Response Theory for Equilibrium and Non-Equilibrium Statistical Mechanics: Causality and Generalized Kramers-Kronig relations

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Abstract

We consider the general response theory recently proposed by Ruelle for describing the impact of small perturbations to the non-equilibrium steady states resulting from Axiom A dynamical systems. We show that the causality of the response functions entails the possibility of writing a set of Kramers-Kronig relations for the corresponding susceptibilities at all orders of nonlinearity. Nonetheless, only a special class of directly observable susceptibilities obey Kramers-Kronig relations. The apparent contradiction with the principle of causality is also clarified. Specific results are provided for the case of arbitrary order harmonic response, which allows for a very comprehensive Kramers-Kronig analysis and the establishment of sum rules connecting the asymptotic behavior of the harmonic generation susceptibility to the short-time response of the perturbed system. These results set in a more general theoretical framework previous findings obtained for optical Hamiltonian systems and simple mechanical models, and shed light on the very general impact of considering the principle of causality for testing self-consistency: the described dispersion relations constitute unavoidable benchmarks that any experimental and model generated dataset must obey. In order to gain a more complete picture, connecting the response theory for equilibrium and non equilibrium systems, we show how to rewrite the classical response theory by Kubo for systems close to equilibrium so that response functions formally identical to those proposed by Ruelle, apart from the measure involved in the phase space integration, are obtained. Finally, we briefly discuss how the presented results, taking into account the chaotic hypothesis by Gallavotti and Cohen, might have relevant implications for climate research. In particular, whereas the fluctuation-dissipation theorem does not work for non-equilibrium systems, because of the non-equivalence between internal and external fluctuations, Kramers-Kronig relations might be more robust tools for the definition of a self-consistent theory of climate change.

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Contents

I. INTRODUCTION

The analysis of how systems respond to external perturbations to their steady state constitutes one of the crucial subjects of investigation in the physical and mathematical sciences. In the case of physical systems near equilibrium, the powerful approach introduced by Kubo [1], based on the generalization up to any order of nonlinearity of the formalism of the Green function, allows for expressing the change in the statistical properties of a general observable due to the introduction of a perturbation in terms of expectation values of suitably defined quantities evaluated at the unperturbed state [2]. These results have had huge impact on statistical mechanics and have allowed detailed treatment of several and rather diverse processes, including, *e.g.* the interaction of radiation with condensed matter. Recently, Ruelle [3, 4] has extended some of the investigations by Kubo to a wide class of systems *far* from equilibrium, and introduced a perturbative approach for computing the response of systems driven away by a small external forcing from their non-equilibrium steady states. More precisely, the results by Ruelle consider perturbations to autonomous Axiom-A flows (and maps) defined in a compact manifold, which possess a chaotic, mixing dynamics, and are associated to an invariant ergodic Sinai-Ruelle-Bown (SRB) measure [5, 6]. We remind that, the - mathematically speaking, special - case of Axiom A systems amounts to being of general physical interest, if one accepts the chaotic hypothesis by Gallavotti and Cohen [7, 8] which states that, for the purpose of computing macroscopic quantities, many-particle systems behave *as though* they were dynamical systems with transitive Axiom-A global attractors. Ruelle shows that, in analogy to what found by Kubo, at all orders of perturbative expansion, the effect of the forcing on the expectation value of a general observable can be expressed in terms of averages of quantities performed at the non-equilibrium steady state, *i.e.* obtained by integrating over the unperturbed SRB measure. Moreover, in the case of linear response, it is shown that it is possible to define formally a susceptibility function, obtained as the Fourier Transform of the linear Green function of the system, and to prove that such susceptibility, basically as a result of the causality principle, obeys Kramers-Kronig (K-K) relations [9, 10], just as in Kubo framework. The K-K relations say that the the real and imaginary part of the linear susceptibility are fundamentally connected, each one being the Hilbert transform of the other one. Hence, these integral properties provide unavoidable constraints for checking the self-consistency of experimental or model-generated data. Furthermore, by applying the K-K relations, it is possible to perform the so-called inversion of data, *i.e.* to acquire knowledge on the real part by measurements of the imaginary part over the whole spectrum or vice versa.

Nevertheless, in spite of such important formal analogies, it is important to stress some qualitative differences between equilibrium and non-equilibrium systems in the physical meaning of the linear response function. Whereas in systems close to equilibrium there is basically equivalence between the natural fluctuations and the linear response to external perturbations, as clarified by the fluctuation-dissipation theorem [11, 12], in the considered non equilibrium systems such symmetry in broken, the mathematical reason being that the SRB measure is smooth only along the unstable manifold. A more geometrical view of this fact is that, whereas natural fluctuations of the system are restricted to the unstable manifold, because, by definition, asymptotically there is no dynamics along the stable manifold, external forcings will cause almost always motions having components - of exponentially decaying amplitude - out of the unstable manifold [3, 4]. For a discussion of this point, see also [22]. It should also be noted that the non-equivalence of forced and free fluctuations in chaotic systems was already pointed out and tackled in heuristic terms in the late '70s by Lorenz [13] when considering the atmospheric system.

Whereas K-K relations for linear processes, thanks to their generality, have become a basic textbook subject and standard tool in many different fields, such as acoustics, signal processing, optics, statistical mechanics, condensed matter physics, material science, relatively little attention has been paid to theoretical and experimental investigation of K-K relations and sum rules of the nonlinear susceptibilities, in spite of the ever increasing scientific and technological relevance of nonlinear physical processes. Recently, several theoretical and experimental results in this direction have been formulated in the context of analyzing nonlinear processes of interaction of radiation with matter [14, 15].

The main goal of this paper is to analyze the formal properties on the n^{th} order perturbative response of Axiom A, non equilibrium steady state systems to external forcings. In particular, we develop a theory of generalized K-K relations that extend, on one side, the results on the linear case given by Ruelle [3] for this class of systems, and on the other side, what obtained for nonlinear processes in electronic systems close to equilibrium [14, 15] and in simple yet prototypical mechanical systems [18]. Special attention is paid to the case of nonlinear susceptibilities describing processes responsible for harmonic generation, whose properties are such that a rather extensive set of important properties - including sum rules - can be deduced. We stress that also in the nonlinear case K-K relations constitute unavoidable benchmarks that any experimental and model generated dataset must obey. K-K relations may prove, as discussed later, useful tools for defining a theory of climate change, because they apply also for systems where the fluctuation-dissipation theorem is not verified.

