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Fluctuations of two-time quantities and non-linear response functions

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Abstract. We study the fluctuations of the autocorrelation and autoresponse functions and, in particular, their variances and covariance. In a first general part of the paper, we show the equivalence of the variance of the response function to the second-order susceptibility of a composite operator, and we derive an equilibrium fluctuation-dissipation theorem beyond linear order, relating it to the other variances. In a second part of the paper we apply the formalism in the study of non-disordered ferromagnets, in equilibrium or in the coarsening kinetics following a critical or sub-critical quench. We show numerically that the variances and the non-linear susceptibility obey scaling with respect to the coherence length ξ in equilibrium, and with respect to the growing length $L(t)$ after a quench, similar to what is known for the autocorrelation and the autoresponse functions.

Keywords: coarsening processes (theory), dynamical heterogeneities (theory), fluctuations (theory)

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1. Introduction

Two-time quantities, such as the autocorrelation function $C(t, t_w)$ and the associated linear response function $\chi(t, t_w)$, describing the effects of a perturbation, are generally considered in experiments, theories and numerical investigations. In equilibrium the fluctuation-dissipation theorem (FDT) holds, providing an important tool for studying coherence lengths and relaxation times by means of susceptibility measurements.

Apart from equilibrium, the pair C and χ has been thoroughly investigated also for slowly relaxing systems, such as supercooled liquids, glasses, spin glasses and quenched ferromagnets, as natural quantities for characterizing and studying the ageing behavior.

In this context, the fluctuation-dissipation ratio $X(t, t_w) = d\chi/dC$ was defined [1] in order to quantify the *distance* from equilibrium, where $X \equiv 1$. Particularly relevant is its limiting value $X_\infty = \lim_{t_w \rightarrow \infty} \lim_{t \rightarrow \infty} X(t, t_w)$ due to its robust universal properties [2]–[5]. Complementary to the concept of X , that of an effective temperature $T_{\text{eff}} = T/X$ has been thoroughly applied in several contexts [6], although the physical meaning has not yet been completely clarified. Moreover, the fluctuation-dissipation ratio was also proved [7] to be related to the overlap probability distribution of the equilibrium state at the final temperature of the quench, providing an important bridge between equilibrium and non-equilibrium. Finally, in the context of coarsening systems, the behavior of the response function was shown to be strictly linked to geometric properties of the interfaces [8, 9], allowing the characterization of their roughness, and, in the case of phase ordering on inhomogeneous substrates, to important topological properties of the underlying graph [10].

Besides this manifold interest in average two-time quantities, more recently considerable attention has been paid also to the study of their local fluctuations, which are now accessible in large scale numerical simulations [11] and, due to new techniques, also in experiments [12]. The reasons for considering these quantities are various:

- For disordered systems, since averaging over the disorder makes the usual two-particle correlation function (structure factor) short ranged even in those cases where a large coherence length ξ is present, quantities related either to the spatial fluctuations of C [13]–[15] or to non-linear susceptibilities [14, 16] have been proposed for detecting and quantifying ξ .
- Local fluctuations of two-time quantities are associated with the dynamical heterogeneities observed in several systems which are believed to be a key to local rearrangements taking place in slowly evolving systems [11, 17]. In the context of spin models, it was shown [18] that these fluctuations can be conveniently used to highlight the heterogeneous nature of the system.
- In [19] it was shown that for a large class of glassy models the action describing the asymptotic dynamics is invariant under the transformation of time $t \rightarrow h(t)$, denoted as time reparameterization. This symmetry is expected to hold true for glassy systems with a finite effective temperature but not for coarsening systems, where $T_{\text{eff}} = \infty$ [20]. Then, restricting to glassy systems, it was proposed [18, 19] that the ageing kinetics could be physically interpreted as the coexistence of different parameterizations $t \rightarrow h_r(t)$ slowly varying in space \mathbf{r} . According to this interpretation, spatial fluctuations of two-time quantities should span the possible values of C and χ associated with different choices of $h(t)$. Since the correlation and the response function transform in the same way under the time reparameterization transformation, the same curve $\chi(C)$ relating the average quantities is expected to hold also for the fluctuations. This property was proposed in [18, 19] as a check on the time reparameterization invariance, and the results tend to conform to this interpretation.
- In [21] it was claimed that, at least in the context of non-disordered coarsening systems, fluctuations of two-time quantities encode the limiting fluctuation-dissipation ratio X_∞ , similarly to the fluctuation-dissipation relation between the fully averaged quantities χ and C .

In the first part of this paper, we discuss the definition of the fluctuating versions $\hat{C}_i, \hat{\chi}_i$ of C_i and χ_i on site i , and consider their (co)variances $V_{ij}^C = \langle \hat{C}_i \hat{C}_j \rangle - C_i C_j$, V_{ij}^χ , and $V_{ij}^{C\chi}$ (defined analogously to V_{ij}^C). We present a rather detailed and complete study of these quantities and their relation to a non-linear susceptibility \mathcal{V}_{ij}^χ (defined in equation (16)) related to the fluctuations of $\hat{\chi}_i$ introduced in [16]. We show that, for $i \neq j$, the variance V_{ij}^χ of $\hat{\chi}_i$ is equal to \mathcal{V}_{ij}^χ . This allows us to derive a relation between V_{ij}^C , \mathcal{V}_{ij}^χ and $V_{ij}^{C\chi}$, which can be regarded as a second-order fluctuation-dissipation theorem (SOFDT) relating these quantities in equilibrium. The SOFDT holds for every choice of t and t_w and of i, j and is completely general for Markov systems. It represents also a relation between the second moments of \hat{C}_i and $\hat{\chi}_j$ for $i \neq j$, but not for $i = j$ because, in this case, \mathcal{V}_{ij}^χ cannot be straightforwardly interpreted as a variance. Prompted by the SOFDT, we argue that \mathcal{V}_{ij}^χ , rather than V_{ij}^χ , is the natural quantity to consider, on an equal footing with the variances V_{ij}^C and $V_{ij}^{C\chi}$, for studying scaling behaviors, and for detecting and quantifying correlation lengths. Being a susceptibility, \mathcal{V} could in principle be accessible in experiments.

These ideas are tested in the second part of the paper, where we study numerically the behavior of V_{ij}^C , $V_{ij}^{C\chi}$ and of \mathcal{V}_{ij}^χ in non-disordered ferromagnets in equilibrium or in the non-equilibrium kinetics following a quench to a final temperature T at or below T_c . Restricting to the cases with $T \geq T_c$ the same problem has been recently addressed analytically by Annibale and Sollich [22] in the context of the soluble spherical model. Here we carry out the analysis using the finite-dimensional Ising model, focusing particularly on the scaling properties. Focusing on the $k = 0$ Fourier component $V_{k=0}^C = (1/N) \sum_{i,j=1}^N V_{ij}^C$ (and similarly for the other quantities) our results show a pattern of behaviors for $V_{k=0}^C$, $V_{k=0}^{C\chi}$ and $\mathcal{V}_{k=0}^\chi$ similar to what is known for C and χ . In particular, in a quench at T_c , one finds the asymptotic scaling form $V_{k=0}^C(t, t_w) \propto V_{k=0}^{C\chi}(t, t_w) \propto \mathcal{V}_{k=0}^\chi(t, t_w) \propto t_w^{b_c} f(t/t_w)$, where the exponent $b_c = (4 - d - 2\eta)/z_c$ can be expressed in terms of the equilibrium static and dynamic critical exponents η and z_c , in agreement with what was found in [22]. In quenches below T_c , in the time sector with $t_w \rightarrow \infty$ and $t/t_w = \text{const}$, usually referred to as the ageing regime, we find a scaling form $V_{k=0}^C(t, t_w) = t_w^{a_C} f(t/t_w)$ (and similarly for $V_{k=0}^{C\chi}$ and $\mathcal{V}_{k=0}^\chi$), where, in contrast to the critical quench case, a_C and f are genuinely non-equilibrium quantities that cannot be straightforwardly related to equilibrium behaviors.

Our results allow us to discuss also the issue of a direct correlation between the fluctuating parts of C and χ , as predicted for glassy systems by the time reparameterization invariance scenario. In the ageing dynamics of coarsening systems, we find that for large t/t_w the ratio \mathcal{V}^χ/V^C diverges, both in the quench at T_c and below T_c . This implies that \hat{C} and $\hat{\chi}$ are not related so as to follow the curve $\chi(C)$, in contrast with the above mentioned scenario.

This paper is organized as follows. In section 2 we introduce and discuss general definitions of the fluctuating quantities, their variances and covariances; in section 3 we discuss the relations among them and with the second-order susceptibility \mathcal{V}^χ . In section 4 we specialize the above concepts to the case of ferromagnetic systems. We study the behavior of V^C , $V^{C\chi}$ and \mathcal{V}^χ in equilibrium in section 4.1, relating their large $t - t_w$ behavior to the coherence length in section 4.1.1. The non-equilibrium kinetics is considered in section 4.2: critical quenches are studied in section 4.2.1, while section 4.2.2 is devoted to sub-critical quenches. The results of these sections are related to the issue

of time reparameterization invariance in section 4.3. Last, in section 5 we summarize, draw our conclusions and discuss some open problems and perspectives. Four appendices contain some technical points.

