

Nonlinear response and fluctuation-dissipation relations

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A unified derivation of the off-equilibrium fluctuation dissipation relations (FDRs) is given for Ising and continuous spins to arbitrary order, within the framework of Markovian stochastic dynamics. Knowledge of the FDRs allows one to develop zero field algorithms for the efficient numerical computation of the response functions. Two applications are presented. In the first one, the problem of probing for the existence of a growing cooperative length scale is considered in those cases, like in glassy systems, where the linear FDR is of no use. The effectiveness of an appropriate second order FDR is illustrated in the test case of the Edwards-Anderson spin glass in one and two dimensions. In the second application, the important problem of the definition of an off-equilibrium effective temperature through the nonlinear FDR is considered. It is shown that, in the case of coarsening systems, the effective temperature derived from the second order FDR is consistent with the one obtained from the linear FDR.

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I. INTRODUCTION

The statistical mechanics of systems out of equilibrium is a rapidly evolving subject, due to the intensive research in the slow relaxation phenomena arising in several different contexts, such as coarsening systems, glassy and granular materials, colloidal systems, etc. Understanding the basic mechanism underlying the slow relaxation is an issue of major importance. In particular, a key question is whether the large time scales are due to cooperative effects on large length scales. For nondisordered coarsening systems this is certainly the case, since the observed power-law relaxation can be directly related to the growth of the time-dependent correlation length, or domain size [1]. In the case of disordered or glassy systems the establishment of such a connection is much more problematic, due to the difficulty of pinpointing the observables fit to the task.

The use of the nonlinear susceptibilities has been advocated [2–4] as an experimental or numerical probe apt to detect the heterogeneous character of the glassy relaxation and, possibly, to uncover the existence of the growing length scale responsible of the slowing down of the relaxation. However, this requires one to establish clearly the relationship between nonlinear susceptibilities and correlation functions in order to make sure what actually do the nonlinear susceptibilities probe. In other words, the problem of the derivation of the nonlinear fluctuation dissipation relations (FDRs) in the out of equilibrium regime needs to be addressed. As a matter of fact, this has been one of the most fruitful lines of investigation in the field of slow relaxation, although mostly limited to the domain of linear response [5,6].

In this paper we approach the problem on fairly general grounds. Within the framework of Markovian stochastic evolution, we bring to the fore the structural elements which are common to discrete and continuous spins. We develop the formal apparatus necessary for a unified derivation of the FDRs in the two cases and to arbitrary order. We also show, expanding on the work of Semerjian *et al.* [7], how the nonlinear FDR of arbitrary order can be derived from a fluctuation principle [8] also in the off-equilibrium regime. This allows one to regard the FDR as a manifestation of the constraint imposed on the dynamics by the requirement of microscopic reversibility.

The immediate application of the FDR is in the development of algorithms for the computation of the response functions without the imposition of an external perturbation, the so-called zero field algorithms. The numerical advantages of a zero field algorithm are remarkable. These have been illustrated and discussed in detail, in the linear case, in a recent paper [9]. In the present paper we apply the zero field algorithm to the computation of the nonlinear response functions. We consider two cases, where knowledge of a nonlinear response function is required. The first one arises in the search for a growing length scale in the context of glassy systems, as mentioned above. The presence of quenched or self-induced disorder makes the linear response function short ranged, compelling one to resort to the nonlinear ones. The second one deals with the extension of the effective temperature concept [10] to nonlinear order. This is an important and difficult problem. Here, we consider it in the context of non-disordered coarsening systems, showing the consistency of the effective temperatures derived from the linear and the second order FDR.

The paper is organized as follows: the formal developments concerning the time evolution, the response functions, the FDR, and the fluctuation principle are presented in Secs. II–V, respectively. In Sec. VI the problem of the detection of a cooperative length through a nonlinear susceptibility is addressed, while the effective temperature to nonlinear order is

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treated in Sec. VII. Concluding remarks are presented in Sec. VIII.

II. FORMALISM AND TIME EVOLUTION

Let us consider a system in contact with a thermal reservoir, whose microscopic states are the configurations $\sigma = [\sigma_i]$ of the N degrees of freedom, discrete or continuous, placed on the discrete set of sites $i = 1, \dots, N$. Assuming a Markovian stochastic dynamics, the time evolution of the system is fully specified once the probability distribution $P(\sigma, t_0)$ at some initial time t_0 is given, together with the transition probability $P(\sigma, t | \sigma', t')$ for any pair of times $t_0 \leq t' \leq t$. Observables, or random variables, are functions $A(\sigma)$ defined over the phase space of the microscopic states, whose expectations are given by

$$\langle A(t) \rangle = \sum_{\sigma} A(\sigma) P(\sigma, t), \quad (1)$$

where $P(\sigma, t) = \sum_{\sigma'} P(\sigma, t | \sigma', t_0) P(\sigma', t_0)$.

In order to keep the notation compact, it is convenient to switch to the operator formalism [11], whereby the microscopic states introduced above are the set of labels of the basis vectors

$$|\sigma\rangle = \otimes |\sigma_i\rangle, \quad i = 1, \dots, N \quad (2)$$

of a vector space. The single site states obey the orthonormality relation $\langle \sigma_i | \sigma'_j \rangle = \delta_{\sigma_i, \sigma'_j} \delta_{i,j}$. With this notation, the probability distributions $P(\sigma, t)$ become the time-dependent vectors $|P(t)\rangle$ such that

$$P(\sigma, t) = \langle \sigma | P(t) \rangle \quad (3)$$

and the transition probability is associated to the propagator of the process $\hat{P}(t|t')$, which is the operator whose matrix elements are given by

$$P(\sigma, t | \sigma', t') = \langle \sigma | \hat{P}(t|t') | \sigma' \rangle. \quad (4)$$

For stochastically continuous processes, through the first order expansion

$$\hat{P}(t + \Delta t | t) = \hat{I} + \hat{W}(t) \Delta t + O(\Delta t^2), \quad (5)$$

where \hat{I} is the identity operator, there remains defined the generator of the process $\hat{W}(t)$. Then, the pair $|P(t_0)\rangle, \hat{W}(t)$ contains all the information on the process, since the propagator can be written as

$$\hat{P}(t|t') = \mathcal{T}(e^{\int_{t'}^t ds \hat{W}(s)}), \quad (6)$$

where \mathcal{T} is the time ordering operator. In differential form this is equivalent to the equations

$$\frac{\partial}{\partial t} \hat{P}(t|t') = \hat{W}(t) \hat{P}(t|t'), \quad (7)$$

$$\frac{\partial}{\partial t'} \hat{P}(t|t') = -\hat{P}(t|t') \hat{W}(t'), \quad (8)$$

from the first one of which follows the equation of motion of the state vector

$$\frac{\partial}{\partial t} |P(t)\rangle = \hat{W}(t) |P(t)\rangle. \quad (9)$$

Notice that the normalization of probabilities imposes on the generator the condition

$$\langle - | \hat{W}(t) = 0, \quad (10)$$

where $\langle - | = \sum_{\sigma} \langle \sigma |$ is called the flat vector. We shall assume that at each instant of time the generator satisfies the detailed balance condition

$$e^{\beta \hat{\mathcal{H}}(t)} \hat{W}(t) e^{-\beta \hat{\mathcal{H}}(t)} = \hat{W}^\dagger(t), \quad (11)$$

where $\hat{\mathcal{H}}(t)$ denotes the Hamiltonian of the system, with a possible time dependence. This implies that the instantaneous Gibbs state

$$|P(t)\rangle_{\beta} = \frac{1}{Z(t)} e^{-\beta \hat{\mathcal{H}}(t)} |-\rangle \quad (12)$$

is an invariant state in the sense that

$$\hat{W}(t) |P(t)\rangle_{\beta} = 0. \quad (13)$$

The time-dependent partition function is given by $Z(t) = \langle - | e^{-\beta \hat{\mathcal{H}}(t)} |-\rangle$, as it follows from the normalization of the state $\langle - | P(t) \rangle_{\beta} = 1$. From now on we shall adopt the notation $|\cdot\rangle_{\beta}$ for the Gibbs states.

Notice that Eq. (1) requires that observables correspond to diagonal operators. Each random function $A(\sigma)$ is mapped into the operator $\hat{A} = A(\hat{\sigma})$, where the operators $\hat{\sigma}_i$ are defined by

$$\hat{\sigma}_i | \sigma \rangle = \sigma_i | \sigma \rangle \quad (14)$$

in such a way that the expectation (1) can be written as

$$\langle \hat{A}(t) \rangle = \langle - | \hat{A} | P(t) \rangle. \quad (15)$$

If \hat{W} and $|P\rangle_{\beta}$ are time independent, one can show that the multitime expectations of observables in the stationary state obey the Onsager relation [12]. Namely, if $\hat{A}_1, \hat{A}_2, \dots, \hat{A}_n$ is a set of observables and $t_n \geq t_{n-1} \dots \geq t_1$ an ordered sequence of instants of time, then

$$\begin{aligned} & \langle \hat{A}_n(t_n) \hat{A}_{n-1}(t_{n-1}) \dots \hat{A}_2(t_2) \hat{A}_1(t_1) \rangle_{\beta} \\ &= \langle \hat{A}_1(t_n) \hat{A}_2[t_n - (t_2 - t_1)] \dots \\ & \quad \times \hat{A}_{n-1}[t_1 + (t_n - t_{n-1})] \hat{A}_n(t_1) \rangle_{\beta}, \end{aligned} \quad (16)$$

where

$$\begin{aligned} & \langle \hat{A}_n(t_n) \hat{A}_{n-1}(t_{n-1}) \dots \hat{A}_2(t_2) \hat{A}_1(t_1) \rangle_{\beta} \\ &= \langle - | \hat{A}_n \hat{P}(t_n | t_{n-1}) \hat{A}_{n-1} \dots \hat{A}_2 \hat{P}(t_2 | t_1) \hat{A}_1 | P \rangle_{\beta}. \end{aligned} \quad (17)$$

Finally, using Eqs. (7) and (8), it is straightforward to show that the time derivative of a multitime expectation is given by

$$\begin{aligned} & \frac{\partial}{\partial t_k} \langle \hat{A}_n(t_n) \cdots \hat{A}_k(t_k) \cdots \hat{A}_1(t_1) \rangle \\ &= \langle \hat{A}_n(t_n) \cdots [\hat{A}_k, \hat{W}(t_k)](t_k) \cdots \hat{A}_1(t_1) \rangle, \end{aligned} \quad (18)$$

namely, the time derivative in front of the expectation amounts to the insertion, at the time t_k , of the commutator $[\hat{A}_k, \hat{W}(t_k)]$ inside the expectation. This applies for all $k = 1, \dots, n$. In particular, in the case of a single observable

$$\frac{\partial}{\partial t} \langle \hat{A}(t) \rangle = \langle -[\hat{A}, \hat{W}(t)]P(t) \rangle = \langle -[\hat{A}, \hat{W}(t)]P(t) \rangle, \quad (19)$$

where the second equality is a consequence of Eq. (10). It should be noticed that, in general, $[\hat{A}, \hat{W}(t)]$ is not an observable.

III. RESPONSE FUNCTIONS

Let us assume that the generator $\hat{W}(t)$ depends on time through an external field $h_i(t)$. Then, upon varying $h_i(t)$, there remains defined a family of stochastic processes and one may ask whether these stochastic processes are related one to the other. In particular, one would like to know whether the process with the generic $h_i(t)$ can be reconstructed from the properties of the *unperturbed* process, the one with the particular choice $h_i(t) \equiv 0$. In order to answer the question, let us start from the statement that all the information in the process, with a given $h_i(t)$, is contained in the full hierarchy of the time-dependent moments

$$M_{i_1, \dots, i_n}(t_1, \dots, t_n, [h_i(t')]) = \langle \hat{\sigma}_{i_1}(t_1) \cdots \hat{\sigma}_{i_n}(t_n) \rangle, \quad (20)$$

each of which is a functional of $h_i(t)$. Assuming analyticity, one can write the formal expansion

$$\begin{aligned} & M_{i_1, \dots, i_n}(t_1, \dots, t_n, [h_i(t')]) \\ &= M_{i_1, \dots, i_n}(t_1, \dots, t_n) + \sum_{m=1}^{\infty} \frac{1}{m!} \sum_{j_1, \dots, j_m} \int_{t_w}^t dt'_1 \cdots \\ & \quad \times \int_{t_w}^{t'_1} dt'_m R_{i_1, \dots, i_n; j_1, \dots, j_m}^{(n,m)}(t_1, \dots, t_n; t'_1, \dots, t'_m) \\ & \quad \times h_{j_1}(t'_1) \cdots h_{j_m}(t'_m), \end{aligned} \quad (21)$$

where $M_{i_1, \dots, i_n}(t_1, \dots, t_n)$ is the unperturbed moment, (t_w, t) is the time interval over which the action of the external field is considered, and

$$\begin{aligned} & R_{i_1, \dots, i_n; j_1, \dots, j_m}^{(n,m)}(t_1, \dots, t_n; t'_1, \dots, t'_m) \\ &= \left. \frac{\delta^m M_{i_1, \dots, i_n}(t_1, \dots, t_n, [h_i(t')])}{\delta h_{j_1}(t'_1) \cdots \delta h_{j_m}(t'_m)} \right|_{h=0} \end{aligned} \quad (22)$$

is the m th order response function of the n th moment. Therefore the question asked above can be positively answered if the response functions can be expressed in terms of quantities computable in the unperturbed process, namely, if the FDR of arbitrary order can be obtained.