Our paper is structured as follows. In Sec. II, we introduce the properties of the general n^{th} susceptibility, resulting as Fourier transform of the n^{th} perturbative order response function of the system. In Sec. III, we present an extension of the theory of nonlinear K-K relations to the dynamical systems considered by Ruelle, showing which class of nonlinear susceptibilities obey K-K relations and deducing rigorous results in the case of harmonic generation processes. In Sec. IV, we discuss our results, present our conclusions and perspectives for future investigations. Two appendices are also included. In App. A we show how the Kubo theory can be formally reconciled with the results by Ruelle, so that the results presented in this work can be applied also for general equilibrium systems. A discussion of the relevance for climate studies of the response theory for Axiom-A systems and of the specific results described in this study is given in App. B.

II. LINEAR AND NONLINEAR RESPONSE OF PERTURBED NON-EQUILIBRIUM STEADY STATES

We consider an autonomous Axiom-A flow $\dot{x} = F(x)$ defined in a compact manifold, such that $x(t) = f^t x$, with $x = x(0)$. The flow is assumed to possess a chaotic, mixing dynamic, and to be associated to an invariant ergodic SRB measure $\rho_{SRB}(\mathrm{d}x)$, such that for any measurable observable $\Phi(x)$ the ensemble average is equal to the time average:

$$\langle \Phi \rangle_0 = \int \rho_{SRB}(\mathrm{d}x)\Phi(x) = \lim_{T\to\infty} \frac{1}{T} \int_0^T \mathrm{d}t\Phi(f^t x) = \lim_{T\to\infty} \int \mathrm{d}x\Phi(f^T x) \tag{1}$$

for almost every initial condition x according to the Lebesgue measure $\mathrm{d}x$; the last equality holds for the special case of mixing dynamics. The SRB measure is usually singular, but smooth along the directions of the unstable manifold [5, 6, 19]. Ruelle has shown that for this specific class of dynamical systems (as well as for the corresponding discrete-time diffeomorphisms) it is possible to differentiate the SRB states [20, 21] when the flow is perturbed by an infinitesimal vector field in the following way:

$$\dot{x} = F(x) + e(t)X(x). \tag{2}$$

Is is then possible to express the perturbed expectation value of $\Phi(x)$ in terms of a perturbation series:

$$\langle \Phi \rangle(t) = \langle \Phi \rangle_0 + \sum_{n=1}^{\infty} \langle \Phi \rangle^{(n)}(t) \tag{3}$$

where, proposing a slight generalization of the formula proposed by Ruelle [4], which considered purely periodic perturbations, the n^{th} term can be expressed as a n-uple convolution integral of the n^{th} order Green function with n terms each representing the suitably delayed time modulation of the perturbative vector field:

$$\langle\Phi\rangle^{(n)}(t) = \int\limits_{-\infty}^{\infty}\int\limits_{-\infty}^{\infty}\ldots\int\limits_{-\infty}^{\infty} \mathrm{d}\sigma_1\mathrm{d}\sigma_2\ldots\mathrm{d}\sigma_n G^{(n)}(\sigma_1,\ldots,\sigma_n)e(t-\sigma_1)e(t-\sigma_2)\ldots e(t-\sigma_n). \quad (4)$$

The n^{th} order Green function is causal, *i.e.* its value is zero if any of the argument is non positive, and can be expressed as time dependent expectation value of an observable evaluated over the unperturbed SRB measure:

$$\begin{aligned} G^{(n)}(\sigma_1,\ldots,\sigma_n) = \int \rho_{SRB}(\mathrm{d}x) \quad & \Theta(\sigma_1)\Theta(\sigma_2-\sigma_1)\ldots\Theta(\sigma_n-\sigma_{n-1}) \times \\ & \times\Lambda\Pi(\sigma_n-\sigma_{n-1})\ldots\Lambda\Pi(\sigma_2-\sigma_1)\Lambda\Pi(\sigma_1)\Phi(x), \end{aligned} \quad (5)$$

where Θ is the usual Heaviside function, $\Lambda(\bullet) = X(x)\nabla(\bullet)$ describes the effect of the perturbative vector field, and Π induces the time evolution along the unperturbed vector field so that $\Pi(\tau)A(x) = A(x(\tau))$ for any observable A. The $n=1$ term describes the linear response of the system to the perturbation field [3], and, thanks to the superposition principle, can be derived also by using the method of impulse perturbation [22]. In App. A we show that it is possible to rephrase the Kubo response theory [1] in such a way to obtain a formula that perfectly matches the formula presented in Eq. (5), provided that the equilibrium canonical distribution is used instead of the SRB measure $\rho_{SRB}(\mathrm{d}x)$.

A. Response of the system in the frequency domain

If we compute the Fourier transform of the n^{th} order perturbation to the expectation value $\langle\Phi\rangle^n(t)$ defined in Eq. (4) we obtain:

$$\langle\Phi\rangle^{(n)}(\omega) = \int\limits_{-\infty}^{\infty}\ldots\int\limits_{-\infty}^{\infty} \mathrm{d}\omega_1\ldots\mathrm{d}\omega_n\chi^{(n)}(\omega_1,\ldots,\omega_n)\, e(\omega_1)\ldots e(\omega_n)\times\delta\left(\omega-\sum_{l=1}^{n}\omega_l\right), \quad (6)$$

where the Dirac δ guarantees that the sum of the arguments of the Fourier transforms of the time modulation functions equals the argument of the Fourier transform of $\langle\Phi\rangle^n(t)$, whereas the susceptibility function is defined as

$$\chi^{(n)}\left(\omega_1,\ldots,\omega_n\right)=\int\limits_{-\infty}^{\infty}\ldots\int\limits_{-\infty}^{\infty}\mathrm{d}t_1\ldots\mathrm{d}t_n G^{(n)}\left(t_1,\ldots,t_n\right)\exp\left[\mathrm{i}\sum_{j=1}^{n}\omega_j t_j\right]. \tag{7}$$

These operations make sense if the Green function is integrable or at least, in a weaker, distributional sense, if it not exponentially increasing. In the linear case, Ruelle [3, 4] has shown that integrability is ensured by proving that both the contributions associated to terms resulting from projections of the perturbative vector field on the unstable and stable manifolds converge, because of the distinct processes of mixing and of exponential contraction, respectively. In the nonlinear $n > 1$ case, we can heuristically use the same arguments - as well as taking into account that in the classical equilibrium case [1] the higher order correlations are typically much weaker and with faster decrease - to exclude the possibility that the operation presented in Eq. (7) is meaningless.