2. Fluctuating quantities and variances

Let us consider a system described by a set of variables σ_i defined on lattice sites i . In order to fix the notation we consider discrete variables, referred to as spins, the evolution of which is described by a master equation. The results of this paper, nonetheless, apply as well to continuous variables subjected to a Langevin equation (specific differences between the two cases will be noticed whatever the case). The autocorrelation function is defined as

$$C_i(t, t_w) = \langle \sigma_i(t) \sigma_i(t_w) \rangle - \langle \sigma_i(t) \rangle \langle \sigma_i(t_w) \rangle. \quad (1)$$

Using the symbol $\hat{\cdot}$ to denote the fluctuating quantities whose average gives the usual functions, one has $\hat{C}_i(t, t_w) = [\sigma_i(t) - \langle \sigma_i(t) \rangle][\sigma_i(t_w) - \langle \sigma_i(t_w) \rangle]$. The (auto)response function is defined as

$$\chi_i(t, t_w) = T \int_{t_w}^t dt' \left. \frac{\delta \langle \sigma_i(t) \rangle_h}{\delta h_i(t')} \right|_{h=0}, \quad (2)$$

where $\langle \dots \rangle_h$ means an average over a process where an impulsive perturbing field h has been switched on at time t' . Notice that a factor T has been included in the definition (2) of the response. The presence of the derivative in equation (2) makes the definition of a fluctuating part of χ_i not straightforward in the case of discrete variables (see appendix A for a discussion of a possible definition of $\hat{\chi}_i$ based on the definition (2), where the perturbation h_i is present). This problem can be bypassed using an out-of-equilibrium fluctuation-dissipation relation

$$\chi_i(t, t_w) = \langle \hat{\chi}_i(t, t_w) \rangle, \quad (3)$$

where in the limit of vanishing h the derivative of equation (2) is worked out analytically, and on the right-hand side there appear specific correlation functions (see e.g. equation (7) and the discussion below) computed in the unperturbed dynamics. Such a relation has been obtained in different forms in [16], [23]–[29]. This allows one to introduce a fluctuating part of the susceptibility defined over an unperturbed process. Equation (3) is the basis of the so called *field-free* methods for the computation of response functions allowing the computation of χ_i without applying any perturbation.

With the quantities introduced above, one can build the following (co)variances:

$$V_{ij}^C(t, t_w) = \langle \widehat{\delta C}_i(t, t_w) \widehat{\delta C}_j(t, t_w) \rangle \quad (4)$$

$$V_{ij}^X(t, t_w) = \langle \widehat{\delta \chi}_i(t, t_w) \widehat{\delta \chi}_j(t, t_w) \rangle \quad (5)$$

$$V_{ij}^{CX}(t, t_w) = \langle \widehat{\delta C}_i(t, t_w) \widehat{\delta \chi}_j(t, t_w) \rangle \quad (6)$$

where, for a generic observable A , we have defined $\widehat{\delta A} \equiv \hat{A} - \langle \hat{A} \rangle$. Notice that we restrict the analysis to variances obtained by taking products of two-time quantities on different sites but with the same choice of times t, t_w . $V_{ij}^C(t, t_w)$ is the four-point correlation function

introduced in [13] for studying cooperative effects in disordered systems, usually denoted as C_4 .

As discussed in [26, 30], for a given unperturbed model, there are many possible choices of the perturbed transition rates, which give rise to different expressions for $\hat{\chi}_i$. However, as shown in [30], and further in appendix A, we expect all these choices to lead to approximately the same values of the variances as were introduced above (with the notable exception of the equal site variance V_{ii}^X , which, however, is not of interest in this paper). Then, in the following, we will consider the expression

$$\hat{\chi}_i(t, t_w) = \frac{1}{2} \left[\sigma_i(t) \sigma_i(t) - \sigma_i(t) \sigma_i(t_w) - \sigma_i(t) \int_{t_w}^t dt_1 B_i(t_1) \right], \quad (7)$$

where $B_i = -\sum_{\sigma'} [\sigma_i - \sigma'_i] w(\sigma'|\sigma)$, $w(\sigma'|\sigma)$ being the transition rate for going from the configuration σ to σ' . This form has been obtained in [26] (and, in an equivalent formulation, for continuous variables in [16, 23]).

The relation (3) with the choice (7) has the advantage of a large generality, holding for Markov processes with generic unperturbed transition rates, both for continuous and discrete variables. Other possible relations between the response and quantities computed on unperturbed trajectories have been proposed [24, 25, 27, 28] but we do not consider them here because, as discussed in [30], in those approaches either the response is not related to correlation functions of observable quantities in the unperturbed system, as in [24, 27, 28], or, in the case of [25], it is restricted to a specific systems (Ising) with a specific (heat bath) transition rate.

The $k = 0$ Fourier components of the correlation and response functions are usually considered to extract physical information, such as spatial coherence or relaxation times, from the (unperturbed) system under study. The $k = 0$ mode $V_{k=0}^C(t, t)$ of the variance of \hat{C} , defined through

$$V_{k=0}^C(t, t_w) = \frac{1}{N} \sum_{i,j=1}^N V_{ij}^C(t, t_w), \quad (8)$$

has been considered to access the same information for disordered systems. This might suggest that the same information is contained in the $k = 0$ component of the other variances. Notice that, for V^X , the sum (8) includes the equal site term V_{ii}^X which, as anticipated, takes different values according to the specific choices of the fluctuating part of the response. We will deal with this problem later.

3. The equilibrium relation between variances and non-linear susceptibilities

In this section we derive a relation between the variances and the non-linear susceptibility \mathcal{V}^X (defined in equation (16)) that will be interpreted as a second-order fluctuation-dissipation theorem (SOFTD) relating these quantities. We sketch here the basic results; further details and formalism are contained in appendix B.

Let us start by recovering the usual FDT. In equilibrium, using time translation and time inversion invariance, namely the Onsager relations, it can be shown [16] that

$$\langle \sigma_i(t) B_i(t_1) \rangle_{\text{eq}} = -\frac{\partial}{\partial t_1} \langle \sigma_i(t) \sigma_i(t_1) \rangle_{\text{eq}}, \quad (9)$$

valid for $t > t_1$. Plugging this relation into equations (3) and (7) one retrieves the usual fluctuation-dissipation theorem

$$\langle \hat{D}_i(t, t_w) \rangle = 0, \quad (10)$$

where we have introduced the quantity

$$\hat{D}_i(t, t_w) = \hat{\chi}_i(t, t_w) + \hat{C}_i(t, t_w) - \hat{C}_i(t, t). \quad (11)$$

Notice that, for Ising spins $\sigma_i = \pm 1$, $\hat{C}_i(t, t) \equiv 1$ and does not fluctuate.

The next step is to seek for a relation holding between the variances. Since the mechanism whereby this relation is obtained is different for equal or different sites i, j (due to the sensitivity of V_{ii}^X to the choice of $\hat{\chi}_i$), we split the arguments into separate sections.

3.1. $i \neq j$

Defining the second moment of \hat{D}_i as $V_{ij}^D(t, t_w) = \langle \delta \hat{D}_i(t, t_w) \delta \hat{D}_j(t, t_w) \rangle$, and using the equilibrium property (9) it is easy to show that

$$V_{ij}^D(t, t_w) = V_{ij}^X(t, t_w) + 2V_{ij}^{C\chi}(t, t_w) + V_{ij}^C(t, t_w) - V_{ij}^C(t, t). \quad (12)$$

Proceeding in a similar way to in the derivation of equation (10), in appendix B we show that, for $i \neq j$, the rhs of equation (12) vanishes in equilibrium. Hence we have the following SOFDT:

$$V_{ij}^D(t, t_w) = 0. \quad (13)$$

This relation holds for every choice of the fluctuating part of χ : indeed, we have already noticed that on different sites i, j the variances involved in the rhs of equation (12) are independent of that choice. Interestingly, equation (13) shows that not only does the first moment of \hat{D}_i vanish (due to the FDT (10)), but also the second moment does too. Moreover, as shown in appendix A, the equal site variance V_{ii}^D is not zero (due to the divergence of the term K_i^X (or \tilde{K}_i^X) appearing in V_{ii}^X ; see equations (A.21) and (A.22)), indicating that \hat{D} is not identically vanishing, and hence it is a truly fluctuating quantity. This leads to the surprising conclusion that \hat{D} is an uncorrelated variable for any choice of i, j and of t, t_w , and in any equilibrium state of any Markovian model. This observation, which might have far reaching consequences, will be enforced in section 4 to disentangle quasi-equilibrium correlation from the genuine non-equilibrium ones in ageing systems.

3.2. $i = j$

For $i = j$ a relation such as equation (10) cannot be satisfied for any choice of the fluctuating part of χ . In order to show that, let us first observe that, recalling equation (12), if equation (13) were to hold also for $i = j$, the quantity $-2V_{ii}^{C\chi}(t, t_w) - V_{ii}^C(t, t_w) + V_{ii}^C(t, t)$ should equal $V_{ii}^X(t, t_w)$. This quantity can be easily computed, yielding

$$-2V_{ii}^{C\chi}(t, t_w) - V_{ii}^C(t, t_w) + V_{ii}^C(t, t) = -\chi_i^2(t, t_w) - \Delta_i(t, t_w), \quad (14)$$

where $\Delta_i(t, t_w) = 2\langle \hat{C}_i(t, t_w) \hat{\chi}_i(t, t_w) \rangle + \langle \hat{C}_i^2(t, t_w) \rangle - \langle \hat{C}_i^2(t, t) \rangle$ is a quantity which vanishes for Ising spins, as can be easily shown using the definitions of \hat{C}_i and $\hat{\chi}_i$ and the

property (B.3). On the other hand, computing V_{ii}^X directly leads to the result (see appendix A)

$$V_{ii}^X(t, t_w) = -\chi_i^2(t, t_w) - \Delta_i(t, t_w) + K_i^X(t, t_w), \quad (15)$$

where K_i , given in equation (A.21), is a quantity that has been studied in specific models in [30] and found to be positive and diverging as $t - t_w$ increases. Expression (15) is different from the rhs of equation (14), thus proving that the SOFTD does not hold for $i = j$. Worse, the quantity K_i^X appearing in equation (15) prevents the possibility of any direct relation between the variances because it introduces an explicit time dependence.

