordinary statistical mechanics itself. Since there is a consensus on the importance and validity of ordinary statistical mechanics, we are tempted to conclude that the inverse power law behavior must be regarded as an idealization of reality as strong as the exact exponential behavior, and that reality must imply a complex superposition of these two ingredients, with ordinary statistical mechanics obtained along the lines here indicated, and with an exact exponential behavior replaced by a behavior which is exponential within the limits of human observation. This would not be a completely satisfactory approach to thermodynamics, and there are serious doubts that such a satisfactory approach is possible within the theoretical framework of the current physical theories, either classical or quantum mechanical [40]. The avenue illustrated here is, in our opinion, the most compatible with the physical laws already known.

According to what we said above, the "weakness" of our theoretical approach to thermodynamics, namely, our inability to guarantee condition (i) in general, can also be regarded as a significant result of this paper: the discovery that a rigorous derivation of LRT is a necessary step to derive statistical mechanics and thermodynamics from mechanics, with no statistical assumptions.

Note that when only condition (a) is satisfied we have a thermodynamics (a temperature) dependence on the frequency of the system of interest and on the correlation function of the booster, which is clearly an unsatisfactory result: condition (a) leads to a very "strange" thermodynamics. On the other hand, when condition (c) applies we are forced to use only systems of interest that are very slow compared to the booster and (see Sec. IV D) the temperature depends on the number of degrees of freedom of the booster. Thus condition (c) also does not yield ordinary thermodynamics, although for real systems where a fluctuation-dissipation process is observed, it would require some additional investigation (for instance, comparing susceptibility and autocorrelation function) to appreciate that the thermodynamics is that typical of condition (c) and not the "canonical" one. It is only when condition (b) is realized, as in the case in which the *standard canonical* Kubo LRT is applicable, that we have temperature independence of the dynamics of the booster and of the kind of system of interest used; this reinforces the idea that the standard canonical Kubo LRT must be a general property of nature, and that it is probably the result of the joint action of chaos and of a large number of degrees of freedom.

Finally, some remarks about the applicability of the perturbation approach on which the theory here developed is based. It is clear that for any weak coupling constant Δ, there exists a time t^* such that for times shorter than t^* the perturbative approach is applicable. The smaller Δ is, the larger t^* becomes. However, a decrease of Δ increases the relaxation time of the system of interest, therefore it is wrong to think that it is always possible to find a small enough Δ such that the perturbation approach gives the correct results for times greater than the relaxation time, i.e., for all times: the final equilibrium state will be affected by how these two limits are actually reached. This is particularly striking in the Hamiltonian case treated here. It is clear (see Fig. 4) in this case that the equilibrium temperature measured in the simulations is independent of the parameter Δ. However, it is also clear that this temperature differs by some 10% from the theoretical temperature expected for the system. Thus also for vanishing coupling Δ, the difference between the theoretical temperature and the measured one does not decrease.

This discrepancy is due to the obvious fact that we coupled a booster with a small number of degrees of freedom and with energy E to a system of interest with zero energy. The coupling, as small as it can be, nevertheless allows a flow of energy from the booster to the system of interest. The equilibrium eventually reached is such that the total energy exchanged is not a small perturbation of the booster energy. So, although the short-time dynamics is well reproduced by the theory, the equilibrium, deduced assuming that the booster is left unperturbed, in this case is not correct. Even so, we *stress* that the equilibrium temperature reached in this situation is much closer to the temperature predicted following our theory than to the temperature predicted using the "standard" Boltzmann principle without any dynamical correction.

We can conclude that, to apply our theory, we must use a small coupling constant Δ *and* we must also check that the booster is never perturbed too much by the system of interest. In the case of a Hamiltonian booster this means that the booster must have a number of degrees of freedom that is fairly large compared to that of the system of interest. In the Hamiltonian case of the numerical simulations of Sec. V A, we see that eight degrees of freedom are perhaps just large enough to be able to apply the theory, and small enough to appreciate the contribution from the dynamical correction to the "standard" Boltzmann principle.