Assuming that, without serious loss of generality, the function $e(t)$ can be expressed as:

$$e(t)=\sum_{k=1}^{m} e_{\omega_j}\exp[-\mathrm{i}\omega_j t]+e_{-\omega_j}\exp[\mathrm{i}\omega_j t] \tag{8}$$

with $e_{\omega_j}=\left[e_{-\omega_j}\right]^*$, we derive that each frequency component in Eq. 6 can be written as:

$$\langle\Phi\rangle^{(n)}(\omega)=\sum_{\{\omega_\Sigma\}}\overline{\langle\Phi\rangle}^{(n)}\left(\omega_\Sigma\right)\delta\left(\omega-\omega_\Sigma\right), \tag{9}$$

where we are summing over all the possible distinct values $\{\omega_\Sigma\}$ of the possible sums of n among the $2m$ frequencies in the spectrum of $e(t)$, which basically formalizes the process of *frequency mixing*. Of course, in the linear $n = 1$ case, no mixing occurs and outputs can be observed at the same frequencies as the input. In general, each term $\overline{\langle\Phi\rangle}^{(n)}\left(\omega_\Sigma\right)$ is given by the following sum:

$$\overline{\langle\Phi\rangle}^{(n)}\left(\omega_\Sigma\right)=\sum_{\sum\omega_{k_j}=\omega_\Sigma}\chi^{(n)}\left(\omega_{k_1},\ldots,\omega_{k_n}\right)e_{w_{k_1}}\ldots e_{w_{k_n}}, \tag{10}$$

where the sum of the arguments of all the contributing susceptibility functions is ω_Σ. Note that, from an experimental point of view, we can measure $\overline{\langle\Phi\rangle}^{(n)}\left(\omega_\Sigma\right)$ by analyzing in the frequency domain the perturbed output of the system, whereas disentangling the various terms contributing to the summation in Eq. (10) is rather hard. Again, this problem is not present in the linear case.

III. GENERALIZED KRAMERS-KRONIG RELATIONS

A. Basic Results

Once we are granted that at every order n the response on the system $\langle\Phi\rangle^{(n)}(t)$ is written as a convolution integral having as Kernel a causal Green function $G^{(n)}(\sigma_1,\ldots,\sigma_n)$, and assuming that the suitable integrability conditions are obeyed, we are in the conditions of writing generalized dispersion relations for the n^{th} order susceptibility presented in Eq. (7), along the lines of what developed in the context of optics in [14, 15]. Therefore, we can apply Titchmarsch's theorem [9, 10, 14, 15] separately to each variable of $G^{(n)}(\sigma_1,\ldots,\sigma_n)$ and deduce that $\chi^{(n)}(\omega_1,\ldots,\omega_n)$ is holomorphic in the upper complex plane of each variable ω_i, $1\le i\le n$. If we consider the first argument ω_1 of the nonlinear susceptibility function (7), the following dispersion relation holds

$$\mathrm{P}\int_{-\infty}^{\infty}\mathrm{d}\omega_1'\frac{\chi^{(n)}\left(\omega_1',\ldots,\omega_n'\right)}{\omega_1'-\omega_1}=\mathrm{i}\pi\chi\left(\omega_1,\ldots,\omega_n'\right), \tag{11}$$

where P indicates that integration is performed in principal part. Repeating the same procedure for all the remaining $n-1$ frequency variables, we obtain

$$\mathrm{P}\int_{-\infty}^{\infty}\ldots\int_{-\infty}^{\infty}\mathrm{d}\omega_1'\ldots\mathrm{d}\omega_n'\frac{\chi^{(n)}\left(\omega_1',\ldots,\omega_n'\right)}{\left(\omega_1'-\omega_1\right)\ldots\left(\omega_n'-\omega_n\right)}=\left(\mathrm{i}\pi\right)^n\chi\left(\omega_1,\ldots,\omega_n\right), \tag{12}$$

which extends to all orders the linear K-K relations already described by Ruelle [3]. K-K relations constitute self-consistency constraints that must be obeyed and allow to reconstruct the real part of the response from the imaginary part, or vice-versa. The principle of causality of the response function is reflected mathematically in the validity of the K-K relations presented in Eq. (12). Note that, as discussed by Peiponen [16, 17], all the functions $\left[\chi^{(n)}\left(\omega_1,\ldots,\omega_n\right)\right]^m$, with $m\ge 1$ obey the very same dispersion relations as that written for $m=1$ in Eq. (12). This implies that the generality of these dispersion relation goes beyond not only the distinction between classical and quantum equilibrium system, as discussed in [14, 15], but also beyond the distinction between equilibrium and non-equilibrium systems, at least when we consider the Axiom A case or adopt the chaotic hypothesis for many particles systems.

The dispersion relations (11) and (12) may be thought of being of doubtful interest from an experimental point of view, since on one side we basically can have access to quantities like

$\overline{\langle\Phi\rangle}^{(n)}(\omega_\Sigma)$, which results from a linear combination of, in general, more than one different susceptibility functions (in the sense that they are evaluated at different values of their arguments). Moreover, most of the physically relevant nonlinear phenomena are described by nonlinear susceptibilities where all or part of the frequency variables are mutually dependent, such in the later described case of n^{th} order harmonic generation at frequency $n\omega$ in the presence of a monochromatic modulation function $e(t) = \exp[-\mathrm{i}\omega_0 t] + \exp[\mathrm{i}\omega_0 t]$ of frequency ω_0. We may, therefore, understand that a more flexible theory is needed in order to provide the effectively relevant dispersion relations for nonlinear phenomena.