3.3. The non-linear susceptibility $\mathcal{V}_{ij}^X(t, t_w)$

In order to remove the asymmetry between $i = j$ and $i \neq j$ and proceed further, the idea is to search for a quantity \mathcal{V}_{ij}^X related to V_{ij}^X such that $\mathcal{V}_{i \neq j}^X = V_{i \neq j}^X$, while on equal sites the equilibrium value of \mathcal{V}_{ii}^X equals the rhs of equation (14). This would allow one to arrive at a pair of relations analogous to equations (13) and (12) for any ij . As shown in appendix C, the second-order susceptibility

$$\mathcal{V}_{ij}^X(t, t_w) \equiv \int_{t_w}^t dt_1 \int_{t_w}^t dt_2 \left[R_{ij;ij}^{(2,2)}(t, t; t_1, t_2) - R_i(t, t_1) R_j(t, t_2) \right], \quad (16)$$

where

$$R_{ij;ij}^{(2,2)}(t, t; t_1, t_2) \equiv T^2 \frac{\delta^2 \langle \sigma_i(t) \sigma_j(t) \rangle_h}{\delta h_i(t_1) \delta h_j(t_2)} \Big|_{h=0} \quad (17)$$

is the non-linear impulsive response function proposed in [16] for studying heterogeneities in disordered systems, meets the requirements above. Then, recalling equation (14), one has the relations

$$\mathcal{V}_{ij}^D(t, t_w) = 0, \quad (18)$$

and

$$\mathcal{V}_{ij}^D(t, t_w) = \mathcal{V}_{ij}^X(t, t_w) + 2V_{ij}^{CX}(t, t_w) + V_{ij}^C(t, t_w) - V_{ij}^C(t, t) \quad (19)$$

formally identical to equations (13) and (12), but holding for every choice of the sites i, j and hence also for the $k = 0$ component, namely

$$\mathcal{V}_{k=0}^D(t, t_w) = 0. \quad (20)$$

In summary, one always has an equilibrium relation (equation (18) or (20)) between the second-order response defined in equations (16) and (17) and the variances V_{ij}^C and V_{ij}^{CX} . In the case of different sites $i \neq j$, this non-linear response is also the variance of $\hat{\chi}$, whereas on equal sites there is no analogous interpretation, and neither is it possible to obtain a relation involving V_{ii}^X directly.

Coming back to the problem discussed at the end of section 2, namely the possibility of extracting physical information on the unperturbed system from the $k = 0$ mode of the variances, some considerations are in order. First, it is clear that, as regards $V_{k=0}^X$, its value changes depending on the way the perturbation is introduced (via the term V_{ii}^X). In this way this quantity mixes information regarding the perturbation with other factors of

interest. The quantity $\mathcal{V}_{k=0}^x$, however, does not suffer from this problem, since its equal site value can always be related to quantities that do not depend on the choice of the perturbation. Moreover, for large times, $V_{k=0}^x$ (defined in analogy to equation (8)) turns out to be dominated by the equal site contribution. Indeed, whatever definition of $\hat{\chi}_i$ is adopted, either the quantity K_i^x or \tilde{K}_i^x comes in (see equations (A.22) and (A.23)), and these are either infinite (\tilde{K}_i^x) or diverging with increasing $t-t_w$ (K_i^x). These considerations suggest the use of $\mathcal{V}_{k=0}^x$. Indeed it has been shown in specific cases [16] that this quantity contains information on relevant properties, such as the coherence length, similarly to the variance V_{ij}^C , and therefore has an important physical meaning.

4. Fluctuations in ferromagnets

Specializing the general definitions given above to the case of ferromagnetic systems, in this section we study the behavior of the $k = 0$ mode of the quantities introduced above in the Ising model in equilibrium (section 4.1) and in the non-equilibrium kinetics following a quench to T_c (section 4.2.1) or below T_c (section 4.2.2). Our main interest is in the scaling of these quantities with respect to the characteristic length of the system. From this perspective, it is quite natural to focus on $\mathcal{V}_{k=0}^x$ rather than on $V_{k=0}^x$. Indeed we will show that in any case $V_{k=0}^C$, $V_{k=0}^{Cx}$ and $\mathcal{V}_{k=0}^x$ obey scaling forms from which a correlation length can be extracted. On the other hand, as already anticipated, these scaling properties are masked in $V_{k=0}^x$ by the term K_i^x or \tilde{K}_i^x .

4.1. Equilibrium behavior

Here we consider the behavior of V^C , V^{Cx} and \mathcal{V}^x in equilibrium states above, at, and below T_c . In the last case, we consider equilibrium within ergodic components, namely in states with broken symmetry.

4.1.1. Limiting behaviors for $t - t_w = 0$ and for $t - t_w \rightarrow \infty$. Before discussing the scaling properties of V^C , V^{Cx} and \mathcal{V}^x , let us compute their limiting behaviors for small and large time differences $t - t_w$. From the definitions (4), (6) and (16) one has $V_{ij}^C(t, t) = V_{ij}^{Cx}(t, t) = \mathcal{V}_{ij}^x(t, t) = 0$, and the same for the $k = 0$ component. One can compute analytically also the limiting values attained in equilibrium by V^C , V^{Cx} and \mathcal{V}^x for $t - t_w \rightarrow \infty$, relating them to the usual static correlation function. Indeed, with the definitions of section 2, all the quantities considered are written in terms of two-time/two-site correlation functions. For large time differences these correlation functions can be factorized as products of one-time quantities resulting in the following behavior (details are given in appendix D):

$$\begin{aligned} V_{ij}^C(\infty) &= \lim_{t-t_w \rightarrow \infty} V_{ij}^C(t - t_w) = C_{ij,eq}(C_{ij,eq} + 2m^2) \\ V_{ij}^{Cx}(\infty) &= \lim_{t-t_w \rightarrow \infty} V_{ij}^{Cx}(t - t_w) = -m^2 C_{ij,eq} \\ \mathcal{V}_{ij}^x(\infty) &= \lim_{t-t_w \rightarrow \infty} \mathcal{V}_{ij}^x(t - t_w) = -C_{ij,eq}^2, \end{aligned} \quad (21)$$

where m is the equilibrium magnetization and $C_{ij,eq} \equiv \langle \sigma_i \sigma_j \rangle_{eq} - m^2$ is the static correlation function.

For the $k = 0$ components, from equations (21) for $T \gtrsim T_c$, using the scaling $C_{ij,\text{eq}} \sim |i - j|^{2-d-\eta} f(|i - j|/\xi)$, where ξ is the equilibrium coherence length and $i - j$ the distance between i and j , one has

$$V_{k=0}^C(\infty) = -\mathcal{V}_{k=0}^\chi(\infty) \propto \xi^{\beta_c}, \quad (22)$$

where

$$\beta_c = 4 - d - 2\eta \quad (23)$$

is an exponent related to the critical exponent η , and

$$V_{k=0}^{C\chi}(\infty) = 0, \quad (24)$$

because $m = 0$. For $V_{k=0}^C(\infty)$ and $\mathcal{V}_{k=0}^\chi(\infty)$ the same result holds true also below (but close to) T_c , since the terms containing the magnetization in equations (21) can be neglected. Interestingly, the behavior of $V_{k=0}^{C\chi}(\infty)$, on the other hand, is discontinuous around the critical temperature: it vanishes identically for $T > T_c$ while it diverges as $-(T_c - T)^{2\beta-\gamma}$ (where $\gamma = (2 - \eta)\nu$ and β are the usual critical exponents) on approaching T_c from below.

4.1.2. Scaling behavior. We turn now to the point that we are mainly interested in, namely the scaling behavior of V^C , $V^{C\chi}$ and \mathcal{V}^χ . To simplify the notation let us introduce the symbol V^X , with $X = C$, $X = C\chi$, and $X = \chi$, to denote V^C , $V^{C\chi}$ and \mathcal{V}^χ , respectively. Approaching the critical temperature the coherence length diverges and hence a finite-size scaling analysis of the numerical data will be necessary in section 4.1.3. Let us discuss here how such an analysis can be performed. For a finite system of linear size \mathcal{L} we expect a scaling form

$$V_{k=0}^X(t - t_w) = \mathcal{L}^{\beta_X} f_X \left(\frac{t - t_w - t_0}{\mathcal{L}^{z_c}}, \frac{\xi}{\mathcal{L}} \right) \quad (25)$$

where t_0 is a microscopic time, z_c is the dynamic critical exponent, and $f_X(x, y)$ a scaling function (in the following, in order to simplify the notation, we will always denote scaling functions with an f , even if, in different cases, they may have different functional forms). Away from the critical point, matching the large $t - t_w$ behavior of equation (25) with the large time difference limits V_∞^C , \mathcal{V}_∞^χ of equation (22) implies $f_C(x, y) \sim f_\chi(x, y) \sim \xi^{\beta_c}/\mathcal{L}^{\beta_X}$. Since only the ratio ξ/\mathcal{L} must enter f_X this fixes the exponents $\beta_C = \beta_\chi = \beta_c$. Finally, equation (20) implies that also $\beta_{C\chi}$ takes the same value and, in conclusion,

$$\beta_X \equiv \beta_c \quad (26)$$

for all the quantities. Letting $\mathcal{L}^{z_c} = (t - t_w - t_0)$ in equation (25) implies

$$V_{k=0}^X(t - t_w) = (t - t_w - t_0)^{b_c} f_X \left(\frac{t - t_w - t_0}{\xi^{z_c}} \right), \quad (27)$$

where $f_X[(t - t_w - t_0)/\xi^{z_c}]$ is shorthand for $f_X[1, (t - t_w - t_0)/\xi^{z_c}]$, and $b_c = \beta_c/z_c$. Assuming that there is no dependence on ξ for small time differences $t - t_w$ leads to $f_X(x) \sim \text{const}$ in this regime. This implies

$$V_{k=0}^X(t - t_w) \sim (t - t_w - t_0)^{b_c} \quad (28)$$

for $(t - t_w - t_0) \ll \xi^{z_c}$.