Without loss of generality, we limit ourselves to work out the response functions for the first moment. For the re-

sponses of the higher moments there is nothing conceptually different, just the formalism gets more involved. As a matter of fact, in Sec. VI we shall deal with the second order response of the second moment. Coming back to the first moment, from

$$M_i(t, [h_j(t')]) = \langle -|\hat{\sigma}_i \hat{P}_h(t|t_w)|P(t_w) \rangle, \quad (23)$$

where $\hat{P}_h(t|t_w)$ is the propagator in the presence of the field, follows

$$\begin{aligned} & R_{i; j_1, \dots, j_m}^{(1,m)}(t, t_1, \dots, t_m) \\ &= \left\langle -|\hat{\sigma}_i \left. \frac{\delta^m \hat{P}_h(t|t_w)}{\delta h_{j_1}(t_1) \cdots \delta h_{j_m}(t_m)} \right|_{h=0} P(t_w) \right\rangle \end{aligned} \quad (24)$$

which obviously vanishes if $t_j \in (t_w, t)$ for any $j = 1, \dots, m$. Let us write explicitly the first two derivatives

$$\frac{\delta \hat{P}_h(t|t_w)}{\delta h_{j_1}(t_1)} = \mathcal{T} \left[e^{\int_{t_w}^t ds \hat{W}(s)} \frac{\partial \hat{W}(t_1)}{\partial h_{j_1}(t_1)} \right] = \hat{P}_h(t|t_1) \frac{\partial \hat{W}(t_1)}{\partial h_{j_1}(t_1)} \hat{P}_h(t_1|t_w) \quad (25)$$

and

$$\begin{aligned} & \frac{\delta^2 \hat{P}_h(t|t_w)}{\delta h_{j_1}(t_1) \delta h_{j_2}(t_2)} \\ &= \mathcal{T} \left\{ e^{\int_{t_w}^t ds \hat{W}(s)} \left[\frac{\partial \hat{W}(t_1)}{\partial h_{j_1}(t_1)} \frac{\partial \hat{W}(t_2)}{\partial h_{j_2}(t_2)} + \frac{\partial^2 \hat{W}(t_1)}{\partial h_{j_1}^2(t_1)} \delta(12) \right] \right\} \\ &= \hat{P}_h(t|t_M) \frac{\partial \hat{W}(t_M)}{\partial h_{j_M}(t_M)} \hat{P}_h(t_M|t_m) \frac{\partial \hat{W}(t_m)}{\partial h_{j_m}(t_m)} \hat{P}_h(t_m|t_w) \\ & \quad + \hat{P}_h(t|t_1) \frac{\partial^2 \hat{W}(t_1)}{\partial h_{j_1}^2(t_1)} \hat{P}_h(t_1|t_w) \delta(12), \end{aligned} \quad (26)$$

where $t_M = \max(t_j)$, $t_m = \min(t_j)$, j_M, j_m are the sites where the field acts at the times t_M or t_m , respectively, and $\delta(np) = \delta_{j_n j_p} \delta(t_n - t_p)$. The third order derivative is written down in Appendix A.

In order to go further, we must specify how $\hat{W}(t)$ depends on the field $h_i(t)$ and that is where the distinction between discrete spins and continuous spins comes in. In the following, in order to keep the derivation as simple as possible we shall specialize to the case of Ising spins with single spin-flip dynamics. The generalization to q -state spins (e.g., clock models) and to dynamical rules with conservation laws, such as Kawasaki spin-exchange, turns out to be straightforward.

A. Ising spins

For Ising spins the state vectors $|\sigma_i = \pm 1\rangle$ are represented by the column vectors

$$|\sigma_i = 1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |\sigma_i = -1\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

A generator of single spin flip dynamics is of the type

$$\hat{W} = \frac{1}{N} \sum_{i=1}^N \hat{W}_i, \quad (27)$$

where \hat{W}_i has nonvanishing matrix elements only between states which differ for the value of σ_i . The form of \hat{W}_i is obtained imposing the detailed balance condition (11). Singling out the site i , the Hamiltonian can be written in the form

$$\hat{\mathcal{H}}(t) = \mathcal{H}([\hat{\sigma}^z]_i, t) + \{h^W([\hat{\sigma}^z]_i) - h_i(t)\} \hat{\sigma}_i^z, \quad (28)$$

where $\hat{\sigma}_i^z$ is the z Pauli matrix

$$\hat{\sigma}_i^z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},$$

$[\hat{\sigma}^z]_i$ stands for the set of all spins except for the one on the i th site and $\hat{h}_i^W = h^W([\hat{\sigma}^z]_i)$ is the Weiss field on the site i . Inserting into the detailed balance condition (11), one finds the generator of the Glauber type [13]

$$\hat{W}_i(t) = (\hat{\sigma}_i^x - \hat{I}) e^{\beta[\hat{h}_i^W - h_i(t)] \hat{\sigma}_i^z}, \quad (29)$$

where $\hat{\sigma}_i^x$ is the x Pauli matrix

$$\hat{\sigma}_i^x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.$$

Hence the derivatives are given by

$$\frac{\partial^n \hat{W}(t_1)}{\partial h_{j_1}^n(t_1)} = (-\beta)^n \hat{W}_{j_1}(t_1) (\hat{\sigma}_{j_1}^z)^n \quad (30)$$

with

$$(\hat{\sigma}_{j_1}^z)^n = \begin{cases} \hat{I} & \text{for } n \text{ even,} \\ \hat{\sigma}_{j_1}^z & \text{for } n \text{ odd.} \end{cases} \quad (31)$$

For later reference, let us write here the identity

$$\hat{W}_i \hat{\sigma}_i^z = \frac{1}{2} [\hat{W}_i, \hat{\sigma}_i^z] + \frac{1}{2} \{\hat{W}_i, \hat{\sigma}_i^z\} \quad (32)$$

obtained by adding the commutator and the anticommutator. It is straightforward to verify that the anticommutator is a diagonal operator and, therefore, is an observable which we will denote by

$$\hat{B}_i(t) = \{\hat{\sigma}_i^z, \hat{W}(t)\}. \quad (33)$$

Due to Eq. (10), the average of the left-hand side of Eq. (32) vanishes and Eq. (19) for $\hat{\sigma}_i^z$ can be rewritten as

$$\frac{\partial}{\partial t} \langle \hat{\sigma}_i^z(t) \rangle = \langle \hat{B}_i(t) \rangle. \quad (34)$$

B. Continuous spins

In order to avoid confusion, here we shall denote by $\varphi = [\varphi_i]$ the set of the N continuous variables. Let us assume an equation of motion of the Langevin type

$$\frac{\partial}{\partial t} \varphi_i(t) = B_i(t) + \eta_i(t), \quad (35)$$

where the drift B_i is related to the Hamiltonian, or free energy functional $\mathcal{H}[\varphi]$, by

$$B_i(t) = - \frac{\partial \mathcal{H}[\varphi(t)]}{\partial \varphi_i}, \quad (36)$$

$\eta_i(t)$ is a Gaussian white noise with expectations

$$\langle \eta_i(t) \rangle = 0, \quad \langle \eta_i(t) \eta_j(t') \rangle = 2T \delta_{ij} \delta(t - t') \quad (37)$$

and T is the temperature of the thermal reservoir. The generator of the corresponding Markov process is the Fokker-Planck operator

$$\hat{W}^{FP} = \sum_i \hat{W}_i^{FP}, \quad (38)$$

where

$$\hat{W}_i^{FP} = -\{T \hat{p}_i^2 + i B_i[\hat{\varphi}] \hat{p}_i + D_i[\hat{\varphi}]\}, \quad (39)$$

$B_i[\hat{\varphi}]$ is defined through Eq. (36) and

$$D_i[\hat{\varphi}] = - \left. \frac{\partial^2 \mathcal{H}[\varphi]}{\partial \varphi_i^2} \right|_{\varphi=\hat{\varphi}}. \quad (40)$$

The conjugated operators $\hat{\varphi}_i$ and \hat{p}_i , defined by

$$\langle \varphi' | \hat{\varphi}_i | \varphi \rangle = \varphi_i \langle \varphi' | \varphi \rangle, \quad (41)$$

$$\langle \varphi' | \hat{p}_i | \varphi \rangle = -i \frac{\partial}{\partial \varphi_i} \langle \varphi' | \varphi \rangle, \quad (42)$$

obey the commutation relation

$$[\hat{\varphi}_i, \hat{p}_j] = i \delta_{ij} \quad (43)$$

and satisfy the equalities

$$\langle - | \hat{p}_i = 0, \quad (44)$$

$$\langle - | \hat{W}_i^{FP} = 0. \quad (45)$$

The external field enters the free energy functional linearly,

$$\mathcal{H}_h[\varphi, t] = \mathcal{H}[\varphi] - \sum_i h_i(t) \varphi_i \quad (46)$$

yielding

$$B_{h,i}[\varphi, t] = B_i[\varphi] + h_i(t), \quad (47)$$

while $D_i[\varphi]$ remains unaltered. Therefore the generator is changed into

$$\hat{W}_{h,i}^{FP} = \hat{W}_i^{FP} - i h_i(t) \hat{p}_i \quad (48)$$

and the derivatives are given by

$$\frac{\partial^n \hat{W}_{h,i}^{FP}}{\partial h_i^n(t)} = \begin{cases} -i \hat{p}_i & \text{for } n = 1, \\ 0 & \text{for } n > 1. \end{cases} \quad (49)$$

Obviously, the identity (32) holds also in this case,

$$\hat{W}_i^{FP} \hat{\phi}_i = \frac{1}{2} [\hat{W}_i^{FP}, \hat{\phi}_i] + \frac{1}{2} \{\hat{W}_i^{FP}, \hat{\phi}_i\} \quad (50)$$

and, using the definition (39) together with the commutation relation (43), it is not difficult to rewrite it in the more convenient form

$$i\hat{p}_i = \frac{\beta}{2} \{[\hat{W}_i^{FP}, \hat{\phi}_i] + B_i[\hat{\phi}_i]\}. \quad (51)$$

Again, since the average of the left-hand side vanishes, we get the analog of Eq. (34)

$$\frac{\partial}{\partial t} \langle \hat{\phi}_i(t) \rangle = \langle B_i[\hat{\phi}_i](t) \rangle \quad (52)$$

showing that the anticommutator (33) for Ising spins and the drift (36) for continuous spins play the same role in the evolution, thus justifying the choice of the same notation.

IV. FLUCTUATION-DISSIPATION RELATIONS

Let us now return to the general treatment, valid for discrete and continuous spins alike, with the operator $\hat{\sigma}$ standing either for $\hat{\sigma}^z$ or for $\hat{\phi}$, depending on the context. Which is the case will be specified whenever necessary.

Comparing the left-hand sides of Eqs. (32) and (51) with the first derivatives (30) and (49), we can write the basic equation in this paper as

$$\frac{\partial \hat{W}}{\partial h_i} = \frac{-\beta}{2} ([\hat{W}_i, \hat{\sigma}_i] + B_i[\hat{\sigma}_i]) \quad (53)$$

where, in the case of continuous spins, the superscript FP on the Fokker-Planck operator has been dropped and, as specified above, \hat{B}_i stands for

$$\hat{B}_i = \begin{cases} \{\hat{\sigma}_i, \hat{W}_i\} & \text{for Ising spins,} \\ B_i[\hat{\phi}_i] & \text{for continuous spins.} \end{cases} \quad (54)$$

We are now in the position to derive the FDR by going through the following steps.