B. A New Definition of Dispersion Relations

We take the following point of view. When considering the n^{th} order nonlinear process, a meaningful dispersion relation involves a line integral in the space of the frequency variables, which entails the choice of a one-dimensional space embedded in a n-dimensional space. This corresponds to the realistic experimental setting where only the frequency of one of the monochromatic fields described in Eq. (8) is changed. Since in the nonlinear setting we have frequency mixing, changing the frequency of one of the components of the forcing will change differently each of the terms $\overline{\langle\Phi\rangle}^{(n)}(\omega_\Sigma)$, depending on whether none, one or more than one arguments of the contributing nonlinear susceptibility functions (see Eq. (10)) are varied. The choice of the parameterization then selects different susceptibilities and so refers to different nonlinear processes. Each component j of the straight line in $\mathbb{R}^n$ can be parameterized as follows:

$$\omega_j = v_j s + w_j, 1 \leq j \leq n, \tag{13}$$

where the parameter $s \in \mathbb{R}$, the vector $\vec{v} \in \mathbb{R}^n$ of its coefficients describes the direction of the straight line, and the vector $\vec{w} \in \mathbb{R}^n$ determines $\vec{\omega}(0)$. Since we know that $\chi^{(n)}(\omega_1, \ldots, \omega_n)$ is holomorphic in the upper complex plane of each variable ω_i, $1 \leq i \leq n$, we have that the extension for complex values of s of the function:

$$\begin{aligned}\chi^{(n)}(s) &= \chi^{(n)}(v_1 s + w_1, \ldots, v_n s + w_n) \\ &= \int_{-\infty}^{\infty} \ldots \int_{-\infty}^{\infty} \mathrm{d}t_1 \ldots \mathrm{d}t_n G^{(n)}(t_1, \ldots, t_n) \exp\left[\mathrm{i}s\sum_{j=1}^{n} v_j t_j + \mathrm{i}\sum_{j=1}^{n} w_j t_j\right]\end{aligned} \tag{14}$$

is holomorphic in the upper complex s plane if all the components of vector $\vec{v}$ are non-negative. This construction has been first proposed in the context of nonlinear optics in [23]. Hence, by applying the Titchmarch theorem, we deduce that for all $m \geq 1$ the following integral relation holds for the susceptibility defined in Eq. (14):

$$\mathrm{i}\pi \left[\chi^{(n)}(s)\right]^m = \mathrm{P}\int_{-\infty}^{\infty} \frac{\left[\chi^{(n)}(s')\right]^m}{s'-s}\mathrm{d}s', \tag{15}$$

which, when the real and imaginary part of the nonlinear susceptibility are considered, results into:

$$\mathrm{Re}\left\{\left[\chi^{(n)}(s)\right]^m\right\} = \frac{1}{\pi}\mathrm{P}\int_{-\infty}^{\infty} \frac{\mathrm{Im}\left\{\left[\chi^{(n)}(s')\right]^m\right\}}{s'-s}\mathrm{d}s', \tag{16}$$

$$\mathrm{Im}\left\{\left[\chi^{(n)}(s)\right]^m\right\} = -\frac{1}{\pi}\mathrm{P}\int_{-\infty}^{\infty} \frac{\mathrm{Re}\left\{\left[\chi^{(n)}(s')\right]^m\right\}}{s'-s}\mathrm{d}s'. \tag{17}$$

The condition on the sign of the directional vectors of the straight line in $\mathbb{R}^n$ implies that only one particular class of nonlinear susceptibilities possess the holomorphic properties required to obey the dispersion relations (16). Hence, causality is not a sufficient condition for the existence of K-K relations between the real and imaginary part of a general nonlinear susceptibility function, *if its arguments are mutually dependent.* We stress that, instead, causality implies that Eq. (12) holds.

C. Harmonic Generation

In order to clarify the results presented in the previous sections, and show how they can be used for analyzing actual data, we concentrate on the simplified setting of a single monochromatic perturbation field such that $e(t) = \exp[-\mathrm{i}\omega_0 t] + \exp[\mathrm{i}\omega_0 t]$. In this case, at each order n, $\omega_\Sigma = \pm(2j+1)$, with $\omega_0, j = 0, \ldots, (n-1)/2$ if n is odd and $\omega_\Sigma = \pm 2j\omega_0$, with $j = 0, \ldots, n/2$ if n is even. Note that for even orders there is always a static response, which, in the optical literature, is known as optical rectification [15]. If we focus, *e.g.*, on the third order of perturbation and consider only the positive frequencies, we have that the observable signal at ω_0, constituting the first correction to the linear response is:

$$\overline{\langle\phi\rangle}^{(3)}(\omega_0) = \chi^{(3)}(-\omega_0, \omega_0, \omega_0) + \chi^{(3)}(\omega_0, -\omega_0, \omega_0) + \chi^{(3)}(\omega_0, \omega_0, -\omega_0); \tag{18}$$

whereas the observable signal, responsible for the third harmonic generation is:

$$\overline{\langle\phi\rangle}^{(3)}(3\omega_0) = \chi^{(3)}(\omega_0, \omega_0, \omega_0); \tag{19}$$

If we change the frequency ω_0 of the perturbation field and study how the output varies, it is clear that for all the three terms comparing on the right hand side of Eq. (18) the vector $\vec{v}$ of the s-parameterization proposed in Eq. (13) has one negative component, whereas $\vec{v} = (1, 1, 1)$ for the only term responsible for harmonic generation in Eq. (19). This implies that, when analyzing the first nonlinear correction to the linear response at frequency ω_0, we cannot expect that K-K relations apply, since poles in the upper complex plane of the $s = \omega_0$ may well be present [24]. In this case, different signal processing techniques, such as the Maximum Entropy Method, have to be adopted [15]. Therefore, the condition on the sign of $\vec{v}$ is in this case useful for giving a negative statement, *i.e. determining when K-K cannot be applied.* On the contrary, we are granted that the susceptibility describing the third harmonic nonlinear response obeys K-K relation. It is clear that the same applies at all orders n, and also it can be easily shown that the only contribution to the observable $\overline{\langle\phi\rangle}^{(n)}(n\omega_0)$ is $\chi^{(n)}(\omega_0, \ldots, \omega_0)$.