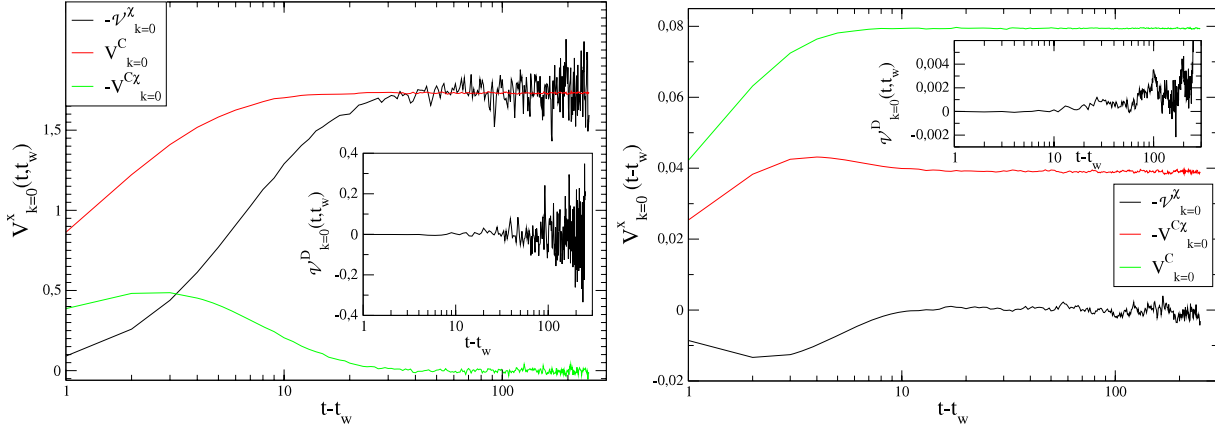


Figure 1. $V_{k=0}^C(t - t_w)$, $-V_{k=0}^X(t - t_w)$ and $-V_{k=0}^{Cx}(t - t_w)$ are plotted against $t - t_w$ in equilibrium conditions at $T = 3.5 > T_c$ (left panel) where $\xi \simeq 1.98$ and at $T = 1.5 < T_c$ (right panel) where $\xi \simeq 0.88$. In the insets $V_{k=0}^D(t, t_w)$ is plotted against $t - t_w$. The system size is $\mathcal{L} = 10^3$ and $l = 10^2$.

4.1.3. Numerical studies. In this section we study numerically the equilibrium behavior of the two-dimensional Ising model, where $z_c \simeq 2.16$ and $b_c \simeq 0.69$, and check the scaling laws derived above.

Before presenting the results let us comment on the method used to compute the $k = 0$ components. For $T \neq T_c$, for any t and t_w , $V_{ij}^X(t - t_w)$ decays over a distance $i - j$ at most of order of ξ . Then, performing the sum in equation (8) over the whole system one introduces a number of order $[(\mathcal{L} - \xi)/\xi]^d$ of terms whose average value is negligible. However, due to the limited statistics of the simulations, such terms are not efficiently averaged and introduce noisy contributions which, with the definition (8), sum up to produce an overall noise of order $[(\mathcal{L} - \xi)/\xi]^{d/2}$. For \mathcal{L} much larger than ξ this quantity is large and lowers the numerical accuracy. Therefore, since one knows that the average of that noise is zero, the most efficient way of computing $V_{k=0}^X$ is to sum only up to distances $i - j = l \gtrsim \xi$. We have checked that the two procedures (namely summing over all the sites i, j of the system or restricting to those with $i - j \leq l$) give the same results within the numerical uncertainty. We anticipate that in the study of non-equilibrium after a quench below T_c presented in section 4.2.2, similar considerations apply with ξ replaced with $L(t)$, the typical size of domains. Clearly, at T_c where $\xi = \infty$ such a procedure cannot be applied and the sum must be performed over the whole system.

Starting from the case $T > T_c$, in the left part of figure 1 we plot V^C , V^{Cx} and V^X as functions of $t - t_w$. $V_{k=0}^C$ and $-V_{k=0}^X$ grow monotonically to the same limit (22), while $V_{k=0}^{Cx}$ has a non-monotonic behavior vanishing for large time differences. In the inset, by plotting $V_{k=0}^D(t, t_w)$ (we recall that $V_{k=0}^C(t, t) \equiv 0$ for Ising spins) we confirm the SOFDT (20).

In the case of quenches below T_c (right part of figure 1), we obtained the broken symmetry equilibrium state by preparing an ordered state (i.e. all spins up) and then letting it relax at the working temperature to the stationary state. In this case the behavior of V^C , V^{Cx} and V^X is similar to the case for $T > T_c$, with the difference that also $V_{k=0}^X$ has a non-monotonic behavior. We have checked that for temperatures close to

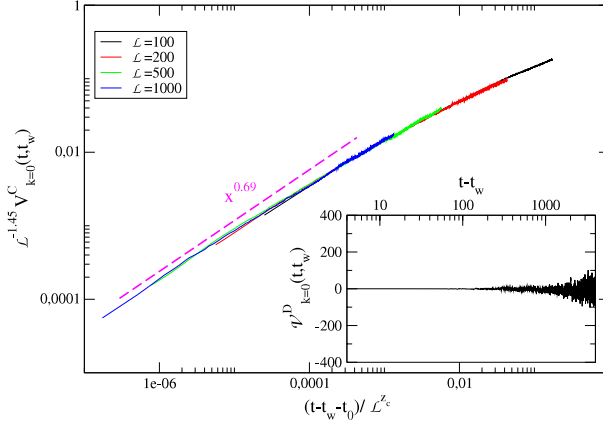


Figure 2. $\mathcal{L}^{-1.45} V_{k=0}^C(t - t_w)$ is plotted against $(t - t_w - t_0)/\mathcal{L}^{z_c}$ (with $t_0 = 0.475$), in equilibrium conditions at T_c for different values of \mathcal{L} . The dashed line is the expected power-law behavior $[(t - t_w - t_0)/\mathcal{L}^{z_c}]^{b_c}$ ($b_c = 0.69$). In the inset $\mathcal{V}_{k=0}^D(t, t_w)$ is plotted against $t - t_w$ for $\mathcal{L} = 10^3$.

T_c , both above and below T_c (i.e. for $T = 2.28$ and $T = 2.25$), V^C , $V^{C,\chi}$ and \mathcal{V}^χ grow as $(t - t_w - t_0)^{b_\chi}$ with b_χ consistent with the expected value b_c , as expressed in equation (28).

In order to study the critical behavior we have equilibrated the system at T_c using the Wolff cluster algorithm [31]. In figure 2 we present a finite-size scaling analysis of the data. In view of equation (25) we plot $\mathcal{L}^{-1.45} V_{k=0}^C$ for different \mathcal{L} against $(t - t_w - t_0)/\mathcal{L}^{z_c}$, where $t_0 = 0.475$ and the exponent 1.45 (in good agreement with the expected value $\beta_c = 1.5$) have been obtained by requiring the best data collapse. All the data exhibit a nice collapse on a unique master curve. The master curve grows initially as a power law with an exponent 0.69 in good agreement with b_c , as expected from equation (28), and then tends toward saturation for $t - t_w + t_0 \gg \mathcal{L}^{z_c}$. A similar behavior is observed for the other V^C , $V^{C\chi}$, apart from the sign, since $\mathcal{V}_{k=0}^\chi$ and $V_{k=0}^{C\chi}$ are negative for large $t - t_w$.

4.2. Non-equilibrium

4.2.1. The critical quench. In this section we consider a ferromagnetic system quenched from an equilibrium state at infinite temperature to T_c . Numerical results are presented for $d = 2$. For $d = 3$ the situation is qualitatively similar although our data are too noisy for extracting precise quantitative information. With $T = T_c$ we expect a scaling form as in equation (25) where the role played by \mathcal{L} is now assumed by $L(t_w) \sim t_w^{1/z_c}$. Letting $t - t_w \gg t_0$, one has

$$V_{k=0}^X(t, t_w) \simeq t_w^{b_c} f_X\left(\frac{t}{t_w}\right), \quad (29)$$

where $f_X(t/t_w)$ is shorthand for $f_X(t/t_w, \infty)$, and the short time behavior (28). Notice that this scaling, like the equilibrium one (27), is consistent with the results of [22] where the same forms are obtained with $b_c = (4 - d - 2\eta)/z_c = (4 - d)/2$, since in the spherical model $\eta = 0$ and $z_c = 2$.