(1) According to Eq. (24), the response function is obtained by appropriate insertions of derivatives of the generator in between propagators, as exemplified in Eqs. (25) and (26).

(2) According to Eq. (53), each first derivative of \hat{W} can be replaced by the sum of the commutator and the drift operator \hat{B}_i .

(3) According to Eq. (18), the insertion of the commutator amounts to a time derivative acting in front of the average.

The above steps exhaust all there is to do in the continuous spin case, since there are no derivatives of the generator of order higher than the first. Higher derivatives do, instead, appear in the Ising case producing singular terms. In order to see how the procedure works in practice, let us carry out the computation up to second order. The explicit result for the third order response function is presented in Appendix A.

A. Linear FDR

Let us begin with the simplest case of the linear response function. From Eqs. (24) and (25) follows

$$R_{i_1 j_1}^{(1,1)}(t, t_1) = \langle - |\hat{\sigma}_i \hat{P}(t|t_1) \frac{\partial \hat{W}(t_1)}{\partial h_{j_1}(t_1)} \Big|_{h=0} \hat{P}(t_1|t_w) | P(t_w) \rangle \quad (55)$$

and, using Eqs. (53) and (18), this becomes the linear FDR

$$R_{i_1 j_1}^{(1,1)}(t, t_1) = \frac{\beta}{2} \left[\frac{\partial}{\partial t_1} M_{i_1 j_1}(t, t_1) - \langle \hat{\sigma}_i(t) \hat{B}_{j_1}(t_1) \rangle \right] \quad (56)$$

due to the appearance of unperturbed correlation functions of observables in the right-hand side. This result has been known for some time for continuous spins, see, e.g., Ref. [6], while for Ising spins it has been derived for the first time in Ref. [9], where it has been exploited to develop the zero field algorithm for the computation of $R_{i_1 j_1}^{(1,1)}(t, t_1)$, mentioned in the Introduction.

If the system is in equilibrium, the averages in the right-hand side are equilibrium averages and, invoking the Onsager relation (16), one gets

$$\langle \hat{\sigma}_i^z(t) \hat{B}_{j_1}(t_1) \rangle_\beta = \langle - [[\hat{\sigma}_{j_1}, \hat{W}] \hat{P}(t|t_1) \hat{\sigma}_i | P \rangle_\beta = - \frac{\partial}{\partial t_1} M_{i_1 j_1}(t, t_1) \quad (57)$$

after using space and time translation invariance in the last equality, Eqs. (32) or (51) to eliminate \hat{B}_{j_1} , together with the normalization conditions (10) or (44). Inserting this into Eq. (56), the equilibrium fluctuation dissipation theorem (FDT) is recovered,

$$R_{i_1 j_1}^{(1,1)}(t, t_1) = \beta \frac{\partial}{\partial t_1} C_{i_1 j_1}(t, t_1), \quad (58)$$

where we have introduced the pair correlation function

$$C_{i_1 j_1}(t, t_1) = M_{i_1 j_1}(t, t_1) - M_i(t) M_{j_1}(t_1) \quad (59)$$

since it is clear that in equilibrium the one time quantities are time independent and the time derivative of $C_{i_1 j_1}(t, t_1)$ coincides with that of $M_{i_1 j_1}(t, t_1)$.

B. Second order FDR

From Eqs. (24) and (26), the second order, or *two kicks* nonlinear response function, is given by

$$\begin{aligned} R_{i_1 j_1 j_2}^{(1,2)}(t, t_1, t_2) &= \langle - |\hat{\sigma}_i \hat{P}(t|t_M) \frac{\partial \hat{W}(t_M)}{\partial h_{j_1}(t_M)} \Big|_{h=0} \hat{P}(t_M|t_w) \\ &\times \frac{\partial \hat{W}(t_M)}{\partial h_{j_2}(t_M)} \Big|_{h=0} \hat{P}_h(t_M|t_w) | P(t_w) \rangle \\ &+ \langle - |\hat{\sigma}_i \hat{P}(t|t_1) \frac{\partial^2 \hat{W}(t_1)}{\partial h_{j_1}^2(t_1)} \Big|_{h=0} \hat{P}(t_1|t_w) \\ &\times | P(t_w) \rangle \delta(12). \end{aligned} \quad (60)$$

Substituting, next, Eq. (53) for the first derivatives and the identity

$$\hat{W}_i = \frac{1}{2} \hat{\sigma}_i^z \hat{B}_i + \frac{1}{2} \hat{\sigma}_i^z [\hat{\sigma}_i^z, \hat{W}_i] \quad (61)$$

for the manipulation of the singular term, eventually one finds the second order FDR

$$\begin{aligned} R_{i;j_1 j_2}^{(1,2)}(t, t_1, t_2) = (\beta/2)^2 & \left\{ \frac{\partial}{\partial t_M} \frac{\partial}{\partial t_m} M_{ij_M j_m}(t, t_M, t_m) \right. \\ & - \frac{\partial}{\partial t_M} \langle \hat{\sigma}_i(t) \hat{\sigma}_{j_M}(t_M) \hat{B}_{j_m}(t_m) \rangle \\ & - \frac{\partial}{\partial t_m} \langle \hat{\sigma}_i(t) \hat{B}_{j_M}(t_M) \hat{\sigma}_{j_m}(t_m) \rangle \\ & \left. + \langle \hat{\sigma}_i(t) \hat{B}_{j_M}(t_M) \hat{B}_{j_m}(t_m) \rangle \right\} \\ & + (\beta^2/2) \left\{ \langle \hat{\sigma}_i^z(t) \hat{\sigma}_{j_M}^z(t_M) \hat{B}_{j_m}(t_m) \rangle \right. \\ & \left. + \frac{\partial}{\partial t_m} M_{ij_M j_m}(t, t_M, t_m) \right\} \delta_{j_M j_m} \delta(t_M - t_m), \quad (62) \end{aligned}$$

where, it is worth recalling, the last singular contribution in the braces is present only for Ising spins.

Again, at stationarity the Onsager relation can be used to eliminate the \hat{B} 's entering with the shortest time in favor of time derivatives. In so doing, the second and the fourth contribution in the right-hand side become identical to the first and the third one, respectively. Furthermore, in the stationary state the last contribution in the right-hand side vanishes, eventually yielding what we may call the second order FDT,

$$\begin{aligned} R_{i;j_1 j_2}^{(1,2)}(t, t_1, t_2) = (\beta^2/2) & \left\{ \frac{\partial}{\partial t_M} \frac{\partial}{\partial t_m} C_{ij_M j_m}(t, t_M, t_m) \right. \\ & \left. - \frac{\partial}{\partial t_m} \langle \hat{\sigma}_i(t) \hat{B}_{j_M}(t_M) \hat{\sigma}_{j_m}(t_m) \rangle_\beta \right\}, \quad (63) \end{aligned}$$

where we have substituted the time derivative of the moment with that of the correlation function. Notice that there remains an ineliminable presence of \hat{B} in the second term in the right-hand side, which carries the information on the specific rule governing the time evolution. This is a distinctive feature of all FDRs of order higher than linear, making them less universal than the linear one, which is \hat{B} dependent only off equilibrium.

V. FLUCTUATION PRINCIPLE

In the following we show that the FDRs obtained in the previous section arise as a consequence of a fluctuation principle [8]. For convenience, the derivation is presented for the continuous spin case, but it can be worked out along the same lines also for Ising spins. The idea of a derivation from the fluctuation principle was implemented by Semerjian *et*

al. [7] in the stationary case. Here we extend the derivation to the more general off-equilibrium case.

Let us call experimental protocol the assigned time dependence of the external field $h(t)$ in some time interval (t_0, t_F) . Then, from the detailed balance condition follows that the probability $P_\beta([\varphi(t)]|\varphi_0, [h(t)])$ of a path $[\varphi(t)]$, taking place under the protocol $[h(t)]$ and conditioned to the initial value $\varphi(t_0) = \varphi_0$, is related to the probability of the reverse path

$$\tilde{\varphi}(t) = \varphi(\bar{t}), \quad \bar{t} = t_F - t + t_0 \quad (64)$$

under the reverse protocol $[\tilde{h}(t)]$ and conditioned to $\tilde{\varphi}(t_0) = \varphi_F$ by

$$\begin{aligned} P_\beta([\varphi(t)]|\varphi_0, [h(t)]) \exp \left\{ -\beta \int_{t_0}^{t_F} dt h(t) \dot{\varphi}(t) \right\} \\ = P_\beta([\tilde{\varphi}(t)]|\varphi_F, [\tilde{h}(t)]) \exp \{ \beta [\mathcal{H}_0(\varphi_0) - \mathcal{H}_0(\varphi_F)] \}, \quad (65) \end{aligned}$$

where the subscript β is there to remind one that the evolution takes place while the system is in contact with a single thermal reservoir at the inverse temperature β . Multiplying both sides by $\varphi_{i,F} P_i(\varphi_0)$, where $P_i(\varphi_0)$ is an arbitrary probability distribution, and summing over the set $\mathcal{C}(t_0, t_F)$ of all paths in the interval (t_0, t_F) one finds

$$\begin{aligned} \int_{\mathcal{C}(t_0, t_F)} d[\varphi(t)] \varphi_{i,F} P_\beta([\varphi(t)]|\varphi_0, [h(t)]) \\ \times \exp \left\{ -\beta \int_{t_0}^{t_F} dt h(t) \dot{\varphi}(t) \right\} P_i(\varphi_0) \\ = Z_{\beta,0} \int_{\mathcal{C}(t_0, t_F)} d[\varphi(t)] P_i(\varphi_0) e^{\beta \mathcal{H}_0(\varphi_0)} P_\beta([\tilde{\varphi}(t)]|\varphi_F, [\tilde{h}(t)]) \\ \times \varphi_{i,F} P_{\beta,0}(\varphi_F), \quad (66) \end{aligned}$$

where $P_{\beta,0}$ and $Z_{\beta,0}$ denote the equilibrium distribution and the corresponding partition function, in absence of the external field. Hence the above result can be rewritten more compactly as

$$\begin{aligned} \left\langle \varphi_i(t_F) \exp \left\{ -\beta \int_{t_0}^{t_F} dt h(t) \dot{\varphi}(t) \right\} \right\rangle_{I \rightarrow \beta, [h(t)]} \\ = Z_{\beta,0} \langle P_i(\varphi(t_F)) e^{\beta \mathcal{H}_0(\varphi(t_F))} \varphi_i(t_0) \rangle_{\beta,0 \rightarrow \beta, [\tilde{h}(t)]}, \quad (67) \end{aligned}$$

where $\langle \cdot \rangle_{I \rightarrow \beta, [h(t)]}$ stands for the average in the process starting with the initial condition P_i , thereafter in contact with the thermal reservoir β and evolving with the protocol $[h(t)]$, while $\langle \cdot \rangle_{\beta,0 \rightarrow \beta, [\tilde{h}(t)]}$ stands for the process in contact with the thermal reservoir β , starting with the unperturbed equilibrium distribution $P_{\beta,0}$ and evolving with the reverse protocol $[\tilde{h}(t)]$.