At every order n, we have that $\chi^{(n)}(-\omega_1, \ldots, -\omega_n) = \left\{\chi^{(n)}(\omega_1, \ldots, \omega_n)\right\}^*$ ($\{Z\}^*$ indicating the complex conjugate of Z), because $\langle\Phi\rangle^{(n)}(t)$ and $e(t)$ are real. It is is easy to show that the following relation holds for all values of $m \geq 1$:

$$\left[\chi^{(n)}(-\omega_1, \ldots, -\omega_n)\right]^m = \left\{\left[\chi^{(n)}(\omega_1, \ldots, \omega_n)\right]^m\right\}^*, \tag{20}$$

We then derive that at all orders $n \geq 1$ and for all $m \geq 1$:

$$-\frac{\pi}{2}\mathrm{Im}\left\{\left[\chi^{(n)}(\omega_0, \ldots, \omega_0)\right]^m\right\} = \omega_0 \mathrm{P}\int_0^\infty \mathrm{d}\omega_0' \frac{\mathrm{Re}\left\{\left[\chi^{(n)}(\omega_0', \ldots, \omega_0')\right]^m\right\}}{\left(\omega_0'^2 - \omega_0^2\right)} \tag{21}$$

$$\frac{\pi}{2}\mathrm{Re}\left\{\left[\chi^{(n)}(\omega_0, \ldots, \omega_0)\right]^m\right\} = \mathrm{P}\int_0^\infty \mathrm{d}\omega_0' \frac{\omega_0'\mathrm{Im}\left\{\left[\chi^{(n)}(\omega_0', \ldots, \omega_0')\right]^m\right\}}{\left(\omega_0'^2 - \omega_0^2\right)} \tag{22}$$

which, albeit in a different perspective from what shown in Eq. (12), generalize the linear K-K at all orders. Note that, if we consider $\lim_{\omega_0 \to 0}$ of Eq. (22) in the linear case and assume that the limits converge, we obtain the following expression for the linear static response of the system:

$$\mathrm{Re}\left\{\left[\chi^{(1)}(0)\right]^{\mathrm{m}}\right\} = \left[\mathrm{Re}\left\{\chi^{(1)}(0)\right\}\right]^{\mathrm{m}} = \frac{2}{\pi}\mathrm{P}\int_0^\infty \mathrm{d}\omega_0' \frac{\mathrm{Im}\left\{\left[\chi^{(1)}(\omega_0')\right]^{\mathrm{m}}\right\}}{\omega_0'}; \tag{23}$$

the finiteness of the integral is consistent with the fact that, by symmetry, $\mathrm{Im}\left\{\left[\chi^{(1)}(\omega_0 = 0)\right]^m\right\} = 0$, which must be obeyed for all values of $m \geq 1$. Note that a detailed verification of linear K-K has been performed in the case of Lorenz system [25]. It is somewhat surprising to observe how the qualitative features of the detected (and reconstructed) susceptibility are similar to what results from a simple oscillator model: the imaginary part has a strong peak for a resonance of system (even if in this case there is no deterministic *natural frequency* for the system), which matches the dispersive structure found for the real part of the susceptibility. Another minor spectral feature is observed, and again, following the spectroscopic paradigm, a peak in the imaginary part is associated to a dispersive structure in the real part. Note also that the Lorenz system is non-Axiom A, which suggests that a wide range of applicability for these relations is still to be explored. Note that, even if several monochromatic forcings are present, Eqs. (21)-(22) still apply, since no other frequency components are involved.

If we plug $\vec{v} = (1, \ldots, 1)$ and $\vec{w} = (0, \ldots, 0)$, and redefine $s = \omega_0$ in Eq. (14), and consider the basic properties of the Fourier Transform, we have that the short time behavior of the n^{th} order Green function determines the asymptotic behavior of the n^{th} order harmonic susceptibility at frequency $n\omega_0$. We perform the following variable change

$$t_j = \sum_{k=1}^{j} \tau_k, \tag{24}$$

assume that $G^{(n)}(t_1(\tau_1), \ldots, t_n(\tau_1, \ldots \tau_n))$ be smooth for all its arguments $\{\tau_j\}$ in 0, and let β be the smallest sum of exponents of $(\tau_1, \ldots \tau_n)$ such that there is a non-vanishing monomial $M_\beta(\tau_1, \ldots, \tau_n)$ in the Taylor expansion $G^{(n)}(t_1(\tau_1), \ldots, t_n(\tau_1, \ldots \tau_n))$. We then have that the following limit exists and is finite [14, 15, 26]:

$$\lim_{\omega_0 \to \infty} \omega_0^{\beta+n} \chi^{(n)}(\omega_0, \ldots, \omega_0) = \alpha \in \mathbb{R} \setminus \{0\}, \tag{25}$$

which implies that the asymptotic behavior of $\chi^{(n)}(\omega_0, \ldots, \omega_0)$ is at least as fast as ω_0^{-n}. Moreover, since $\mathrm{Re}\left\{\chi^{(n)}(\omega_0, \ldots, \omega_0)\right\}$ is an even function of ω_0 and, from Eq. (25), determines the asymptotic behaviour ($\mathrm{Im}\left\{\chi^{(n)}(\omega_0, \ldots, \omega_0)\right\}$ has a faster asymptotic decrease), we derive that $\beta + n$ must be even, so that $\beta + n = 2\gamma$. Therefore, dispersion theory provides us with indirect information also about the short time behavior of the Green function. Furthermore, the knowledge of the asymptotic behavior allows a further generalization of what presented in (21)-(22). In fact, we have that all the (independent) functions $\omega^{2p}\chi^{(n)}(\omega_0, \ldots, \omega_0)$, $p = 0, \ldots, \gamma - 1$ are holomorphic in the upper complex plane of ω_0 and obey suitable integrability conditions allowing for writing the following set of generalized