VII. CONCLUSION

In this paper we derived equilibrium and nonequilibrium statistical mechanics from deterministic mechanics, using systems with a finite (and small) number of degrees of freedom. From equilibrium statistical mechanics we derived thermodynamics, reversing the order normally followed to derive statistical mechanics, where thermodynamics is assumed. Our dynamical derivation yields an expression for the temperature which is only a function of the mechanical properties (Fourier transform of the correlation function at a given frequency, susceptibility) of the system.

The comparison of our expression for the temperature with the "standard" expression for the temperature (obtained using the Boltzmann principle) shows that the latter is corrected by a factor connected to the dynamics of the system studied, and which vanishes when the limit of a system with many degree of freedom is taken. The theory is based on the distinction between variables for the system of interest and irrelevant variables, following the standard approach to derive the FPE. Notably, however, in our approach the irrelevant part is not a thermodynamical system on its own but rather a (small) dynamical system with chaotic solutions. Numerical simulations performed for two model systems strongly support our theoretical arguments.

In conclusion we are convinced that this paper provides a satisfactory derivation, and generalization, of the Boltzmann principle, and of ordinary statistical mechanics, in terms of dynamical properties with no thermodynamical assumption whatsoever.

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APPENDIX: DERIVATION OF SOME QUANTITIES OF INTEREST

Let $\boldsymbol{f}$ be a vector of differentiable functions of the variables $\boldsymbol{q}$ of the system under study. Let O be a generic operator of the form

$$O \equiv \frac{\partial}{\partial \boldsymbol{q}} \cdot \boldsymbol{f}(\boldsymbol{q}) \tag{A1}$$

and let O^+

$$O^+ \equiv -\boldsymbol{f}(\boldsymbol{q}) \cdot \frac{\partial}{\partial \boldsymbol{q}} \tag{A2}$$

be its adjoint. The equalities

$$(O^+ g(\boldsymbol{q})) = (O^+)^\times [g(\boldsymbol{q})] = -O^\times [g(\boldsymbol{q})] \tag{A3}$$

hold true, where we used the definition of Eq. (42) and g is a generic analytic function of $\boldsymbol{q}$.

To prove the equalities in Eq. (A3), it is simply necessary to explicitly carry out the commutations and work out the resulting derivatives. If $O = \mathcal{L}$, i.e., it is the differential operator responsible for the time translations, it follows from Eq. (A3) that Eq. (45) is true; furthermore, for Hamiltonian systems, if $\boldsymbol{q}$ is a vector of canonical variables, then $O^+ = -O$, and the last equality in Eq. (A3) becomes an identity.

We now prove Eq. (44), written here for convenience:

$$e^{\mathcal{L}_a^\times u}\left[\frac{\partial}{\partial v}\right] = \left(\frac{\partial}{\partial x}x_a(t-u)\right)\frac{\partial}{\partial v} - \left(\frac{\partial}{\partial v}x_a(t-u)\right)\frac{\partial}{\partial x}. \tag{A4}$$

To this end, we map the canonically conjugate variables x, v to some new variables $E, \tilde{x}$ defined as

$$\begin{aligned} E &\equiv m\frac{v^2}{2} + V(x) \\ \tilde{x} &\equiv x. \end{aligned} \tag{A5}$$

The inverse mapping is given by

$$\begin{aligned} v &= \sqrt{\frac{2}{m}[E - V(\tilde{x})]}, \\ x &= \tilde{x}, \end{aligned} \tag{A6}$$

from which

$$\begin{aligned} \frac{\partial}{\partial x} &= \frac{\partial}{\partial \tilde{x}} + V'(\tilde{x})\frac{\partial}{\partial E}, \\ \frac{\partial}{\partial v} &= mv(E,\tilde{x})\frac{\partial}{\partial E}. \end{aligned} \tag{A7}$$

Hence the Liouvillian operator $\mathcal{L}_a$, defined as

$$\mathcal{L}_a \equiv -v\frac{\partial}{\partial x} + \frac{V'(x)}{m}\frac{\partial}{\partial v}, \tag{A8}$$

becomes, under the transformation, the new operator $\mathcal{G}$ defined as

$$\mathcal{G} \equiv -v(E,\tilde{x})\frac{\partial}{\partial \tilde{x}}, \tag{A9}$$

where

$$v(E,\tilde{x}) \equiv \sqrt{\frac{2}{m}[E - V(\tilde{x})]}. \tag{A10}$$

From now on, for simplicity we omit the tilde on the new variable $\tilde{x}$.