The behavior of V^C , $V^{C,\chi}$ and \mathcal{V}^χ is shown in figure 3. By plotting $t_w^{-0.66} V_{k=0}^X(t, t_w)$ versus $(t - t_w)/t_w$ one observes a good collapse of the curves for $(t - t_w)/t_w$ sufficiently

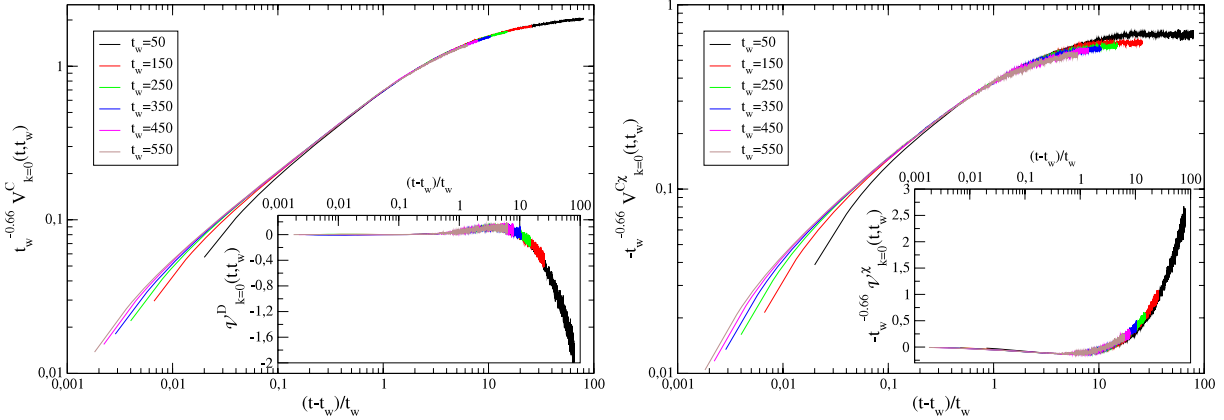


Figure 3. $t_w^{-0.66} V_{k=0}^C(t-t_w)$ (left panel, log-log scale), $-t_w^{-0.66} V_{k=0}^{C\chi}(t-t_w)$ (right panel, log-log scale) and $-t_w^{-0.66} \mathcal{V}_{k=0}^\chi(t-t_w)$ (inset of the right panel, log-linear scale) are plotted against $(t-t_w)/t_w$ for a quench to T_c for $d = 2$. In the inset of the left panel $\mathcal{V}_{k=0}^D(t, t_w)$ is plotted against $(t-t_w)/t_w$.

large. Lack of collapse for $t-t_w \lesssim t_0$ is expected due to the t_0 dependence in the scaling form (25) and those derived from it. The exponent 0.66 is in good agreement with the expected one $b_c \simeq 0.69$, and this confirms that the scaling (29) is obeyed. In the short time difference regime, for $t-t_w \ll t_w$, these quantities behave as in equilibrium, and in particular the relation (20) is obeyed, as is shown in the inset of the left panel of figure 3. For $t-t_w \gtrsim t_w$ the relation (20) breaks down and the asymptotic regime is entered. In this time domain V^C and $V^{C\chi}$ approach constant values in the large t limit. For $V_{k=0}^C$ this can be understood as follows: writing the sum (8) as an integral

$$V_{k=0}^C(t, t_w) = \int d\mathbf{r} V^C(r, t, t_w) \quad (30)$$

where $r = |i-j|$, and invoking the clustering property, by factorizing $V^C(r, t, t_w)$ for $t \rightarrow \infty$, one has

$$V_{k=0}^C(t, t_w) \simeq \int d\mathbf{r} C_r(t_w) C_r(t). \quad (31)$$

Using the scaling of the correlation function $C_r(t) = t^{-(d-2+\eta)/z_c} f(r/t^{1/z_c})$, with the small x behavior $f(x) \sim x^{-(d-2+\eta)}$, equation (31) becomes

$$\lim_{t \rightarrow \infty} V_{k=0}^C(t, t_w) = c t_w^{b_c} \quad (32)$$

with $c = \int d^d x x^{-(d-2+\eta)} f(x)$. Notice that the asymptotic values (32) approached by $V_{k=0}^C$ (and $V_{k=0}^{C\chi}$) are increasing functions of t_w . This mechanism makes $\lim_{t_w \rightarrow \infty} \lim_{t \rightarrow \infty} V_{k=0}^C(t, t_w) = \infty$, and in this sense the limit (22) is recovered, bearing in mind that $\xi = \infty$. Moreover, $\lim_{t_w \rightarrow \infty} \lim_{t \rightarrow \infty} V_{k=0}^{C\chi}(t, t_w)/V_{k=0}^C(t, t_w)$ is a t_w independent constant as was found in [21]. We also observe that $V_{k=0}^{C\chi}$ going to a constant value is a different behavior with respect to the spherical model [22], where this quantity vanishes for $t \rightarrow \infty$. The quantity $\mathcal{V}_{k=0}^\chi$ has a different behavior, in that it diverges for $t \rightarrow \infty$ for any value of t_w . Therefore, at variance with the case for $V_{k=0}^C$ and $V_{k=0}^{C\chi}$, the limit (22) is always

recovered, irrespectively of t_w . This is a general property of susceptibilities. Considering the linear case for simplicity, from equation (A.2) one sees that χ_i can be written as an average of a one-time quantity over a process where the Hamiltonian is changed at t_w . Since the average of a one-time quantity must tend to its (perturbed) equilibrium value for large t (even if the Hamiltonian has been modified at t_w), this explains why $\lim_{t \rightarrow \infty} \chi_i(t, t_w)$ is independent of t_w . An analogous argument holds for \mathcal{V}_{ij}^X . Indeed, recalling equations (A.4) and (A.14), for $i \neq j$ also this quantity can be written as an average of a one-time quantity. The same property holds for the equal site contribution since, according to equation (14), it is $\mathcal{V}_{ii}^X(t, t_w) = -\chi_i^2(t, t_w)$. The limit (22) is then satisfied irrespectively of t_w .

4.2.2. The quench below T_c . In this section we consider a ferromagnetic system quenched from an equilibrium state at infinite temperature to $T < T_c$, for $d = 1, 2$.

Let us recall the behavior of C and χ in a quench from $T = \infty$ to $T < T_c$. In the large t_w limit C obeys the following additive structure [32]:

$$C(t, t_w) \simeq C_{\text{st}}(t - t_w) + C_{\text{ag}}(t, t_w). \quad (33)$$

Here C_{st} is the contribution provided by bulk spins which are in local equilibrium. This term vanishes for quenches to $T = 0$. $C_{\text{ag}}(t, t_w)$ is the ageing contribution originated by the presence of interfaces which scales as

$$C_{\text{ag}}(t, t_w) = t_w^{-b} f\left(\frac{t}{t_w}\right), \quad (34)$$

with $b = 0$ and the property [5]

$$f(x) \sim x^{-\lambda} \quad (35)$$

for large x , where λ is related to the Fisher–Huse exponent.

A decomposition analogous to equation (33) holds for $\chi(t, t_w)$, with $\chi_{\text{st}}(t - t_w) = \chi_{\text{eq}}(t - t_w) = C_{\text{eq}}(t, t) - C_{\text{eq}}(t, t_w)$ and

$$\chi_{\text{ag}}(t, t_w) = t_w^{-a} g\left(\frac{t}{t_w}\right), \quad (36)$$

with g behaving as [5]

$$g(x) \sim x^{-a} \quad (37)$$

for large x . The exponent a depends on the spatial dimensionality such that $a > 0$ for $d > d_1$, d_1 being the lower critical dimensionality, and $a = 0$ for quenches at $d = d_1$ with $T = 0$ [5, 8, 10, 33]. Notice that, at variance with the critical quench case, the non-equilibrium exponents are not related to the equilibrium ones, since the additive form (33) splits them into separate terms.

The additive structure (33), which is expected also for the V^X , opens the problem of disentangling the stationary from the ageing contributions to allow the separate analysis of their scaling properties. In order to do this one usually enforces the knowledge of the time sectors where the stationary and the ageing terms contribute significantly. Specifically, working in the short time difference regime, namely with $t_w \rightarrow \infty$ and $t - t_w$ finite, the ageing term is constant and one can study the behavior of the stationary one. In

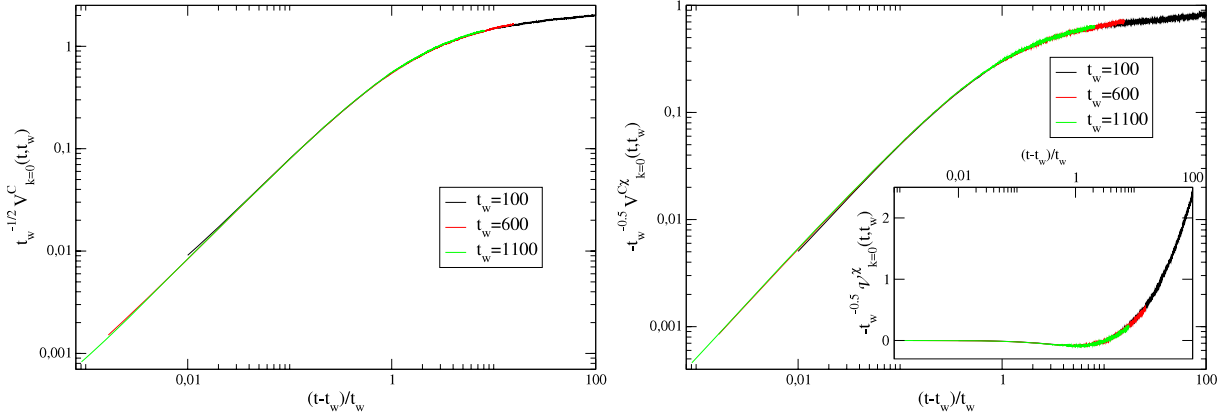


Figure 4. $t_w^{-1/2} V_{k=0}^C(t - t_w)$ (left panel, log-log scale), $-t_w^{-1/2} V_{k=0}^{C\chi}(t - t_w)$ (right panel, log-log scale) and $-t_w^{-1/2} \eta_{k=0}^\chi(t - t_w)$ (inset of the right panel, log-linear scale) are plotted against $(t - t_w)/t_w$ for different values of t_w in the key in a quench to $T = 0$ for $d = 1$.

contrast, in the ageing regime with $t_w \rightarrow \infty$ and t/t_w finite, $C_{\text{st}}(t - t_w) \simeq 0$ and one has direct access to C_{ag} . The same procedure can be applied to isolate the stationary and ageing contributions to the V^X , as will be done in section 4.2.2. However, in so doing one effectively separates the two contributions only in the limit $t_w \rightarrow \infty$. In numerical simulations, where finite values of t_w are used, a certain mixing of the two is unavoidable and may affect the results. Furthermore, this technique fails in systems where (in contrast to the ferromagnetic model case considered here) we do not have a precise knowledge of the time sectors where stationary and ageing terms contribute.