K-K relations:

$$-\frac{\pi}{2}{\omega_0}^{2p+1}\mathrm{Im}\left\{\left[\chi^{(n)}\left(\omega_0,\ldots,\omega_0\right)\right]^m\right\} = \mathrm{P}\int_0^\infty \mathrm{d}\omega_0' \frac{{\omega_0'}^{2p}\mathrm{Re}\left\{\left[\chi^{(n)}\left(\omega_0',\ldots,{\omega'}_0\right)\right]^m\right\}}{(({\omega_0'}^2-\omega_0^2)}, \tag{26}$$

$$\frac{\pi}{2}{\omega_0}^{2p}\mathrm{Re}\left\{\left[\chi^{(n)}\left(\omega_0,\ldots,\omega_0\right)\right]^m\right\} = \mathrm{P}\int_0^\infty \mathrm{d}\omega_0' \frac{{\omega_0'}^{2p+1}\mathrm{Im}\left\{\left[\chi^{(n)}\left(\omega_0',\ldots,{\omega'}_0\right)\right]^m\right\}}{({\omega_0'}^2-\omega_0^2)}. \tag{27}$$

with $p = 0,\ldots,m\gamma-1$. Comparing the asymptotic behavior given in Eq. (25) with those obtained by applying the superconvergence theorem [27] to the general K-K relations (26)-(27), we derive the following set of general sum rules

$$\int_0^\infty {\omega_0}'^{2p}\mathrm{Re}\left\{\left[\chi^{(n)}\left(\omega_0',\ldots,\omega_0'\right)\right]^m\right\}\mathrm{d}\omega' = 0, \quad 0 \le p \le m\gamma-1, \tag{28}$$

$$\int_0^\infty {\omega_0}'^{2p+1}\mathrm{Im}\left\{\left[\chi^{(n)}\left(\omega_0',\ldots,\omega_0'\right)\right]^m\right\}\mathrm{d}\omega' = 0, \quad 0 \le p \le m\gamma-2, \tag{29}$$

$$\int_0^\infty {\omega_0}'^{2p+1}\mathrm{Im}\left\{\left[\chi^{(n)}\left(\omega_0',\ldots,\omega_0'\right)\right]^m\right\}\mathrm{d}\omega' = -\alpha^m\frac{\pi}{2}, \quad p = m\gamma-1. \tag{30}$$

All the moments of the n^{th} order harmonic generation susceptibility vanish except that of order $2\gamma-1$ of the imaginary part. This latter sum rule creates a conceptual bridge between the measurements of the imaginary part of the susceptibility under examination throughout the spectrum to the short term behavior of the n^{th} Green function. These results hold for all values of $m \geq 1$. The generalized K-K relations and sum rules here presented constitute a rather extensive set of stringent integral constraints that must be obeyed by experimental data and model simulations. These results generalize what obtained for general optical systems near equilibrium [26] and for simple mechanical systems [18]. Note that both the generalized K-K relations (26)-(27) and the sum rules (28)-(30) have been verified in detail on experimental data in the case of optical processes near equilibrium [28].

IV. SUMMARY AND CONCLUSIONS

In this paper we have considered the general response function $G^{(n)}(t_1,\ldots,t_n)$ recently proposed by Ruelle [3, 4] for describing the impact of small time-dependent forcings to the non-equilibrium steady states resulting from Axiom A dynamical systems, which, when taking into account the chaotic hypothesis by Gallavotti and Cohen [7, 8], are of general physical interest. At all orders of perturbative expansion, the effect of the forcing on the expectation value of a general observable can be expressed in terms of means of quantities performed at non-equilibrium steady state.

Since, at every order of perturbation, the response function is causal, it is possible to write a set of Kramers-Kronig relations for the corresponding susceptibility, defined as the multivariable Fourier Transform of the response function $\chi^{(n)}(\omega_1, \ldots, \omega_n)$. These dispersion relations are of little applicability because they cannot be used to effectively analyze the output signal, which is the change in the expectation observable of the considered observable.

In practice, it is interesting to consider the case of one or more monochromatic forcings and to be in the condition of analyzing what happens when the frequency of one of them is changed. Since in the nonlinear setting of order n we have frequency mixing, such frequency tuning will affect differently the various frequency components of the observed output signal, depending on whether none, one or more than one arguments of the nonlinear susceptibility functions responsible for the observed frequency components of the output are varied. Therefore, following this approach, the dispersion relation becomes a parameterized line integral in the n-dimensional space of frequency variables. K-K relations apply only for special forms of parameterizations, which correspond to a specific family of susceptibility functions. These results are system-independent and derive strictly from complex analysis.

Among the phenomena which can be treated using the K-K formalism, we concentrate on the n^{th} order process by which the system responds at frequency $n\omega_0$ when forced by a monochromatic vectorial field with angular frequency ω_0. Such a process is described by the harmonic generation susceptibility $\chi^{(n)}(\omega_0, \ldots, \omega_0)$, which is holomorphic in the upper complex ω_0 plane and obeys K-K relations. For any given system, the asymptotic behavior for large frequencies is shown to depend on the short-time response and to be of the form $\omega_0^{-2\gamma}$. It is then proved that all functions $\omega^{2p}\chi^{(n)}(\omega_0, \ldots, \omega_0)$ with $p = 0, \ldots, \gamma - 1$ obey K-K relations, so that more stringent , generalized constraints are established. Furthermore, using symmetry arguments and the superconvergence theorem on the generalized K-K relations, and comparing the results with the asymptotic behavior for large values of ω_0, new sum rules are obtained. We derive that all even moments of the real part and all odd moments of the imaginary parts are null, except for the highest converging odd moment of the imaginary part of the susceptibility, which is directly related to the short time behavior of the system. Furthermore, these results are also extended to the powers $\left[\chi^{(n)}(\omega_0, \ldots, \omega_0)\right]^m$, $m \geq 1$ of the susceptibility, and additional constraints are derived. The obtained generalized K-K relations and sum rules can be used to check any experimental data and approximate theory of nonlinear phenomena, because they are necessary constraints which have to be obeyed.