The next step is to expand both sides in powers of $[h(t)]$

about $h(t) \equiv 0$ and to compare terms of the same order. This is done in Appendix B, obtaining to zero order

$$Z_{\beta,0} \langle P_I(\varphi(t_F)) e^{\beta \mathcal{H}_0(\varphi(t_F))} \varphi_i(t_0) \rangle_{\beta,0} = \langle \varphi_i(t_F) \rangle_{I \rightarrow \beta,0}, \quad (68)$$

where $\langle \cdot \rangle_{I \rightarrow \beta,0}$ stands for the average in the off-equilibrium process starting with P_I and evolving in contact with the thermal reservoir in absence of the external field. At higher orders one gets

$$Z_{\beta,0} \frac{\delta^n \langle P_I(\varphi(t_F)) e^{\beta \mathcal{H}_0(\varphi(t_F))} \varphi_i(t_0) \rangle_{\beta,0 \rightarrow \beta, [\tilde{h}(t)]}}{\delta \tilde{h}_{j_1}(\tilde{t}_1) \cdots \delta \tilde{h}_{j_n}(\tilde{t}_n)} \Big|_{\tilde{h}=0} = \sum_{p=0}^n (-\beta)^{n-p} \sum_{\mathcal{P}(j_1, \dots, j_{n-p} | j_{n-p+1}, \dots, j_n)} \frac{\delta^p \langle \varphi_i(t_F) \dot{\varphi}_{j_1}(t_1) \cdots \dot{\varphi}_{j_{n-p}}(t_{n-p}) \rangle_{I \rightarrow \beta, [h(t)]}}{\delta h_{j_{n-p+1}}(t_{n-p+1}) \cdots \delta h_{j_n}(t_n)} \Big|_{h=0}, \quad (69)$$

where the second summation is over all the distinct permutations $\mathcal{P}(j_1, \dots, j_{n-p} | j_{n-p+1}, \dots, j_n)$ between the two sets of indices (j_1, \dots, j_{n-p}) and (j_{n-p+1}, \dots, j_n) . For instance, at the first two orders the above formula reads

$$\begin{aligned} Z_{\beta,0} \frac{\delta \langle P_I(\varphi(t_F)) e^{\beta \mathcal{H}_0(\varphi(t_F))} \varphi_i(t_0) \rangle_{\beta,0 \rightarrow \beta, [\tilde{h}(t)]}}{\delta \tilde{h}_{j_1}(\tilde{t}_1)} \Big|_{\tilde{h}=0} \\ = -\beta \frac{\partial}{\partial t_1} \langle \varphi_i(t_F) \varphi_{j_1}(t_1) \rangle_{I \rightarrow \beta,0} + \frac{\delta \langle \varphi_i(t_F) \rangle_{I \rightarrow \beta, [h(t)]}}{\delta h_{j_1}(t_1)} \Big|_{h=0} \end{aligned} \quad (70)$$

and

$$\begin{aligned} Z_{\beta,0} \frac{\delta^2 \langle P_I(\varphi(t_F)) e^{\beta \mathcal{H}_0(\varphi(t_F))} \varphi_i(t_0) \rangle_{\beta,0 \rightarrow \beta, [\tilde{h}(t)]}}{\delta \tilde{h}_{j_1}(\tilde{t}_1) \delta \tilde{h}_{j_2}(\tilde{t}_2)} \Big|_{\tilde{h}=0} \\ = \beta^2 \frac{\partial}{\partial t_1} \frac{\partial}{\partial t_2} \langle \varphi_i(t_F) \varphi_{j_1}(t_1) \varphi_{j_2}(t_2) \rangle_{I \rightarrow \beta,0} \\ - \beta \frac{\partial}{\partial t_1} \frac{\delta \langle \varphi_i(t_F) \varphi_{j_1}(t_1) \rangle_{I \rightarrow \beta, [h(t)]}}{\delta h_{j_2}(t_2)} \Big|_{h=0} \\ - \beta \frac{\partial}{\partial t_2} \frac{\delta \langle \varphi_i(t_F) \varphi_{j_2}(t_2) \rangle_{I \rightarrow \beta, [h(t)]}}{\delta h_{j_1}(t_1)} \Big|_{h=0} \\ + \frac{\delta^2 \langle \varphi_i(t_F) \rangle_{I \rightarrow \beta, [h(t)]}}{\delta h_{j_1}(t_1) \delta h_{j_2}(t_2)} \Big|_{h=0}. \end{aligned} \quad (71)$$

From these two equations the off-equilibrium FDRs (56) and (62) can be recovered. Here we show this explicitly in the linear case, the extension to higher orders being straightforward.

Recalling the definition (22) of the response functions and making the replacements $t_F \rightarrow t$ and $t_0 \rightarrow t_w$, Eq. (70) can be rewritten as

$$\begin{aligned} R_{i;j_1}^{(1,1)}(t, t_1) = \beta \frac{\partial}{\partial t_1} \langle \varphi_i(t) \varphi_{j_1}(t_1) \rangle_{I \rightarrow \beta,0} \\ + Z_{\beta,0} \frac{\delta \langle P_I(\varphi(t)) e^{\beta \mathcal{H}_0(\varphi(t))} \varphi_i(t_w) \rangle_{\beta,0 \rightarrow \beta, [\tilde{h}(t)]}}{\delta \tilde{h}_{j_1}(\tilde{t}_1)} \Big|_{\tilde{h}=0}. \end{aligned} \quad (72)$$

According to Eq. (49), the derivative with respect to $\tilde{h}_{j_1}(\tilde{t}_1)$ can be replaced by the insertion of $-\dot{p}_{j_1}(\tilde{t}_1)$ and, using Eq. (51), the second term in the right-hand side can be rewritten as

$$\begin{aligned} Z_{\beta,0} \frac{\delta \langle P_I(\varphi(t)) e^{\beta \mathcal{H}_0(\varphi(t))} \varphi_i(t_w) \rangle_{\beta,0 \rightarrow \beta, [\tilde{h}(t)]}}{\delta \tilde{h}_{j_1}(\tilde{t}_1)} \Big|_{\tilde{h}=0} \\ = Z_{\beta,0} \frac{\beta}{2} \frac{\partial}{\partial t_1} \langle P_I(\varphi(t)) e^{\beta \mathcal{H}_0(\varphi(t))} \varphi_{j_1}(\tilde{t}_1) \varphi_i(t_w) \rangle_{\beta,0} \\ - Z_{\beta,0} \frac{\beta}{2} \langle P_I(\varphi(t)) e^{\beta \mathcal{H}_0(\varphi(t))} B_{j_1}(\tilde{t}_1) \varphi_i(t_w) \rangle_{\beta,0}. \end{aligned} \quad (73)$$

Furthermore, since after setting to zero the external field the averages become equilibrium averages, using the Onsager relation we get

$$\begin{aligned} Z_{\beta,0} \frac{\delta \langle P_I(\varphi(t_F)) e^{\beta \mathcal{H}_0(\varphi(t_F))} \varphi_i(t_0) \rangle_{\beta,0 \rightarrow \beta, [\tilde{h}(t)]}}{\delta \tilde{h}_{j_1}(\tilde{t}_1)} \Big|_{\tilde{h}=0} \\ = -Z_{\beta,0} \frac{\beta}{2} \frac{\partial}{\partial t_1} \langle \varphi_i(t) \varphi_{j_1}(t_1) P_I(\varphi(t_w)) e^{\beta \mathcal{H}_0(\varphi(t_w))} \rangle_{\beta,0} \\ - Z_{\beta,0} \frac{\beta}{2} \langle \varphi_i(t) B_{j_1}(t_1) P_I(\varphi(t_w)) e^{\beta \mathcal{H}_0(\varphi(t_w))} \rangle_{\beta,0}. \end{aligned} \quad (74)$$

The next step consists in the recognition that for an arbitrary observable A

$$Z_{\beta,0} \langle A(t) P_I(\varphi(t_w)) e^{\beta \mathcal{H}_0(\varphi(t_w))} \rangle_{\beta,0} = \langle A(t) \rangle_{I \rightarrow \beta,0}, \quad (75)$$

since the factor $Z_{\beta,0} P_I(\varphi(t_w)) e^{\beta \mathcal{H}_0(\varphi(t_w))}$ in the left-hand side has the effect of undoing the equilibrium initial condition and replacing it with P_I . Hence Eq. (74) can be rewritten as

$$\begin{aligned} & Z_{\beta,0} \frac{\delta \langle P_i(\varphi(t_F)) e^{\beta \mathcal{H}_0(\varphi(t_F))} \varphi_i(t_0) \rangle_{\beta,0 \rightarrow \beta, [\tilde{h}(t)]}}{\delta \tilde{h}_i(\tilde{t}_1)} \Bigg|_{\tilde{h}=0} \\ &= -\frac{\beta}{2} \frac{\partial}{\partial t_1} \langle \varphi_i(t) \varphi_{j_1}(t_1) \rangle_{I \rightarrow \beta,0} - \frac{\beta}{2} \langle \varphi_i(t) B_{j_1}(t_1) \rangle_{I \rightarrow \beta,0} \end{aligned} \quad (76)$$

and inserting it into Eq. (72), eventually one finds

$$R_{i;j_1}^{(1,1)}(t, t_1) = \frac{\beta}{2} \frac{\partial}{\partial t_1} \langle \varphi_i(t) \varphi_{j_1}(t_1) \rangle_{I \rightarrow \beta,0} - \frac{\beta}{2} \langle \varphi_i(t) B_{j_1}(t_1) \rangle_{I \rightarrow \beta,0}, \quad (77)$$

thus recovering Eq. (56).

VI. NONLINEAR SUSCEPTIBILITY AND GROWING LENGTH SCALE

In this section we consider the use of the response functions in the diagnostics of cooperative effects taking place over large length scales during the relaxation, referring to the case of Ising spin systems. A partial and preliminary account of the material in this section has been presented in Ref. [14].

In nondisordered coarsening systems, such as a ferromagnet quenched to or to below the critical point, the existence of a growing dynamical correlation length is well-captured through the scaling properties of the equal time correlation function $C_{ij}(t) = M_{ij}(t, t)$ [1], recalling that in this kind of processes $M_i(t) \equiv 0$. In glassy systems, instead, quenched or self-induced disorder renders the two body correlation function short ranged, making it necessary to resort to higher order correlation functions. Attention has been particularly focused on the four-point correlation function [15]

$$C_{ij}^{(4)}(t, t_w) = M_{ijij}(t, t_w, t, t_w) - M_{ii}(t, t_w) M_{jj}(t, t_w), \quad (78)$$

which describes the so-called heterogeneities [16], namely the space fluctuations associated to the local time decorrelation. Although quite convenient in the numerical simulations, $C_{ij}^{(4)}(t, t_w)$ has the shortcoming of being hardly accessible in the experiments. Conversely, susceptibilities are more easily measurable and this has prompted the investigation of the nonlinear FDR.

Here, we expand on the proposals [2–4, 14] to investigate dynamic scaling through higher order susceptibilities. Let us begin by considering the second order response of the second moment at equal times

$$R_{ij;j_1 j_2}^{(2,2)}(t, t; t_1, t_2) = \frac{\delta^2 M_{ij}(\mathbf{t}, t, [h_i(t')])}{\delta h_{j_1}(t_1) \delta h_{j_2}(t_2)} \Bigg|_{h=0}. \quad (79)$$

Proceeding exactly as in the derivation of Eq. (62), the corresponding FDR is given by

$$\begin{aligned} R_{ij;j_1 j_2}^{(2,2)}(t, t; t_1, t_2) &= (\beta/2)^2 \left\{ \frac{\partial}{\partial t_M} \frac{\partial}{\partial t_m} M_{ijj_M j_m}(t, t, t_M, t_m) \right. \\ &\quad - \frac{\partial}{\partial t_M} \langle \hat{\sigma}_i^z(t) \hat{\sigma}_j^z(t) \hat{\sigma}_{j_M}^z(t_M) \hat{B}_{j_m}(t_m) \rangle \\ &\quad - \frac{\partial}{\partial t_m} \langle \hat{\sigma}_i^z(t) \hat{\sigma}_j^z(t) \hat{B}_{j_M}(t_M) \hat{\sigma}_{j_m}^z(t_m) \rangle \\ &\quad \left. + \langle \hat{\sigma}_i^z(t) \hat{\sigma}_j^z(t) \hat{B}_{j_M}(t_M) \hat{B}_{j_m}(t_m) \rangle \right\} \\ &\quad + (\beta^2/2) \left\{ \langle \hat{\sigma}_i^z(t) \hat{\sigma}_j^z(t) \hat{\sigma}_{j_M}^z(t_M) \hat{B}_{j_m}(t_m) \rangle \right. \\ &\quad \left. + \frac{\partial}{\partial t_m} M_{ijj_M j_m}(t, t, t_M, t_m) \right\} \delta_{j_M j_m} \delta(t_M - t_m). \end{aligned} \quad (80)$$

Looking at the above equation, it may seem farfetched to relate the properties of $C^{(4)}$ to those of $R^{(2,2)}$, since the fourth order moment appears explicitly only in the first term in the right-hand side and in the singular term. Nonetheless, information on the existence of a growing correlation length can be obtained through a scaling argument, as it will be shown below. Let us consider the more manageable integrated response function

$$\begin{aligned} -\chi_{ij}^{(2,2)}(t, t_w) &= \int_{t_w}^t dt_1 \int_{t_w}^{t_1} dt_2 R_{ij;ij}^{(2,2)}(t, t; t_1, t_2) \\ &\quad - \chi_i^{(1,1)}(t, t_w) \chi_j^{(1,1)}(t, t_w), \end{aligned} \quad (81)$$

where the $\chi_i^{(1,1)}$ in the subtraction are the time integrals of the linear response function (56), i.e.,

$$\chi_i^{(1,1)}(t, t_w) = \int_{t_w}^t dt_1 R_{ii}^{(1,1)}(t, t_1). \quad (82)$$

The reason for this subtraction and for the minus sign on the left-hand side will be clear shortly. Assuming that eventually an equilibrium state is reached, from equilibrium statistical mechanics follows

$$T^2 \lim_{t \rightarrow \infty} \chi_{ij}^{(2,2)}(t, t_w) = C_{ij,eq}^2, \quad (83)$$

where, for simplicity, we have taken $\langle \hat{\sigma}_i^z \rangle_{eq} = 0$. The scaling relation $C_{ij,eq} = \xi^{2-d-\eta} F_{C,eq}(|i-j|/\xi)$, where $\xi(T)$ is the equilibrium correlation length, suggests a finite time scaling behavior of the form

$$T^2 \chi_{ij}^{(2,2)}(t, t_w) = \xi^x F\left(\frac{|i-j|}{\xi}, \frac{t^{1/z}}{\xi}, \frac{t_w}{t}\right), \quad (84)$$

where $x = 4 - 2d - 2\eta$ and z is the dynamical exponent.