For the V^X a more elegant and effective technique for isolating the ageing from the stationary terms relies on the SOFDT. Indeed, according to equation (18), an exact cancelation occurs in \mathcal{V}^D between the stationary (equilibrium) terms, so only the ageing behavior is reflected by \mathcal{V}^D . In other words, recalling the discussion at the end of section 3.1, the quantity \hat{D} does not produce any correlation in equilibrium and hence what is left in \mathcal{V}^D is the correlation due to ageing. This fact will be enforced in section 4.2.2.

Let us now consider the behavior of V^C , $V^{C,\chi}$ and \mathcal{V}^χ for $d = 1, 2$.

$d = 1$, quenching to $T = 0$

As explained in [5] the dynamical features of a system at the lower critical dimension quenched to $T = 0$ are those of a quench into the ordered region, rather than those of a critical quench, due to a non-vanishing Edwards–Anderson order parameter $q_{\text{EA}} = \lim_{t \rightarrow \infty} \lim_{t_w \rightarrow \infty} C(t, t_w)$. Since at $T = 0$ there are no stationary contributions we expect $V_{k=0}^X(t, t_w) = V_{k=0, \text{ag}}^X(t, t_w)$, with the scaling

$$V_{k=0, \text{ag}}^X(t, t_w) = t_w^{a_X} f_X \left(\frac{t}{t_w} \right). \quad (38)$$

The behavior of these quantities is shown in figure 4. By plotting $t_w^{-1/2} V^X(t, t_w)$ versus t/t_w one observes an excellent collapse of the curves (tiny deviations from the master curve for small values of $t - t_w$ are due to the t_0 dependence, as discussed above). This

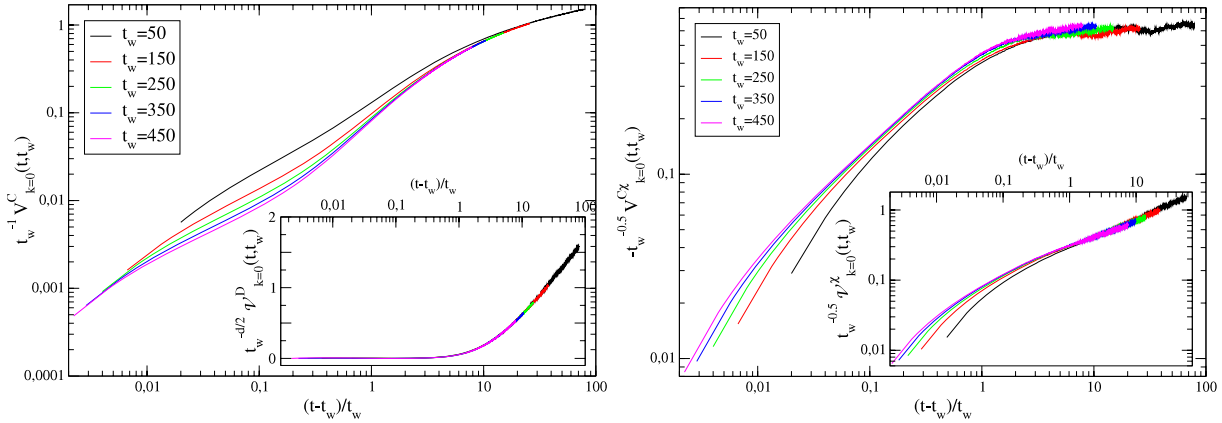


Figure 5. $t_w^{-1} V_{k=0}^C(t - t_w)$ (left panel), $-t_w^{-1/2} V_{k=0}^{C\chi}(t - t_w)$ (right panel) and $t_w^{-1/2} \mathcal{V}_{k=0}^\chi(t - t_w)$ (inset of the right panel) are plotted against $(t - t_w)/t_w$ for different values of t_w in the key in a quench to $T = 1.5$ for $d = 2$. In the inset of the left panel $\mathcal{V}_{k=0}^D(t, t_w)$ is plotted against $(t - t_w)/t_w$.

implies that equation (38) is obeyed with $a_\chi = 1/2$. Notice that, for large values of t/t_w , V^C and $V^{C\chi}$ seem to approach constant values whereas $\mathcal{V}_{k=0}^\chi$ grows as $\mathcal{V}^\chi \propto t^{1/2}$. Then one has the limiting behavior $f_X(x) \sim x^{\lambda_X}$, with values of the exponents consistent with $\lambda_C = \lambda_{C\chi} = 0$ and $\lambda_\chi = 1/2$.

$d = 2$, quenching to $0 < T < T_c$

In this case we consider quenches to finite temperatures, and hence stationary contributions are present. We expect that one can select between the stationary and the ageing contributions to $V^X(t, t_w)$ by considering the short time limit and the ageing regimes separately. In the former case, only the stationary terms contribute and then we expect the relation (20) to be obeyed. This is shown in the inset of the left panel of figure 5 where the relation (20) is observed to hold for $t - t_w \lesssim t_w$. For the ageing regime one selects the ageing contribution scaling as in equation (38). Indeed, on plotting, in figure 5, $t_w^{-a_\chi} V^X(t, t_w)$ versus $(t - t_w)/t_w$ one observes an asymptotic collapse of the curves with $a_C = 1$ and $a_{C\chi} = a_\chi = 1/2$. A residual t_w dependence can be observed (particularly for V^C) that tends to reduce on increasing t_w . This suggests interpreting this correction as being produced by the stationary contributions which, due to the limited values of t_w used in the simulations, are not yet completely negligible. A clear confirmation of this interpretation comes from the inspection of the behavior of $V_{k=0}^D$ in the inset of the left panel of figure 5. Indeed one observes that, at variance with $V_{k=0}^C$, this quantity exhibits an excellent scaling for every value of t_w , due to the fact that the stationary contributions do not contribute to $V_{k=0}^D$. This suggests the use of $V_{k=0}^D$ to study ageing behaviors in more complex non-equilibrium systems, such as spin glasses, where the nature of the stationary contribution has not yet been clarified.

The results for V^C for $d = 1$ and 2 suggest that the scaling exponent depends on the space dimension as $a_C = d/2$. This can be understood on the basis of an argument which, for simplicity, is presented below for the case $d = 1$. Let us consider an interface I at position $x_I(t_w)$ at time t_w . Suppose that at time t , I has moved to a new position

$x_I(t) > x_I(t_w)$. To start with, let us suppose that I is the only interface present in the system and that $t - t_w \ll t_w$. Let us indicate by \mathcal{R}_I the region where $\hat{C}_i(t, t_w) = -1$ (in the present case the region $x(t_w) < i < x(t)$ swept out by the interface). Since V_{ij}^C is the correlation function of the C_i s and the quench is effectively made to below T_c , $V_{k=0}^C$ is proportional to the volume $V(\mathcal{R}_I) = x_I(t) - x_I(t_w)$ of the region \mathcal{R}_I . For $t - t_w \ll t_w$ interfaces can be considered as yielding independent contributions and the above argument can be extended to the physical case with many interfaces. In doing that one simply has to replace $V(\mathcal{R}_I)$ with its typical value $V(\mathcal{R})$ obtained by averaging over the behavior of all the interfaces. Since the typical value of $V(\mathcal{R})$ is $L(t) - L(t_w)$ one obtains $V_{k=0}^C(t, t_w) \propto L(t) - L(t_w)$. Repeating the argument for generic d one finds $V_{k=0}^C(t, t_w) \propto L^d(t) - L^d(t_w)$. For $t - t_w \gtrsim t_w$ the situation is more complex because in this time domain another interface J may move into the region swept out by the interface I and one cannot disentangle their contributions. The situation simplifies again in the limit $t - t_w \rightarrow \infty$, because $x_I(t) \gg x_I(t_w)$ (we assume, without loss of generality, that I has moved in the direction of increasing i). In this case, in the region swept out by the interface, the configuration of the system at t_w was characterized by many domains of different sign. For an interface separating positive spins on the left of it from positive ones, $\hat{C}_i(t, t_w)$ is equal to the sign of the domain to which the i th spin belonged at t_w . Then, almost all the contributions to $V_{k=0}^C$ cancel, because of these alternating signs. The only imbalance between positive and negative contributions comes from the region around $x_I(t)$. Indeed, the interface can build up a positive contribution to $V_{k=0}^C$ if it is not centered on the middle of the domain located there at t_w . This contribution is of order $L(t_w)$ ($V(\mathcal{R}) \sim L^d(t_w)$, for generic d) leading to the saturation of $V_{k=0}^C$ to a t_w -dependent value for large t . In conclusion, from the argument above we obtain, in both of the regimes $t - t_w \ll t_w$ and $t - t_w \gg t_w$, a behavior consistent with equation (38) with $a_C = d/2$ and $f_C(x) \simeq (x^{d/2} - 1)$ for $t - t_w \ll t_w$ and $\lim_{x \rightarrow \infty} f_C(x) = \text{const}$. The same result is found for the soluble large N model [20]. Another way to understand the behavior of V^C is the following: factorizing for $t - t_w \rightarrow \infty$ as $V_{k=0}^C = \int d\mathbf{r} \langle \sigma_i(t) \sigma_j(t) \rangle \langle \sigma_i(t_w) \sigma_j(t_w) \rangle$, using the scaling $\langle \sigma_i(t) \sigma_j(t) \rangle = g(r/L(t))$ and performing the integral, one has