These results generalize and extend what obtained by Ruelle [3, 4] for Axiom A systems, set in a much more general theoretical framework previous findings obtained for near equilibrium optical processes [14, 15] and and simple yet prototypical mechanical systems near equilibrium [18], and shed light on the generality of the constraints deriving from the principle of causality, which can be used for testing model outputs and experimental data, both for equilibrium and non-equilibrium systems. Note that, as discussed in [10, 14, 15], basically all K-K relations and sum rules can be rephrased, after lengthy but straightforward calculations, in terms of absolute value and phase of the susceptibility function, which in some cases may be of easier experimental observation.

It is somewhat surprising, and encouraging in the perspective of the theory here developed, to see that the linear susceptibility of the Lorenz system investigated in [25] looks a lot like the result of an optical experiment: the peaks of the imaginary part, corresponding to the resonances of system (even if in this case there are no deterministic *natural frequencies*) match the dispersive structures found for the real part of the susceptibility. Note that, far from being a curiosity, it is through this approach that the optical constants of most solids have been actually computed [29, 30].

In order to clarify and complete the picture, we have shown, in App. A, that the functions derived for non equilibrium steady states are formally equivalent, at all perturbative orders, to what obtained with the Kubo formalism for the response of systems close to equilibrium, apart from the measure involved in the phase space integration. In the case of near to equilibrium system, the measure is the one describing the canonical distribution, whereas in the setting analyzed by Ruelle, the SRB measure of the unperturbed flow is involved. Therefore, all the results presented in the paper apply, *a fortiori*, for these equilibrium systems.

The response theory for Axiom A systems can have interesting implications for climate studies. In fact, the possibility of defining a response function basically poses the problem of climate change is well-defined context, and, when considering the procedures aimed at improving climate models, justifies rigorously the procedures of tuning and adjusting of the free parameters. Furthermore, qualitative differences between different and widespread *ensemble simulation* practices can be interpreted in this context. Moreover, the non-equivalence of free and forced fluctuations explains why many attempts of applying the fluctuation-dissipation theorem in climate studies have basically failed. Instead, it may be that the general theory of Kramers-Kronig relations described in this paper, which, in the case of non-equilibrium system, is decoupled form the fluctuation-dissipation theorem, may provide a viable way of defining a comprehensive self-consistent theory of climate change, ensured by the integral relations connecting the in-phase and our of phase components of the response of the system to external perturbations. This is discussed in some greater detail in App. B.

We conclude with some practical caveats. As well known, it is surely not trivial in practical terms to effectively verify the K-K relations and sum rules on experimental or model generated data. One general problem is their integral formulation, which requires that data are available on a rather extensive spectral range and with a reasonable resolution. This may raise issue of computational costs and/or experimental set-up. The extrapolations in K-K analysis can be a serious source of errors [30, 31]. Recently, King [32] presented an efficient numerical approach to the evaluation of K-K relations, and singly and multiply subtractive K-K relations have been proposed in order to relax the limitations caused by finite-range data [33, 34]. It should be noted that K-K relations for higher-order susceptibilities are, somewhat counter-intuitively, sometimes easier to verify than the linear K-K relations, because they have typically a much faster asymptotic decrease. Whereas we have shown that at all orders large families of K-K relations hold for the various moments and various powers of the susceptibility functions, it should be expected that they do not converge at the same rate when data of finite precisions coming from a finite spectral range are used. See the discussion in [14, 15]. Furthermore, when considering chaotic systems, further problems in signal detection of the system response at specific frequencies are related to the presence of a continuous spectrum in the background; this latter issue may become more serious when nonlinear processes are examined and the observed monochromatic signal is weaker. Nevertheless, along the line of Reick [25] these problems may result to be manageable.

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APPENDIX A: RECONCILING KUBO'S AND RUELLE'S GENERAL PERTURBATIVE RESPONSE FUNCTIONS

In this appendix we show how to reconcile formally the n^{th} order perturbative response for general systems characterized by non-equilibrium steady state presented in Eq. (5) with the classical results obtained with the Kubo formalism [1] for the response for systems close to equilibrium. Therefore, all the results presented in the paper apply, *a fortiori*, for these equilibrium systems.

We consider a system of N degrees of freedom described by the canonical coordinates $q = (q_1, \ldots, q_N)$ and $p = (p_1, \ldots, p_N)$ and evolving under the action of the Hamiltonian operator $H(q,p) = H_0(q,p) + h(q,p,t)$, composed of the unperturbed Hamiltonian $H_0(q,p)$ plus the time dependent perturbation (weak) Hamiltonian expressed in the form $h(q,p,t) = -e(t)B(q,p)$ [2]. The evolution equation of the system can then be written as:

$$\dot{x} = F(x) + e(t)X(x) \tag{A1}$$

where $x = (q,p)$; $F(x) = \Omega\nabla H(x)$, $X(x) = -\Omega\nabla B(x)$, with Ω indicating the symplectic matrix. We assume that, if the perturbation is set to 0, the expectation value of any observable Φ can be expressed as the following:

$$\langle\Phi\rangle_0 = \int \mathrm{d}x\rho_0(x)\Phi(x) = \int \rho_0(\mathrm{d}x)\Phi(x) \tag{A2}$$

where integration is performed in the phase space of the system, and the canonical distribution, which is absolutely continuous with respect to the Lebesgue measure of the phase space, is defined as usual as:

$$\rho_0(\mathrm{d}x) = \rho_0(x)\mathrm{d}x = \frac{\exp\left[-H_0(x)/kT\right]}{\int \mathrm{d}\Gamma \exp\left[-H_0(x)/kT\right]}\mathrm{d}x = \frac{\exp\left[-H_0(x)/kT\right]}{\int \rho_0(\mathrm{d}x)}\mathrm{d}x. \tag{A3}$$