Another quantity, which has been recently [3] considered in relation to $C^{(4)}$, is the third order integrated response of the first moment

$$\chi_{ij}^{(1,3)}(t, t_w) = -\frac{1}{2} \int_{t_w}^t dt_1 dt_2 dt_3 R_{i;ijj}^{(1,3)}(t; t_1, t_2, t_3), \quad (85)$$

where $R_{i;ijj}^{(1,3)}$ is given by Eq. (A2) of Appendix A. Again, from the large time result

$$T^3 \lim_{t \rightarrow \infty} \chi_{ij}^{(1,3)}(t, t_w) = C_{ij,eq}^2 \quad (86)$$

we may infer the scaling behavior

$$T^3 \chi_{ij}^{(1,3)}(t, t_w) = \xi^x G\left(\frac{|i-j|}{\xi}, \frac{t^{1/z}}{\xi}, \frac{t_w}{t}\right). \quad (87)$$

Notice that the prefactor in the definition (85) has been arranged in such a way that the large time limits of $T^2 \chi^{(2,2)}$ and $T^3 \chi^{(1,3)}$ are the same.

These patterns of behavior have been checked numerically in the one-dimensional Ising model. The simulation has been carried out through standard Monte Carlo techniques with Glauber transition rates, where $\hat{B}_i = \hat{\sigma}_i^z - \tanh(\beta \sum_{\langle j \rangle_i} J_{ij} \hat{\sigma}_j^z)$ and the sum runs over the nearest neighbors $\langle j \rangle_i$ of i . Taking $J_{ij} = 1$, we have prepared the system in a high temperature uncorrelated state and then quenched it to the final temperature T at time $t=0$. In this case $z=2$ [1], and $\xi(T) = -1/\ln[\tanh(1/T)]$ [13]. The integrated response functions $\chi_{ij}^{(2,2)}(t, 0)$ and $\chi_{ij}^{(1,3)}(t, 0)$ have been computed using the FDRs (80) and (A2), following the zero field method of Ref. [9]. It must be stressed that, due to the extremely noisy nature of the response functions, the numerical computation of these quantities through the FDRs is by far more convenient than the computation based on the application of a small external field. In fact, in addition to the incomparably better signal-to-noise ratio, the $h \rightarrow 0$ limit is built in the FDRs.

In order to verify the scaling relations (84) and (87), first of all we have taken $t_w=0$ in order to reduce the variables from three to two in the right-hand sides. Then, recalling that for the 1D Ising model $\eta=1$ implies $x=0$ and varying the temperature and the distance in such a way to keep $|i-j|/\xi$ fixed, it is matter of showing that $T^2 \chi_{ij}^{(2,2)}(t, 0)$ and $T^3 \chi_{ij}^{(1,3)}(t, 0)$ are functions only of $t^{1/z}/\xi$. This is shown, with good accuracy, in Fig. 1 for the quenches to the three final temperatures $T_1=0.6$, $T_2=0.7572$, and $T_3=1.0239$ and with six different values of $|i-j|/\xi$. Both $T^2 \chi_{ij}^{(2,2)}(t, 0)$ and $T^3 \chi_{ij}^{(1,3)}(t, 0)$ grow from zero to the same asymptotic value $C_{ij,eq}^2 = \exp\{-2|i-j|/\xi\}$ on the same time scale, as expected. Note that the data for $\chi^{(1,3)}$ are much more noisy than those for $\chi^{(2,2)}$. Since the same numerical resources have been allocated in the computation of each of these two quantities, we conclude that investigations based on $\chi^{(2,2)}$ are more efficient, at least numerically.

We now discuss how $\chi^{(2,2)}$ can be effectively used for the measurement of a cooperative length in disordered systems. In order to improve the statistics further, it is convenient to consider the $\vec{k}=0$ component of the space Fourier transform

$$\chi_{\vec{k}=0}^{(2,2)}(t, t_w) = (1/N^2) \sum_{i,j} \chi_{ij}^{(2,2)}(t, t_w), \quad (88)$$

which, using Eq. (84), scales as

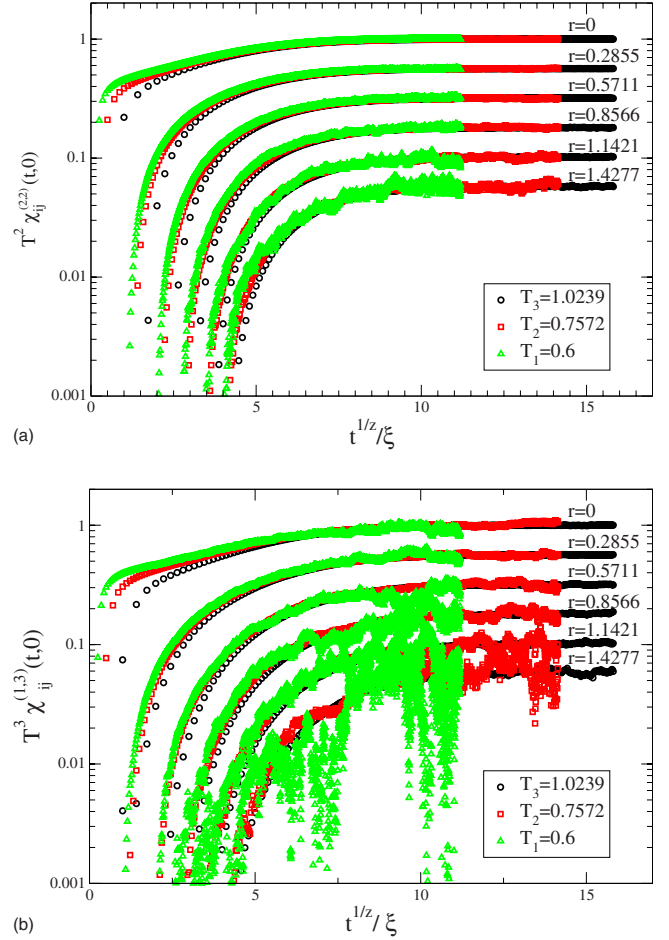


FIG. 1. (Color online) Upper panel: The quantity $T^2 \chi_{ij}^{(2,2)}(t, 0)$ is plotted against $t^{1/z}/\xi$ ($z=2$) for six fixed values of $r=|i-j|/\xi$ ($r=0, 0.2855, 0.5711, 0.8566, 1.1421, 1.4277$ from top to bottom) and three temperatures $T_1=0.6$, $T_2=0.7572$, and $T_3=1.0239$ such that $\xi(T_1)/\xi(T_2)=2$ and $\xi(T_1)/\xi(T_3)=4$. Lower panel: Same for $T^3 \chi_{ij}^{(1,3)}(t, 0)$.

$$\chi_{\vec{k}=0}^{(2,2)}(t, t_w) = \xi^{4-d-2\eta} \mathcal{F}\left(\frac{t^{1/z}}{\xi}, \frac{t_w}{t}\right). \quad (89)$$

In Ref. [14] we have computed numerically this quantity, with $t_w=0$, in the Edwards-Anderson (EA) model with Hamiltonian $\hat{\mathcal{H}} = \sum_{ij} J_{ij} \hat{\sigma}_i^z \hat{\sigma}_j^z$ and $d=1, 2$. The data have been analyzed as follows: for large t the curves saturate to the equilibrium value $\chi_{\vec{k}=0,eq}^{(2,2)} \sim \xi^{4-d-2\eta}$. Using the known values of η , one can extract ξ . In the off-equilibrium regime $t^{1/z} \ll \xi$ the growing correlation length $L(t) \sim t^{1/z}$ is expected not to depend on ξ . Enforcing this condition from Eq. (89) one must have $\mathcal{F}(t^{1/z}/\xi, 0) \sim [\xi/L(t)]^{2\eta+d-4}$, which yields

$$\chi_{\vec{k}=0}^{(2,2)}(t, 0) \sim L(t)^{4-d-2\eta}. \quad (90)$$

This allows one to determine $L(t)$. After doing this, we checked for the data collapse by plotting $\xi^{-4+d+2\eta} \chi_{\vec{k}=0}^{(2,2)}(t, 0)$ vs $L(t)/\xi$ for all the temperatures considered (see Figs. 2 and 3).

Let us consider first the $d=1$ EA model with bimodal distribution of the coupling constants $J_{ij} = \pm 1$. This system is

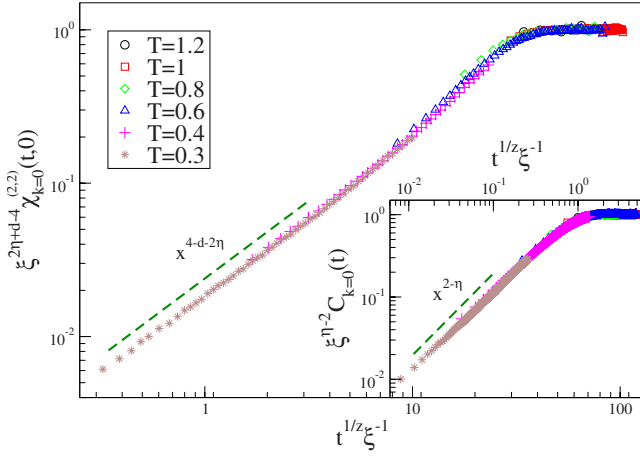


FIG. 2. (Color online) Data collapse of $\chi_{k=0}^{(2,2)}$ ($C_{k=0}$ in the inset) for several temperatures in the $d=1$ EA model ($\eta=1$, $z=2$). The dashed lines are the expected power laws in the nonequilibrium regime.

considered in order to test the method, since it can be mapped onto the ferromagnetic system, just considered above. Moreover, in this simple case, in addition to $\chi_{k=0}^{(2,2)}(t,0)$, one can check the scaling of the equal time structure factor $C_{k=0}(t)$, obtaining independent determinations of $L(t)$ and ξ to compare with. This shows that the sets of data for $L(t)$ and ξ , obtained in both ways, are in agreement with each other and with the analytical behaviors up to the numerical uncertainty. The data collapse of $\chi_{k=0}^{(2,2)}(t,0)$ and of $C_{k=0}(t)$ are shown in Fig. 2. Here, one clearly observes the off-equilibrium regime, characterized by the power-law behavior of $\chi_{k=0}^{(2,2)}(t,0)$ and $C_{k=0}(t)$ with exponents $4-d-2\eta$ and $2-\eta$, respectively. In the large time regime equilibration takes place with the convergence of $\chi_{k=0}^{(2,2)}(t,0)$ and $C_{k=0}(t)$ to $\chi_{k=0,eq}^{(2,2)}$ and to $C_{k=0,eq}(t)$.