$$\int d^d r g(r/L(t)) g(r/L(t_w)) = L(t_w)^d \int d^d x g(xL(t_w)/L(t)) g(x), \quad (39)$$

i.e. $V_{k=0}^C = L(t_w)^d f(t/t_w)$, with $\lim_{t \rightarrow \infty} f(t/t_w) = \text{const}$. This behavior has been derived in the sector of large $t - t_w$ but the scaling (38) implies its general validity. A similar result but for a somewhat different definition of V^C is found in [34]. Going back to the data, the saturation for large t predicted by the above arguments is better observed for $d = 1$ (figure 4) while for $d = 2$, due to computer time limitations, the data of figure 5 only show a tendency.

The data for $V_{k=0, \text{ag}}^{C\chi}(t, t_w)$ and $\mathcal{V}_{k=0, \text{ag}}^\chi(t, t_w)$ collapse with an exponent consistent with $a_{C\chi} = a_\chi = 1/2$. For large values of $(t - t_w)/t_w$, $\mathcal{V}_{k=0}^\chi$ grows as $\mathcal{V}^\chi \propto t^{1/2}$ while $V^{C\chi}$ approaches a constant value, similarly to V^C . In conclusion, our data show that $a_C = d/2$, $a_{C\chi} = a_\chi = 1/2$, and $\lambda_C = \lambda_{C\chi} = 0$, $\lambda_\chi = 1/2$ hold for $d = 1, 2$, suggesting that this might be the generic behavior for all d .⁴

⁴ In order to check this point further we have also computed the V^C , $V^{C,\chi}$ and \mathcal{V}^χ for $d = 3$. Preliminary results seem to substantiate the dependence of the exponents discussed in the text.

4.3. Time reparameterization invariance

In a series of papers [19] it was shown that the action describing the long time slow dynamics of spin glasses is invariant under a reparameterization of time $t \rightarrow h(t)$. Since C and χ have the same scaling dimension, the parametric form $\chi(C)$ is also invariant under time reparameterizations. Elaborating on this, it was claimed that the long time physics of ageing systems is characterized by Goldstone modes in the form of slowly spatially varying reparameterizations $h_r(t)$, like for spin waves in $O(N)$ models. According to this physical interpretation, it was conjectured that fluctuating two-time functions measured locally by spatially averaging over a box of size l centered on \mathbf{r} , i.e. $\hat{C}_r(t, t_w) = \sum_i \hat{C}_i(t, t_w) \theta(l - |i - r|)$ and similarly for $\hat{\chi}_r(t, t_w)$, should fall on the master curve $\chi(C)$ of the average quantities in the asymptotic limit where t and t_w are large. This was checked to be consistent with numerical results for glassy models in [18]. The choice of l should be such that $l \sim R(t)$, where $R(t)$ is the typical length over which the $h_r(t)$ variations occur.

Let us first observe that, with the definitions (8) and the discussion of l at the beginning of section 4.1.3, the variances $V_{k=0}^C$ and $V_{k=0}^X$ considered in this paper coincide with the variances of the fluctuating quantities \hat{C}_r , $\hat{\chi}_r$ introduced above, provided that l is the same in the two cases. Our results for $V_{k=0}^X$, therefore, allow us to comment on this issue. Before doing so, however, let us recall once again that \mathcal{V}^X is not the variance of the fluctuating $\hat{\chi}$. Hence, from the analysis of $\mathcal{V}_{k=0}^X$ one cannot directly infer the properties of $\hat{\chi}$. On the other hand, it is clear that $\hat{\chi}$ cannot fit *a priori* into the time reparameterization invariance scenario, since its variance contains the diverging terms K_i^X or \tilde{K}_i^X of equations (15) and (A.23), according to equations (A.19) and (A.22). Hence, the numerical results contained in [18], which are obtained by switching on the perturbation, can only be consistent with that scenario if a sufficiently large value of the perturbation h is used in the simulations, such that the first contribution on the rhs of equation (A.23) can be neglected.

The results of section 4.2 show that $\lim_{t_w \rightarrow \infty} \lim_{t \rightarrow \infty} \mathcal{V}_{k=0}^X / V_{k=0}^C = \infty$, both in the quench to T_c and below T_c . Since $V^X \geq \mathcal{V}^X$ (see equation (A.19) or (A.22)) this implies that the fluctuations $\hat{\chi}$ and \hat{C} cannot be constrained to follow the $\chi(C)$ curve, at least in this particular order of the large time limits, as already noticed in [21]. Hence the interpretation of [18, 19] cannot be strictly obeyed. This may indicate either that the symmetry $t \rightarrow h(t)$ is not obeyed in coarsening systems, as claimed in [20], or that its physical interpretation misinterprets the effects of time reparameterization invariance in phase-ordering kinetics. Actually, the results of [21] show that at least the limiting slope X_∞ of $\chi(C)$ is encoded in the distribution of \hat{C} and $\hat{\chi}$. Whether this feature might be physically interpreted as a different realization of time reparameterization invariance in a coarsening system is as yet unclear.

5. Conclusions

In this paper we have considered the fluctuations of two-time quantities by studying their variances and the related second-order susceptibility. In doing that a first problem arises already at the level of their definition. While C_i is quite naturally associated with the fluctuating quantity $[\sigma_i(t) - \langle \sigma_i(t) \rangle][\sigma_i(t_w) - \langle \sigma_i(t_w) \rangle]$, for χ_i the situation is not as clear. Actually, referring to the very meaning of a response function the straightforward

way to associate a fluctuation with χ_i would be via the choice of equation (A.3) which is defined for a perturbed process. The quantity $\hat{\chi}_i$ introduced in this way, however, has diverging moments. A way out of this problem is to resort to fluctuation-dissipation theorems. One may enforce a relation between χ_i and the average of a fluctuating quantity $\hat{\chi}_i$, equation (3), which holds also out of equilibrium. We have shown that the variances involving $\hat{\chi}_i$ have a very weak dependence on the particular choice of this fluctuating part, with the exception of the equal sites variance V_{ii}^X . For $i \neq j$, V_{ij}^X is also a second-order susceptibility \mathcal{V}_{ij}^X , which allows one to derive an equilibrium relation between variances, the SOFDT, analogous to the FDT for the averages. Interestingly, the FDT and the SOFDT can be written in a rather similar form, namely equations (10) and (13), expressing the vanishing of the first two moments of the quantity $\hat{D}_i(t, t_w)$ defined in equation (11). The SOFDT holds also for $i = j$ but in this case V_{ii}^X cannot be interpreted as a variance.

The SOFDT relates, in a quite natural way, \mathcal{V}_{ij}^X to V_{ij}^C , promoting the former to a role analogous to that advocated for the latter in the context of disordered systems. This suggests considering \mathcal{V}_{ij}^X on an equal footing with V_{ij}^C and V_{ij}^{CX} , to study scaling behaviors and cooperativity. This we have done in the second part of the paper, considering ferromagnetic systems in and out of equilibrium. We have shown that \mathcal{V}^X , V^C and V^{CX} obey scaling forms involving the coherence length ξ in equilibrium or the growing length $L(t)$ after a quench, similarly to what is known for C and χ . Our results are in good agreement with what is found analytically for the spherical model [22]. They show that the time reparameterization invariance scenario proposed for glassy dynamics does not hold strictly for ferromagnets, as already guessed in [20, 21]. This we find both for critical and for sub-critical quenches, if the large time limit is taken in the order $\lim_{t_w \rightarrow \infty} \lim_{t \rightarrow \infty}$. Such a conclusion relies on the fact that $\mathcal{V}_{k=0}^X / V_{k=0}^C \rightarrow \infty$ in this particular limit and, hence, the fluctuations of $\hat{\chi}$ cannot be exclusively triggered by those of \hat{C} . Notice that this is true also for critical quenches where X_∞ is finite, showing that, quite obviously, a finite limiting effective temperature does not guarantee that the scenario proposed in [18, 19] necessarily holds.

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Appendix A

In this appendix we first discuss a possible definition of the fluctuating part of χ_i in a perturbed process (namely, after equation (2)) and then show that for every choice of $\hat{\chi}_i$ one obtains the same variances except for V_{ii}^X .