We note that

$$\begin{aligned} \mathcal{G}^\times\left[\frac{\partial}{\partial E}\right] &= -v(E,x)\frac{\partial}{\partial x}\frac{\partial}{\partial E} + \frac{\partial}{\partial E}v(E,x)\frac{\partial}{\partial x} \\ &= \frac{1}{mv(E,x)}\frac{\partial}{\partial x} = -\frac{1}{mv(E,x)^2}\mathcal{G}. \end{aligned} \tag{A11}$$

It follows that

$$\begin{aligned} e^{\mathcal{L}_a^\times u}\left[\frac{\partial}{\partial v}\right] &= m\, e^{\mathcal{G}^\times u}\left[v(E,x)\frac{\partial}{\partial E}\right] \\ &= m\, e^{\mathcal{G}^\times u}[v(E,x)]\left\{\frac{\partial}{\partial E} + \sum_{n=1}^{\infty}\frac{u^n}{n!}\left(\mathcal{G}^\times\right)^n\left[\frac{\partial}{\partial E}\right]\right\} \\ &= m\, v_a(t-u)\left\{\frac{\partial}{\partial E} + \sum_{n=1}^{\infty}\frac{u^n}{n!}\left(\mathcal{G}^\times\right)^{n-1}\left[\mathcal{G}^\times\left[\frac{\partial}{\partial E}\right]\right]\right\} \\ &= v_a(t-u)\left\{m\frac{\partial}{\partial E} + \sum_{n=1}^{\infty}\frac{u^n}{n!}\left(\mathcal{G}^\times\right)^{n-1}\left[-\frac{1}{v(E,x)^2}\mathcal{G}\right]\right\} \\ &= v_a(t-u)\left\{m\frac{\partial}{\partial E} - \sum_{n=1}^{\infty}\frac{u^n}{n!}\left(\mathcal{G}^\times\right)^{n-1}\left[\frac{1}{v(E,x)^2}\right]\mathcal{G}\right\} \\ &= v_a(t-u)\left\{m\frac{\partial}{\partial E} - \int_0^u e^{\mathcal{G}^\times u'}\left[\frac{1}{v(E,x)^2}\right]du'\mathcal{G}\right\} \\ &= v_a(t-u)\left\{m\frac{\partial}{\partial E} - \int_0^u \frac{1}{v_a(t-u')^2}du'\mathcal{G}\right\}. \end{aligned} \tag{A12}$$

The last equality in Eq. (A12) follows from Eq. (A3). Note now that

$$v_a(t-u)\int_0^u \frac{1}{v_a(t-u')^2}du'$$
$$= -v_a(t-u)\int_{x_a(t-u)}^{x} m\frac{\partial}{\partial E}\frac{1}{v(E,x')}dx'. \quad \text{(A13)}$$

As function of the old canonically conjugate variables x and v, Eq. (A13) becomes

$$v_a(t-u)\int_0^u \frac{1}{v_a(t-u')^2}du'$$
$$= -\frac{v_a(t-u)}{v}\left(\frac{\partial}{\partial v}u(x,x_a(t-u),v)\right), \quad \text{(A14)}$$

where

$$u(x,x_a(t-u),v) \equiv \int_{x_a(t-u)}^{x}\frac{1}{v(E,x')}dx'. \quad \text{(A15)}$$

It follows that

$$\begin{aligned}\frac{\partial}{\partial v}u(x,x_a(t-u),v) &= -\frac{\partial x_a(t-u)}{\partial v}\left(\frac{\partial x_a(t-u)}{\partial u}\right)^{-1}\\ &= \frac{1}{v_a(t-u)}\frac{\partial x_a(t-u)}{\partial v}.\end{aligned} \quad \text{(A16)}$$