After this explicit verification, we have turned to the $d=2$ case, where the independent information on the structure factor is not available. Both with bimodal and Gaussian dis-

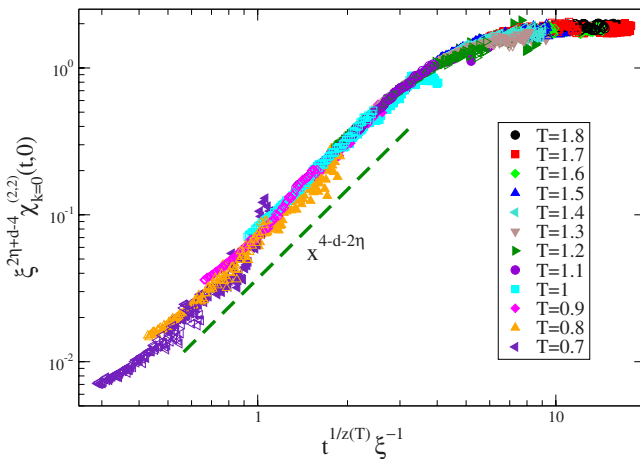


FIG. 3. (Color online) Data collapse of $\chi_{k=0}^{(2,2)}$ for several T in the $d=2$ EA model with bimodal (open symbols) or Gaussian (closed symbols) bond distribution, with $z(T)=4/T$ and $\eta=0$. The dashed line is the expected power law in the nonequilibrium regime.

tributions of J_{ij} , the behavior of ξ extracted from $\chi_{k=0,eq}^{(2,2)}$ using $\eta=0$ [17], has been found consistent with previous results [17,18]. The nonequilibrium behavior is compatible with a power law $L(t) \sim t^{1/z(T)}$ with a temperature-dependent exponent in agreement with $z(T) \approx 4/T$, as reported in Ref. [19]. The data collapse of $\chi_{k=0}^{(2,2)}(t,0)$ is shown in Fig. 3. Notice also the additional collapse of the curves with bimodal and Gaussian bond distribution, further suggesting that the two models may share the same universality class at finite temperatures [17].

VII. EFFECTIVE TEMPERATURE

One of the most interesting developments in the study of the linear FDR out of equilibrium has been the introduction of the concept of effective temperature T_{eff} [10]. The idea is that the off-equilibrium behavior observed during slow relaxation can be accounted for by the separation of the time scales for different subsets of degrees of freedom. Each of these is regarded as in equilibrium with a different virtual thermostat at some appropriate effective temperature, which depends on the time scale and is different from the physical temperature of the real thermostat driving the relaxation. The value of T_{eff} can be inferred by forcing the off-equilibrium linear FDR in the form of the equilibrium FDT. Although appealing, this idea has turned out not to be applicable *tout court*, since T_{eff} might turn out to be observable dependent [20]. Nonetheless, with the proper caveats, the concept remains quite useful and suggestive. In this section we make a preliminary exploration of another open end in the important question of how general T_{eff} can be, investigating whether it is possible to extend to the nonlinear FDR the effective temperature concept, consistently with what it has done in the linear case.

Let us first recall how T_{eff} is defined from the linear FDR. For definiteness, the Ising spin case will be considered. Writing explicitly the time integral in Eq. (82), one has

$$\chi_i^{(1,1)}(t, t_w) = \frac{\beta}{2} \int_{t_w}^t dt_1 \left[\frac{\partial}{\partial t_1} M_{ii}(t, t_1) - \langle \sigma_i^z(t) \hat{B}_i(t_1) \rangle \right]. \quad (91)$$

Assuming $M_i(t) \equiv 0$ throughout the dynamical evolution, and replacing $M_{ii}(t, t_1)$ with the autocorrelation function $C(t, t_1)$, the quantity

$$\psi^{(1)}(t, t_w) = \int_{t_w}^t dt_1 \frac{\partial}{\partial t_1} C(t, t_1) = 1 - C(t, t_w) \quad (92)$$

for fixed t_w is a monotonously increasing function of time, which allows one to reparametrize t in terms of $\psi^{(1)}$ and to write $\chi_i^{(1,1)}(t, t_w)$ in the form

$$\chi_i^{(1,1)}(t, t_w) = \chi_i^{(1,1)}(\psi^{(1)}, t_w). \quad (93)$$

In equilibrium, where time translation invariance holds, the dependence on t_w disappears and the parametric representation becomes linear,

$$\chi_i^{(1,1)}(\psi^{(1)}) = \beta \psi^{(1)} \quad (94)$$

with the obvious consequence

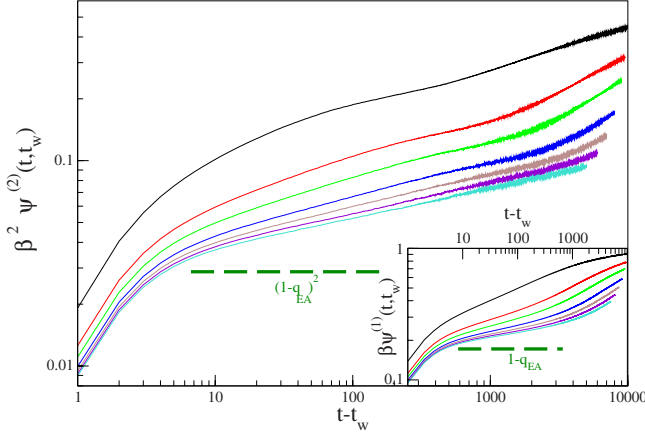


FIG. 4. (Color online) The quantity $\psi^{(2)}$ is plotted against $t-t_w$ for $t_w=100, 500, 1000, 2000, 3000, 4000,$ and 5000 from top to bottom. Data refer to a 2D Ising system of size 1800^2 quenched to $T=2$ ($T_c \approx 2.269$). The dashed horizontal line is the large- t_w height of the plateau [$y=(1-q_{EA})^2$]. In the inset the quantity $\psi^{(1)}$ is shown (same t_w of the main figure).

$$\beta = \frac{d\chi_i^{(1,1)}(\psi^{(1)})}{d\psi^{(1)}}. \quad (95)$$

Off equilibrium, the parametric representation will not be linear and an effective temperature can be defined by the generalization of the above relation,

$$\beta_{eff}(\psi^{(1)}, t_w) = \frac{\partial \chi_i^{(1,1)}(\psi^{(1)}, t_w)}{\partial \psi^{(1)}} \quad (96)$$

with $\beta_{eff} = 1/T_{eff}$.

In order to see how $T_{eff} \neq T$ arises in a simple context, let us consider the relaxation to a low temperature phase characterized by ergodicity breaking and, therefore, by a nonvanishing Edwards-Anderson order parameter q_{EA} . In particular, let us think of the already mentioned coarsening process, like in a ferromagnet quenched to below the critical point and relaxing via domain growth. In that case q_{EA}^2 coincides with the spontaneous magnetization squared M_{eq}^2 .

As $t_w \rightarrow \infty$, the separation of time scales takes place. The short, or quasiequilibrium, time regime holds for $C > M_{eq}^2$, that is $\psi^{(1)} < 1 - M_{eq}^2$, while the large time scale sets in when $C < M_{eq}^2$, or $\psi^{(1)} > 1 - M_{eq}^2$. The existence of this latter regime makes evident the failure of equilibration, even in the $t_w \rightarrow \infty$ limit, since the autocorrelation function falls below the Edwards-Anderson plateau. The behavior of $\psi^{(1)}$, obtained from numerical simulations of the Ising model in $d=2$, is shown in the inset of Fig. 4. Starting from zero, there is a fast growth in the short time regime, followed by a plateau, more evident for large t_w , and finally there is convergence, with the power-law behavior $1 - \psi^{(1)}(t, t_w) \sim t^{-\lambda/z}$, toward the asymptotic value $\psi^{(1)} = 1$. Notice that λ is the Fisher-Huse exponent [21] and that the plateau flattens over the asymptotic value $1 - q_{EA}$ as $t_w \rightarrow \infty$.

Correspondingly, the integrated response function can be written as the sum of two pieces [22]

$$\chi_i^{(1,1)}(\psi^{(1)}, t_w) = \chi_{st}^{(1,1)}(\psi^{(1)}) + \chi_{ag}^{(1,1)}(\psi^{(1)}, t_w), \quad (97)$$

where $\chi_{st}^{(1,1)}$ is the stationary contribution arising from the equilibrated bulk of domains, while $\chi_{ag}^{(1,1)}$ is the aging contribution due to the off-equilibrium domain walls. The stationary contribution obeys Eq. (94) in the short time regime, saturates to its equilibrium value, and remains constant in the large time regime, while the aging contribution vanishes as $t_w \rightarrow \infty$ according to

$$\chi_{ag}^{(1,1)}(\psi^{(1)}, t_w) = t_w^{-a} F(\psi^{(1)}), \quad (98)$$

where $a > 0$ [23]. Hence the full response function obeys the asymptotic form

$$\lim_{t_w \rightarrow \infty} \chi_i^{(1,1)}(\psi^{(1)}, t_w) = \begin{cases} \beta \psi^{(1)} & \text{for } 0 \leq \psi^{(1)} \leq 1 - M_{eq}^2, \\ \beta(1 - M_{eq}^2) & \text{for } 1 - M_{eq}^2 < \psi^{(1)} \leq 1, \end{cases} \quad (99)$$

which, on account of Eq. (96), leads to

$$\lim_{t_w \rightarrow \infty} \beta_{eff}(\psi^{(1)}, t_w) = \begin{cases} \beta & \text{for } 0 \leq \psi^{(1)} \leq 1 - M_{eq}^2, \\ 0 & \text{for } 1 - M_{eq}^2 < \psi^{(1)} \leq 1. \end{cases} \quad (100)$$

Namely, the effective temperature coincides with the physical temperature in the short time regime, where the system appears equilibrated, while it is drastically different from it in the off-equilibrium large time regime.

Let us now carry out the parallel analysis on the $\vec{k}=0$ component of the second order integrated response function

$$\chi_{\vec{k}=0}^{(2,2)}(t, t_w) = \frac{1}{N^2} \sum_{i,j} \int_{t_w}^t dt_1 \int_{t_w}^t dt_2 R_{ij;ij}^{(2,2)}(t, t; t_1, t_2). \quad (101)$$

Notice that, although we use the same notation, this quantity differs from the one in Eq. (88) because of the overall sign and of the absence of the subtraction. Let us introduce the quantity

$$\psi^{(2)}(t, t_w) = \frac{1}{2} \frac{1}{N^2} \sum_{i,j} \int_{t_w}^t dt_1 \int_{t_w}^t dt_2 \left[\frac{\partial^2}{\partial t_M \partial t_m} M_{ij;ij}(t, t, t_M, t_m) + \langle \sigma_i^z(t) \sigma_j^z(t) \hat{B}_i(t_M) \hat{B}_j(t_m) \rangle \right] \quad (102)$$

with properties similar to those of $\psi^{(1)}(t, t_w)$, as shown in Fig. 4. The main feature is the monotonous increase from zero to an asymptotic value well above the limiting value $(1 - q_{EA})^2$ that one would get from the equilibrium calculation. This is the value at which a plateau develops as t_w gets large, signaling the separation of time scales. Using $\psi^{(2)}$ to reparametrize the time t , from Eq. (63) it follows that at equilibrium the FDR becomes linear,

$$\chi_{\vec{k}=0}^{(2,2)}(\psi^{(2)}) = \beta^2 \psi^{(2)}. \quad (103)$$

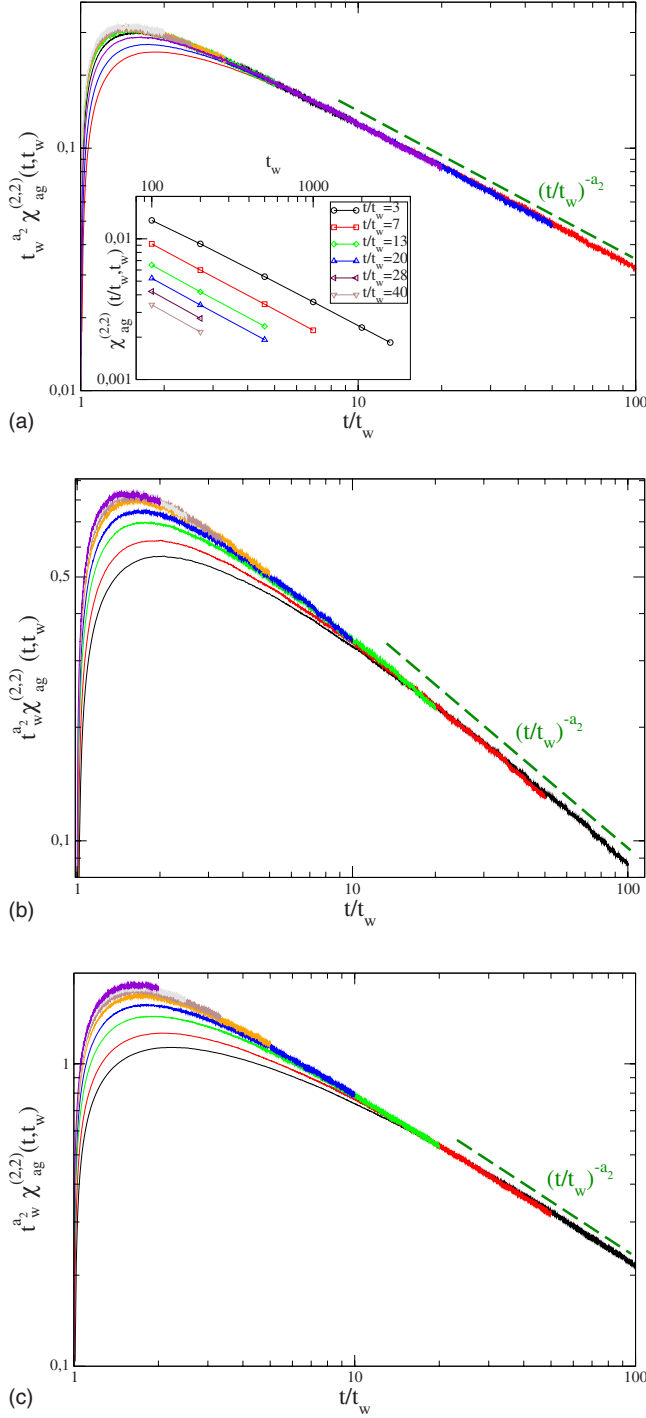


FIG. 5. (Color online) $t_w^{a_2} \chi_{ag}^{(2,2)}(t, t_w)$ is plotted against t/t_w for $t_w = 100, 200, 500, 1000, 2000, 3000, 4000,$ and 5000 (from bottom to top) and three temperatures $T=1, 1.5,$ and 2 (upper, central, and lower panel). The exponent a_2 is extracted as discussed in the text, finding $a_2=0.61$ for $T=1$, and $a_2=0.62$ for $T=1.5$ and 2 . The dashed lines represent the asymptotic behavior $\chi_{ag}^{(2,2)}(t, t_w) \sim (t/t_w)^{-a_2}$ for large t/t_w . In the inset the quantity $\chi_{ag}^{(2,2)}(t, t_w)$ is plotted against t_w with t/t_w fixed.