Following the perturbative approach introduced by Kubo [1], we have that, for small perturbations, the expectation value of Φ at time t can be written as:

$$\langle\Phi\rangle(t) = \langle\Phi\rangle_0 + \sum_{n=1}^{\infty}\langle\Phi\rangle^{(n)}(t) \tag{A4}$$

where the terms under summation describe the non-equilibrium properties - for a system which is close to equilibrium - at all orders of perturbation; in particular the $n = 1$ terms provides information of the linear response of the system. The perturbative terms can be expressed as follows [1, 2]:

$$
\begin{aligned}
\langle \Phi \rangle^{(n)}(t) = & \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \ldots \int_{-\infty}^{\infty} \mathrm{d}\sigma_1 \mathrm{d}\sigma_2 \ldots \mathrm{d}\sigma_n \times \\
& \times \Theta(\sigma_1)\Theta(\sigma_2 - \sigma_1) \ldots \Theta(\sigma_n - \sigma_{n-1}) f(t-\sigma_1) f(t-\sigma_2) \ldots f(t-\sigma_n) \times \\
& \times \langle [B(x), \ldots [B(x(\sigma_n - \sigma_2)), \ldots [B(x(\sigma_n - \sigma_1)), \Phi(x(\sigma_n))]] \ldots] \rangle_0 = \\
& = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \ldots \int_{-\infty}^{\infty} \mathrm{d}\sigma_1 \mathrm{d}\sigma_2 \ldots \mathrm{d}\sigma_n G^{(n)}(\sigma_1, \ldots, \sigma_n) e(t-\sigma_1) e(t-\sigma_2) \ldots e(t-\sigma_n), \quad \text{(A5)}
\end{aligned}
$$

where the time evolution of the observables B and Φ is due to the unperturbed Hamiltonian H_0. The two main are that the non-equilibrium response is expressed as a convolution integral where the Kernel, which is the n^{th} order Green function $G^{(n)}(\sigma_1, \ldots, \sigma_n)$ is causal.

Note that the Kernel operator in the quantum case, where we deal with N-particles Hilbert space and observables are replaced by operators, is formally obtained by simply substituting each Poisson brackets $[\bullet, \bullet]$ with $1/(\mathrm{i}\hbar)$ times the commutator $\{\bullet, \bullet\}$, and by redefining the expectation value at equilibrium of a generic operator P as follows:

$$
\langle P \rangle_0 = \frac{\sum_a \langle a|P|a\rangle \exp\left[-E_a/kT\right]}{\sum_b \exp\left[-E_b/kT\right]}. \quad \text{(A6)}
$$

where $|a\rangle$ is the eigenstate with eigenvalue E_a of the Hamiltonian operator H_0.

Since the following trivial identity holds:

$$
[B(x), \bullet] = X(x)\nabla(\bullet) = \Lambda(\bullet) \quad \text{(A7)}
$$

and since, by definition, the evolution of any observable A driven by the unperturbed Hamiltonian H_0 can be formally represented as follows:

$$
A(x(\tau)) = \exp(i\tau L)A(x) = \Pi(\tau)A(x), \quad \text{(A8)}
$$

where $iLA(x) = [A(x), H_0(x)]$, the n^{th} order Green function can be formally written in the following compact and form:

$$
G^{(n)}(\sigma_1, \ldots, \sigma_n) = \int \rho_0(\mathrm{d}x)\Lambda\Pi(\sigma_n - \sigma_{n-1}) \ldots \Lambda\Pi(\sigma_2 - \sigma_1)\Lambda\Pi(\sigma_1)\Phi(x). \quad \text{(A9)}
$$

which is fully equivalent to the formula shown in Eq. (5), provided that the measure describing the equilibrium canonical distribution is substituted with the general SRB measure.

APPENDIX B: RESPONSE THEORY FOR NON-EQUILIBRIUM STEADY STATES AND CLIMATE RESEARCH

When adopting the chaotic hypothesis, the possibility of defining a response function of a perturbed non-equilibrium steady state and its actual properties seem to have very interesting impacts in climate studies. On one side, this creates a context where the problem of climate change is well-posed at mathematical level and where, when considering the procedures aimed at improving climate models, the tuning and adjustment of the free parameters - at least locally - may be considered as a well-defined operation devoid of catastrophic impacts on the statistical properties of the system. On the other hand, straightforward applications of fluctuation-dissipation theorem [35, 36], or the idea that climate change signals project on the natural modes of climate variability [37] seem inadequate, as discussed in [38]. Instead, it seems that the theory of Kramers-Kronig relations described in this paper may provide a viable way of defining a comprehensive self-consistent theory of climate change, ensured by the integral relations connecting the in-phase and our of phase components of the response of the system to external perturbations. As an example, we may interpret Eq. (23) as the fact that the static response function - measuring *climate sensitivity* - can be related to the out-of-phase response to same forcing at all frequencies, at least in first approximation.

The concepts behind the Ruelle response theory also clarify the meaning of some common *ensemble simulation* practices, which are widely adopted by the climate modelling community with the goal of estimating the uncertainty on the statistical properties of the model outputs, when a specific set of observables is considered [39–41]. Three different strategies, which are nevertheless more and more hybridized, can be pointed out:

- Each simulation is performed with the same climate model, but starting from slightly different initial state;
- Each simulation is performed with the same climate model, but with slightly different values of some key uncertain parameters characterizing the global climatic properties,
- Each simulation is performed with a different climate model (*multi-model ensemble*).

Under the chaotic hypothesis, the first procedure seems useful, since a more detailed exploration of the phase space of the system, with a better sampling - on a finite time - of the attractor of the model. The significance of the second procedure seem to be reinforced by the response theory for non equilibrium steady states, because in this case the variously tuned models basically explore parameterically deformed ergodic measures, and the macroscopic *sensitivity* of the model is thus explored. As for the third procedure, whereas it surely allows for climate model intercomparison, aggregating information from from rather different attractors seems ill-defined.

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