Comparing now Eq. (A16) with Eq. (A14) we can write

$$v_a(t-u)\int_0^u \frac{1}{v_a(t-u')^2}du' = -\frac{1}{v}\left(\frac{\partial}{\partial v}x_a(t-u)\right). \quad \text{(A17)}$$

Using this result in Eq. (A12) and going back to the old canonically conjugate variables x, v, we have

$$\begin{aligned}e^{\mathcal{L}_a^{\times}u}\left[\frac{\partial}{\partial v}\right] &= \frac{v_a(t-u)}{v}\left\{\frac{\partial}{\partial v}+\frac{1}{v}\left(\frac{\partial}{\partial v}x_a(t-u)\right)\right\}\mathcal{L}_a\\ &= \frac{1}{v}\left[v_a(t-u)+\left(\frac{V'(x)}{m}\frac{\partial}{\partial v}x_a(t-u)\right)\right]\frac{\partial}{\partial v}\\ &\quad -\left(\frac{\partial}{\partial v}x_a(t-u)\right)\frac{\partial}{\partial x}.\end{aligned} \quad \text{(A18)}$$

Noting that

$$\begin{aligned}\frac{V'(x)}{m}\frac{\partial}{\partial v}x_a(t-u) &= \mathcal{L}_a x_a(t-u)+v\left(\frac{\partial}{\partial x}x_a(t-u)\right)\\ &= -\frac{d}{dt}x_a(t-u)+v\left(\frac{\partial}{\partial x}x_a(t-u)\right)\\ &= -v_a(t-u)+v\left(\frac{\partial}{\partial x}x_a(t-u)\right),\end{aligned} \quad \text{(A19)}$$

we obtain Eq. (A4) from Eq. (A18).

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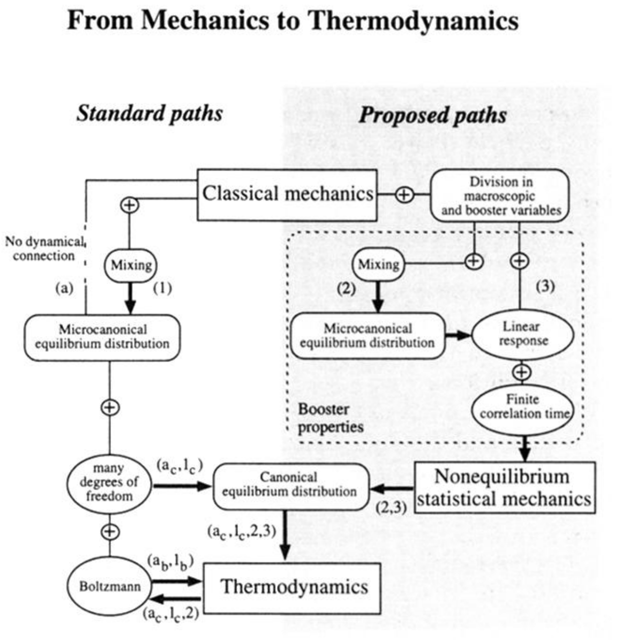
From Mechanics to Thermodynamics
Standard paths
Proposed paths
Classical mechanics
Division in macroscopic and booster variables
No dynamical connection
(a)
Mixing
(1)
Microcanonical equilibrium distribution
Mixing
(2)
(3)
Microcanonical equilibrium distribution
Linear response
Finite correlation time
Booster properties
many degrees of freedom
(a_c, l_c)
Canonical equilibrium distribution
Nonequilibrium statistical mechanics
(2,3)
$(a_c, l_c, 2, 3)$
(a_b, l_b)
Boltzmann
Thermodynamics
$(a_c, l_c, 2)$

FIG. 1. Diagrammatic view of the standard approach to thermodynamics (left) and of the approach to thermodynamics presented here (right): for details, see text.