Hence by following the same reasoning as in the linear case, in the off-equilibrium regime an effective temperature can be introduced by the analog of Eq. (96),

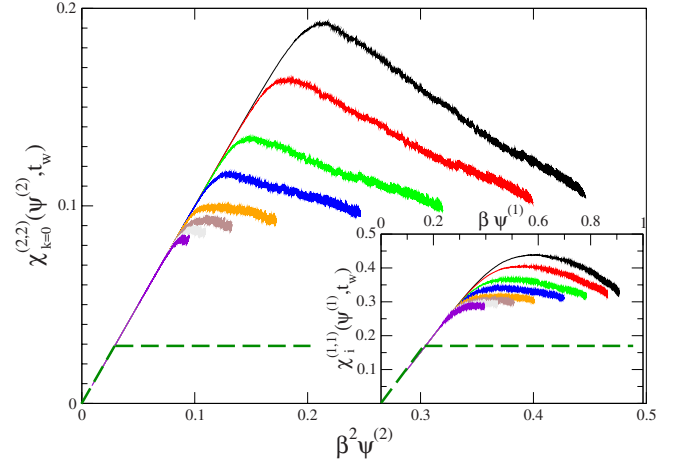


FIG. 6. (Color online) The parametric plot of $\chi_{k=0}^{(2,2)}(t, t_w)$ against $\beta^2 \psi^{(2)}$ [$\chi_{k=0}^{(1,1)}(t, t_w)$ against $\beta \psi^{(1)}$ in the inset] is shown for $T=2$ and $t_w = 100, 200, 500, 1000, 2000, 3000, 4000,$ and 5000 , from top to bottom. The dashed line is the expected asymptotic behavior.

$$\beta_{eff}^2(\psi^{(2)}, t_w) = \frac{\partial \chi_{k=0}^{(2,2)}(\psi^{(2)}, t_w)}{\partial \psi^{(2)}}. \quad (104)$$

The question, now, is whether the two β_{eff} defined by Eqs. (96) and (104) are consistent or not, that is whether the equality

$$\lim_{t_w \rightarrow \infty} \beta_{eff}(\psi^{(2)}, t_w) = \lim_{t_w \rightarrow \infty} \beta_{eff}(\psi^{(1)}, t_w) \quad (105)$$

holds or not. This is a difficult question to answer in general, we shall limit ourselves to the consideration of the particular coarsening process analyzed above in the linear case.

The short and the large time scales, in terms of $\psi^{(2)}$, correspond to $\psi^{(2)}$ smaller or larger than $(1 - M_{eq}^2)^2$, respectively. Writing $\chi_{k=0}^{(2,2)}$ as the sum of two pieces, as in Eq. (97),

$$\chi_{k=0}^{(2,2)}(\psi^{(2)}, t_w) = \chi_{st}^{(2,2)}(\psi^{(2)}) + \chi_{ag}^{(2,2)}(\psi^{(2)}, t_w), \quad (106)$$

the same considerations made on $\chi_{st}^{(1,1)}$ apply exactly to $\chi_{st}^{(2,2)}$, since this is an equilibrium contribution. Namely, after obeying Eq. (103) in the short time regime, it saturates to the equilibrium value $(1 - M_{eq}^2)^2$ and then remains constant in the large time regime. For $\chi_{ag}^{(2,2)}(\psi^{(2)}, t_w)$ there are no previous results to rely on. We have, then, measured $\chi_{ag}^{(2,2)}(\psi^{(2)}, t_w)$ numerically in the quench of a two-dimensional Ising model below T_C evolving with Glauber dynamics. The aging contribution $\chi_{ag}^{(2,2)}$ has been isolated using the method based on the no-bulk-flip dynamics discussed in [23,25–27].

In order to check if a scaling form of the type (98) is obeyed,

$$\chi_{ag}^{(2,2)}(\psi^{(2)}, t_w) = t_w^{-a_2} F_2(t/t_w), \quad (107)$$

we have plotted $\chi_{ag}^{(2,2)}(t, t_w)$ for a fixed value of t/t_w against t_w , as shown in the inset of the upper panel of Fig. 5. From

the observed power-law behavior we have extracted the exponent a_2 , finding values in the range [0.59–0.62]. We have, then, carried out the data collapse by plotting $t_w^{a_2} \chi_{ag}^{(2)}(t, t_w)$ against t/t_w . For large t_w the collapse (Fig. 5) is quite good, confirming that the scaling form (107) is obeyed with an exponent $a_2 \approx 0.61$ –0.62. For small values of t_w and t/t_w deviations are observed due to preasymptotic effects, similarly to what was already observed in the linear case [23,27]. Notice, also, that for large t/t_w one has a power-law decay of the scaling function $F_2(t/t_w) \sim (t/t_w)^{-a_2}$ with the same exponent a_2 entering Eq. (107), exactly as it was observed in the linear case [27].

In conclusion, like in the linear case, the existence of the scaling behavior (107) with $a_2 > 0$ implies that the aging contribution vanishes asymptotically, yielding the analog of Eq. (99),

$$\lim_{t_w \rightarrow \infty} \chi_{k=0}^{(2,2)}(\psi^{(2)}, t_w) = \begin{cases} \beta^2 \psi^{(2)} & \text{for } \psi^{(2)} \leq (1 - M_{eq}^2)^2, \\ \beta^2 (1 - M_{eq}^2)^2 & \text{for } (1 - M_{eq}^2)^2 < \psi^{(2)}. \end{cases} \quad (108)$$

The approach to this asymptotic behavior is shown in Fig. 6. Hence, using the definition (104), we find

$$\lim_{t_w \rightarrow \infty} \beta_{eff}(\psi^{(2)}, t_w) = \begin{cases} \beta & \text{for } \psi^{(2)} \leq (1 - M_{eq}^2)^2, \\ 0 & \text{for } (1 - M_{eq}^2)^2 < \psi^{(2)}. \end{cases} \quad (109)$$

The comparison with Eq. (100) suggests that the consistency condition (105) is satisfied.

VIII. CONCLUSIONS

In this paper we have derived the off-equilibrium FDRs of arbitrary order for systems evolving with Markovian stochastic dynamics. The main effort has been to put the FDRs in the same form for both continuous and discrete spins. In order to stress the generality of the result, we have also

shown how the whole hierarchy of FDRs can be made to descend from the fluctuation principle. Once the FDRs are available, response functions of arbitrary order are expressed in terms of unperturbed correlation functions of observables. The payoff is in the development of simple and efficient zero field algorithms for the numerical simulations.

As an application, we have considered the problem of detecting the existence of a growing length in those cases, like in glassy systems, where standard methods based on two-point correlation functions and the corresponding linear response functions are of no use. In these cases the simplest object carrying useful information, in principle, would be a four-point correlation function which, however, is not directly accessible to experiment. Instead, experimentally accessible are the nonlinear response functions involving the four-point correlation function through the nonlinear FDRs. The choice of which response function and, therefore, of which FDR to use is not univocal, once the realm of the nonlinear response functions is entered. Then the choice is matter of convenience. We have made the proposal to use the second order response of a two-point correlation function, rather than the third order response of the magnetization, as advocated elsewhere in the literature. We have, then, demonstrated the numerical advantage of our choice through the implementation of the zero field algorithm.

Finally, we have made a first step into the important but difficult problem of the definition of the effective temperature through the nonlinear FDR. We have considered the domain coarsening process ensuing the quench of a ferromagnet below its critical point. Indeed, in that case we have found that it is possible to extract from the nonlinear FDR an effective temperature which is consistent with the effective temperature obtained from the much studied linear FDR.

APPENDIX A

Proceeding like in the derivation of Eq. (26), the third order derivative of the propagator is given by

$$\begin{aligned} \frac{\delta^3 \hat{P}_h(t|t_w)}{\delta h_{j_1}(t_1) \delta h_{j_2}(t_2) \delta h_{j_3}(t_3)} &= \hat{P}_h(t|t_M) \frac{\partial \hat{W}(t_M)}{\partial h_{j_M}(t_M)} \hat{P}_h(t_M|t_I) \frac{\partial \hat{W}(t_I)}{\partial h_{j_I}(t_I)} \hat{P}_h(t_I|t_m) \frac{\partial \hat{W}(t_m)}{\partial h_{j_m}(t_m)} \hat{P}_h(t_m|t_w) \\ &+ \hat{P}_h(t|t_M) \frac{\partial^2 \hat{W}(t_I)}{\partial h_{j_I}^2(t_I)} \hat{P}_h(t_I|t_m) \frac{\partial \hat{W}(t_m)}{\partial h_{j_m}(t_m)} \hat{P}_h(t_m|t_w) \delta_{j_M j_I} \delta(t_M - t_I) \\ &+ \hat{P}_h(t|t_M) \frac{\partial \hat{W}(t_M)}{\partial h_{j_M}(t_M)} \hat{P}_h(t_M|t_I) \frac{\partial^2 \hat{W}(t_I)}{\partial h_{j_I}^2(t_I)} \hat{P}_h(t_I|t_w) \delta_{j_I j_m} \delta(t_I - t_m) + \hat{P}_h(t|t_1) \frac{\partial^3 \hat{W}(t_1)}{\partial h_{j_1}^3(t_1)} \hat{P}_h(t_1|t_w) \delta(12) \delta(23), \end{aligned} \quad (A1)$$

where $t_M = \max(t_j)$, $t_m = \min(t_j)$, $t_m \leq t_I \leq t_M$, j_M, j_I , and j_m are the sites where the field acts at the times t_M , t_I , or t_m , respectively, and $\delta(np) = \delta_{j_n j_p} \delta(t_n - t_p)$. Inserting this into Eq. (24) and using Eq. (53), we get the third order response of the first moment:

$$\begin{aligned}
R_{i_1 j_1 i_2 j_2 i_3 j_3}^{(1,3)}(t, t_1, t_2, t_3) = & \left(\frac{\beta}{2}\right)^3 \left\{ \frac{\partial^3}{\partial t_M \partial t_I \partial t_m} M_{ij_M j_i j_m}(t, t_M, t_I, t_m) - \frac{\partial^2}{\partial t_M \partial t_I} \langle \hat{\sigma}_i(t) \hat{\sigma}_{j_M}(t_M) \hat{\sigma}_{j_1}(t_I) \hat{B}_{j_m}(t_m) \rangle \right. \\
& - \frac{\partial^2}{\partial t_M \partial t_m} \langle \hat{\sigma}_i(t) \hat{\sigma}_{j_M}(t_M) \hat{B}_{j_1}(t_I) \hat{\sigma}_{j_m}(t_m) \rangle - \frac{\partial^2}{\partial t_I \partial t_m} \langle \hat{\sigma}_i(t) \hat{B}_{j_M}(t_M) \hat{\sigma}_{j_1}(t_I) \hat{\sigma}_{j_m}(t_m) \rangle + \frac{\partial}{\partial t_m} \langle \hat{\sigma}_i(t) \hat{B}_{j_M}(t_M) \hat{B}_{j_1}(t_I) \hat{\sigma}_{j_m}(t_m) \rangle \\
& + \frac{\partial}{\partial t_I} \langle \hat{\sigma}_i(t) \hat{B}_{j_M}(t_M) \hat{\sigma}_{j_1}(t_I) \hat{B}_{j_m}(t_m) \rangle + \frac{\partial}{\partial t_M} \langle \hat{\sigma}_i(t) \hat{\sigma}_{j_M}(t_M) \hat{B}_{j_1}(t_I) \hat{B}_{j_m}(t_m) \rangle - \langle \sigma_i(t) B_{j_M}(t_M) B_{j_1}(t_I) B_{j_m}(t_m) \rangle \left. \right\} \\
& + \frac{\beta^3}{4} \left\{ \left(\frac{\partial}{\partial t_m} \langle \hat{\sigma}_i(t) \hat{\sigma}_{j_1}(t_I) \hat{B}_{j_1}(t_I) \hat{\sigma}_{j_m}(t_m) \rangle + \frac{\partial}{\partial t_m} \frac{\partial}{\partial t_I} M_{ij_M j_i j_m}(t, t_M, t_I, t_m) - \langle \hat{\sigma}_i(t) \hat{\sigma}_{j_1}(t_I) \hat{B}_{j_1}(t_I) \hat{B}_{j_m}(t_m) \rangle \right. \right. \\
& - \frac{\partial}{\partial t_I} \langle \hat{\sigma}_i(t) \hat{\sigma}_{j_M}(t_M) \hat{\sigma}_{j_1}(t_I) \hat{B}_{j_m}(t_m) \rangle \left. \right) \delta_{j_M j_I} \delta(t_M - t_I) + \left(\frac{\partial}{\partial t_M} \langle \hat{\sigma}_i(t) \hat{\sigma}_{j_M}(t_M) \hat{\sigma}_{j_1}(t_I) \hat{B}_{j_1}(t_I) \rangle \right. \\
& + \frac{\partial}{\partial t_M} \frac{\partial}{\partial t_m} M_{ij_M j_i j_m}(t, t_M, t_I, t_m) - \langle \hat{\sigma}_i(t) \hat{B}_{j_M}(t_M) \hat{\sigma}_{j_1}(t_I) \hat{B}_{j_1}(t_I) \rangle - \frac{\partial}{\partial t_m} \langle \hat{\sigma}_i(t) \hat{B}_{j_M}(t_M) \hat{\sigma}_{j_1}(t_I) \hat{\sigma}_{j_m}(t_m) \rangle \left. \right) \delta_{j_I j_m} \delta(t_I - t_m) \left. \right\} \\
& + \frac{\beta^3}{2} \left(\frac{\partial}{\partial t_I} M_{ij_1}(t, t_1) - \langle \hat{\sigma}_i(t) \hat{B}_{j_1}(t_1) \rangle \right) \delta_{j_1 j_2} \delta_{j_2 j_3} \delta(t_1 - t_2) \delta(t_2 - t_3). \tag{A2}
\end{aligned}$$

At stationarity this becomes

$$\begin{aligned}
R_{i_1 j_1 i_2 j_2 i_3 j_3}^{(1,3)}(t, t_1, t_2, t_3) = & \frac{\beta^3}{4} \left\{ \frac{\partial^3}{\partial t_M \partial t_I \partial t_m} M_{ij_M j_i j_m}(t, t_M, t_I, t_m) - \frac{\partial^2}{\partial t_M \partial t_m} \langle \hat{\sigma}_i(t) \hat{\sigma}_{j_M}(t_M) \hat{B}_{j_1}(t_I) \hat{\sigma}_{j_m}(t_m) \rangle - \frac{\partial^2}{\partial t_I \partial t_m} \langle \hat{\sigma}_i(t) \hat{B}_{j_M}(t_M) \hat{\sigma}_{j_1}(t_I) \hat{\sigma}_{j_m}(t_m) \rangle \right. \\
& + \frac{\partial}{\partial t_m} \langle \hat{\sigma}_i(t) \hat{B}_{j_M}(t_M) \hat{B}_{j_1}(t_I) \hat{\sigma}_{j_m}(t_m) \rangle \left. \right\} + \frac{\beta^3}{2} \left\{ \frac{\partial}{\partial t_m} \langle \hat{\sigma}_i(t) \hat{\sigma}_{j_1}(t_I) \hat{B}_{j_1}(t_I) \hat{\sigma}_{j_m}(t_m) \rangle \right. \\
& + \frac{\partial}{\partial t_m} \frac{\partial}{\partial t_I} M_{ij_M j_i j_m}(t, t_M, t_I, t_m) \left. \right\} \delta_{j_M j_I} \delta(t_M - t_I) + \beta^3 \frac{\partial}{\partial t_1} M_{ij_1}(t, t_1) \delta_{j_1 j_2} \delta_{j_2 j_3} \delta(t_1 - t_2) \delta(t_2 - t_3). \tag{A3}
\end{aligned}$$

It should be recalled that the singular terms in the last two equations are present only in the Ising spin case.

APPENDIX B

The expansion of the left-hand side of Eq. (67) can be done in two steps. Expanding first the exponential we get

$$\begin{aligned}
\left\langle \varphi_i(t_F) \exp \left\{ -\beta \int_{t_0}^{t_F} dt h(t) \dot{\varphi}(t) \right\} \right\rangle_{I \rightarrow \beta, [h(t)]} &= \sum_{m=0}^{\infty} \frac{(-\beta)^m}{m!} \sum_{j_1 \dots j_m} \int_{t_0}^{t_F} dt_1 \dots dt_m \langle \varphi_i(t_F) \dot{\varphi}_{j_1}(t_1) \dots \dot{\varphi}_{j_m}(t_m) \rangle_{I \rightarrow \beta, [h(t)]} \\
&\times h_{j_1}(t_1) \dots h_{j_m}(t_m) \tag{B1}
\end{aligned}$$

and expanding the individual averages

$$\langle \varphi_i(t_F) \dot{\varphi}_{j_1}(t_1) \dots \dot{\varphi}_{j_m}(t_m) \rangle_{I \rightarrow \beta, [h(t)]} = \sum_{p=0}^{\infty} \frac{1}{p!} \sum_{q_1 \dots q_p} \int_{t_0}^{t_F} dt'_1 \dots dt'_p \frac{\mathcal{P} \langle \varphi_i(t_F) \dot{\varphi}_{j_1}(t_1) \dots \dot{\varphi}_{j_m}(t_m) \rangle_{I \rightarrow \beta, [h(t)]}}{\delta h_{q_1}(t'_1) \dots \delta h_{q_p}(t'_p)} \Bigg|_{h=0} h_{q_1}(t'_1) \dots h_{q_p}(t'_p), \tag{B2}$$

all together these two contributions give

$$\begin{aligned}
\left\langle \varphi_i(t_F) \exp \left\{ -\beta \int_{t_0}^{t_F} dt h(t) \dot{\varphi}(t) \right\} \right\rangle_{I \rightarrow \beta, [h(t)]} &= \sum_{m=0}^{\infty} \sum_{p=0}^{\infty} \frac{(-\beta)^m}{m! p!} \sum_{j_1 \dots j_m} \sum_{q_1 \dots q_p} \int_{t_0}^{t_F} dt_1 \dots dt_m dt'_1 \dots dt'_p \\
&\times \frac{\mathcal{P} \langle \varphi_i(t_F) \dot{\varphi}_{j_1}(t_1) \dots \dot{\varphi}_{j_m}(t_m) \rangle_{I \rightarrow \beta, [h(t)]}}{\delta h_{q_1}(t'_1) \dots \delta h_{q_p}(t'_p)} \Bigg|_{h=0} h_{j_1}(t_1) \dots h_{j_m}(t_m) h_{q_1}(t'_1) \dots h_{q_p}(t'_p). \tag{B3}
\end{aligned}$$

Reorganizing the double sum

$$\sum_{m=0}^{\infty} \sum_{p=0}^{\infty} \frac{(-\beta)^m}{m!p!} \sum_{j_1 \dots j_m} \sum_{q_1 \dots q_p} = \sum_{n=0}^{\infty} \sum_{p=0}^n \frac{(-\beta)^{n-p}}{(n-p)!p!} \sum_{j_1 \dots j_{n-p}} \sum_{q_1 \dots q_p} \quad (\text{B4})$$

the above result can be rewritten as

$$\begin{aligned} \left\langle \varphi_i(t_F) \exp \left\{ -\beta \int_{t_0}^{t_F} dt h(t) \dot{\varphi}(t) \right\} \right\rangle_{I \rightarrow \beta, [h(t)]} &= \langle \varphi_i(t_F) \rangle_{I \rightarrow \beta, 0} \times \sum_{n=1}^{\infty} \frac{1}{n!} \sum_{p=0}^n (-\beta)^{n-p} \left[\frac{n!}{(n-p)!p!} \right] \\ &\times \sum_{j_1 \dots j_{n-p}} \sum_{q_1 \dots q_p} \int_{t_0}^{t_F} dt_1 \dots dt_{n-p} dt'_1 \dots dt'_p \\ &\times \frac{\mathcal{D}^i \langle \varphi_i(t_F) \dot{\varphi}_{j_1}(t_1) \dots \dot{\varphi}_{j_{n-p}}(t_{n-p}) \rangle_{I \rightarrow \beta, [h(t)]}}{\delta h_{q_1}(t'_1) \dots \delta h_{q_p}(t'_p)} \Bigg|_{h=0} h_{j_1}(t_1) \dots h_{j_{n-p}}(t_{n-p}) h_{q_1}(t'_1) \dots h_{q_p}(t'_p). \end{aligned} \quad (\text{B5})$$

Notice that the combinatorial factor in the square bracket gives the number of the distinct permutations among the two sets of indices (j_1, \dots, j_{n-p}) and (q_1, \dots, q_p) .

Going over to the right-hand side of Eq. (67) and introducing the shorthand

$$\langle P_i(\varphi(t_F)) e^{\beta \mathcal{H}_0(\varphi(t_F))} \varphi_i(t_0) \rangle_{\beta, 0 \rightarrow \beta, [\tilde{h}(t)]} = \langle \text{RHS} \rangle_{\beta, 0 \rightarrow \beta, [\tilde{h}(t)]} \quad (\text{B6})$$

one gets

$$\begin{aligned} \langle \text{RHS} \rangle_{\beta, 0 \rightarrow \beta, [\tilde{h}(t)]} &= \langle \text{RHS} \rangle_{\beta, 0} + \sum_{n=1}^{\infty} \frac{1}{n!} \sum_{j_1 \dots j_n} \int_{t_0}^{t_F} dt_1 \dots dt_n \\ &\times \frac{\mathcal{D}^i \langle \text{RHS} \rangle_{\beta, 0 \rightarrow \beta, [\tilde{h}(t)]}}{\delta \tilde{h}_{j_1}(\tilde{t}_1) \dots \delta \tilde{h}_{j_n}(\tilde{t}_n)} \Bigg|_{h=0} h_{j_1}(t_1) \dots h_{j_n}(t_n) \quad (\text{B7}) \end{aligned}$$

and, since $\tilde{h}_j(\tilde{t}) = h_j(t)$, this can be rewritten as

$$\begin{aligned} \langle \text{RHS} \rangle_{\beta, 0 \rightarrow \beta, [\tilde{h}(t)]} &= \langle \text{RHS} \rangle_{\beta, 0} + \sum_{n=1}^{\infty} \frac{1}{n!} \sum_{j_1 \dots j_n} \int_{t_0}^{t_F} dt_1 \dots dt_n \\ &\times \frac{\mathcal{D}^i \langle \text{RHS} \rangle_{\beta, 0 \rightarrow \beta, [\tilde{h}(t)]}}{\delta \tilde{h}_{j_1}(\tilde{t}_1) \dots \delta \tilde{h}_{j_n}(\tilde{t}_n)} \Bigg|_{h=0} h_{j_1}(t_1) \dots h_{j_n}(t_n), \quad (\text{B8}) \end{aligned}$$

where $\langle \cdot \rangle_{\beta, 0}$ stands for the equilibrium average at the temperature β and without external field. Therefore comparing with Eq. (B5), one arrives at Eqs. (68) and (69).

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