A.1. The definition of $\hat{\chi}_i$ in a perturbed process

From equation (2) one has

$$\langle \sigma_i \rangle_h = \langle \sigma_i \rangle + \sum_j \chi_{ij}(t, t_w) h_j(t_w), \quad (\text{A.1})$$

where now we consider a perturbing field switched on from t_w onwards, and χ_{ij} is the two-point susceptibility. Using a random field with $\bar{h}_j = 0$ and $\overline{h_i h_j} = h^2 \delta_{ij}$ (where $\overline{\quad}$ means an average over the field realizations) one can single out the equal site susceptibility as [35]

$$\chi_i(t, t_w) = \frac{1}{h^2} \overline{\langle \sigma_i(t) \rangle_h h_i(t_w)}. \quad (\text{A.2})$$

We stress here that, on doing this, for computing χ_i the perturbation does not need to be switched on only on the site i as in equation (2), and this allows one to consider higher moments, such as the variances V_{ij}^χ , where the field must be switched on on both sites i and j . Indeed one can introduce a (perturbed) fluctuating part of the susceptibility as

$$\hat{\chi}_i(t, t_w) = \frac{1}{h^2} \sigma_i(t) h_i(t_w), \quad (\text{A.3})$$

and the correlator

$$\langle \hat{\chi}_i(t, t_w) \hat{\chi}_j(t, t_w) \rangle = \frac{1}{h^4} \overline{\langle \sigma_i(t) \sigma_j(t) \rangle_h h_i(t_w) h_j(t_w)}. \quad (\text{A.4})$$

A.2. Independence of the variances of the choice of $\hat{\chi}_i$

For the sake of simplicity, let us consider a discrete time dynamics with two-time conditional probability given by

$$P(\sigma, t | \sigma', t_w) = \prod_{t'=t_w}^{t-1} w_h(\sigma(t'+1) | \sigma(t')), \quad (\text{A.5})$$

where $\sigma(t)$ is the configuration of the system at time t and the w_h are the transition rates in the perturbed evolution. The linear susceptibility can always be written in the form

$$\chi_i(t, t_w) = \sum_{t'=t_w}^t \langle \sigma_i(t) a_i(t') \rangle \quad (\text{A.6})$$

with [28]

$$a_i(t') = \left. \frac{\delta \ln w_h(\sigma(t'+1) | \sigma(t'))}{\delta h_i(t')} \right|_{h=0} \quad (\text{A.7})$$

from which the fluctuating susceptibility can be defined in terms of unperturbed quantities as

$$\hat{\chi}_i(t, t_w) = \sigma_i(t) \sum_{t'=t_w}^t a_i(t'). \quad (\text{A.8})$$

Notice that a_i depends on the particular form of the perturbed transition probabilities w_h . Then, since for a given unperturbed model there is an arbitrariness in the choice of the perturbed transition rates [16, 26], one has different definitions of $\hat{\chi}_i$ and, in principle, different χ_i . However, as discussed in [26, 30], once the average is taken in equation (A.6), all of these definitions are expected to yield essentially the same determination of χ_i , apart

from very tiny differences which exactly vanish in equilibrium or in the large time regime. With the definition (A.8) the following correlators can be built:

$$\langle \hat{\chi}_i(t, t_w) \hat{\chi}_j(t, t_w) \rangle = \sum_{t'=t_w}^{t-1} \sum_{t''=t_w}^{t-1} \langle \sigma_i(t) \sigma_j(t) a_i(t') a_j(t'') \rangle, \quad (\text{A.9})$$

and

$$\langle \hat{C}_i(t, t_w) \hat{\chi}_j(t, t_w) \rangle = \sum_{t'=t_w}^{t-1} \langle \sigma_i(t) \sigma_i(t_w) \sigma_j(t) a_j(t') \rangle. \quad (\text{A.10})$$

Even though these quantities explicitly depend on the particular choice of a_i , we show in the following that they can all be written as (non-linear) response functions, which, therefore, are not expected to depend on the form of a_i , in the sense discussed above for χ_i . Indeed, considering for simplicity a single-spin dynamics, using equation (A.5) and proceeding analogously to in the derivation of χ_i (equation (A.6)), for $i \neq j$ one can compute the following response functions:

$$R_{ij;ij}^{(2,2)}(t, t; t', t'') \equiv \left. \frac{\delta^2 \langle \sigma_i(t) \sigma_j(t) \rangle_h}{\delta h_i(t') \delta h_j(t'')} \right|_{h=0} = \langle \sigma_i(t) \sigma_j(t) a_i(t') a_j(t'') \rangle \quad (\text{A.11})$$

and

$$R_{ij;j}^{(3,1)}(t, t_w, t; t') \equiv \left. \frac{\delta \langle \sigma_i(t) \sigma_i(t_w) \sigma_j(t) \rangle_h}{\delta h_j(t')} \right|_{h=0} = \langle \sigma_i(t) \sigma_i(t_w) \sigma_j(t) a_j(t') \rangle. \quad (\text{A.12})$$

Comparing equations (A.9) and (A.10) with equations (A.11) and (A.12) one concludes that the correlators (A.9) and (A.10) can both be related to response functions whose values, as for χ_i , are not expected to depend significantly on the choice of the form of the w_h (and hence of a_i). The same holds, therefore, for the variances $V_{i,j}^X$ and V_{ij}^{CX} . Incidentally, equations (A.9), (A.11) and (16) show also that $V_{ij}^X = \mathcal{V}_{ij}^X$ for $i \neq j$. We stress that the above argument holds for every ij for V_{ij}^{CX} whilst it cannot be extended to the equal site variance V_{ii}^X , as we will show in section A.3. Along the same lines, one can show that also the variances obtained with the perturbed fluctuating part (A.3) are related to the same response functions (A.11) and (A.12), and hence take the same values. For instance, for the correlator (A.4), since

$$\lim_{h \rightarrow 0} \frac{1}{h^4} \overline{\langle \sigma_i(t) \sigma_j(t) \rangle_h h_i(t_w) h_j(t_w)} = \sum_{t_1=t_w}^{t-1} \sum_{t_2=t_w}^{t-1} \left. \frac{\delta^2 \langle \sigma_i(t) \sigma_j(t) \rangle_h}{\delta h_i(t_1) \delta h_j(t_2)} \right|_{h=0} \quad (\text{A.13})$$

one has again

$$\langle \hat{\chi}_i(t, t_w) \hat{\chi}_j(t, t_w) \rangle = \sum_{t_1=t_w}^{t-1} \sum_{t_2=t_w}^{t-1} R_{ij;ij}^{(2,2)}(t, t; t_1, t_2). \quad (\text{A.14})$$

A.3. Equal sites

In order to discuss the behavior of V_{ii}^X we compute explicitly this quantity and \mathcal{V}_{ii}^X making the specific choice of w_h which leads to equation (7). Using the second-order fluctuation-dissipation relations derived in [16], for Ising spins $R_{ij;ij}^{(2,2)}(t, t; t_1, t_2)$ can be rewritten as

$$\begin{aligned} R_{ij;ij}^{(2,2)}(t, t; t_1, t_2) = & \frac{1}{4} \left\{ \frac{\partial}{\partial t_1} \frac{\partial}{\partial t_2} \langle \sigma_i(t) \sigma_j(t) \sigma_i(t_1) \sigma_j(t_2) \rangle - \frac{\partial}{\partial t_1} \langle \sigma_i(t) \sigma_j(t) \sigma_i(t_1) B_j(t_2) \rangle \right. \\ & - \frac{\partial}{\partial t_2} \langle \sigma_i(t) \sigma_j(t) B_i(t_1) \sigma_j(t_2) \rangle + \langle \sigma_i(t) \sigma_j(t) B_i(t_1) B_j(t_2) \rangle \Big\} \\ & + \frac{1}{2} \delta(t_1 - t_2) \delta_{ij} \langle \sigma_i(t)^2 B_i(t_1) \sigma_i(t_1) \rangle. \end{aligned} \quad (\text{A.15})$$

Using the property $\sigma_i^2 = 1$ the term $\langle \sigma_i(t)^2 B_i(t_1) \sigma_i(t_1) \rangle$ can be cast as $\frac{1}{2} \langle \sigma_i(t)^2 \tilde{B}_i(t_1) \rangle$, where $\tilde{B}_i = -\sum_{\sigma'} [\sigma' - \sigma]^2 w(\sigma' | \sigma)$. Writing this term in this form, equation (A.15) holds generally for generic discrete or continuous variables. We will use this expression in the following. Integrating over t_1 and t_2 one obtains

$$\begin{aligned} \mathcal{V}_{ij}^X = & \frac{1}{4} \left\{ \langle \sigma_i(t) \sigma_j(t) [\sigma_i(t) - \sigma_i(t_w)] [\sigma_j(t) - \sigma_j(t_w)] \rangle \right. \\ & - \int_{t_w}^t dt_2 \langle \sigma_i(t) \sigma_j(t) [\sigma_i(t) - \sigma_i(t_w)] B_j(t_2) \rangle \\ & - \int_{t_w}^t dt_1 \langle \sigma_i(t) \sigma_j(t) B_i(t_1) [\sigma_j(t) - \sigma_j(t_w)] \rangle \\ & + \int_{t_w}^t dt_1 \int_{t_w}^t dt_2 \langle \sigma_i(t) \sigma_j(t) B_i(t_1) B_j(t_2) \rangle \Big\} \\ & + \frac{1}{4} \delta_{ij} \int_{t_w}^t dt_1 \langle \sigma_i(t)^2 \tilde{B}_i(t_1) \rangle - \chi_i(t, t_w) \chi_j(t, t_w). \end{aligned} \quad (\text{A.16})$$

On the other hand, from the definitions (7) and (5) one has

$$\begin{aligned} V_{ij}^X(t, t_w) = & \langle \hat{\chi}_i(t, t_w) \hat{\chi}_j(t, t_w) \rangle - \chi_i(t, t_w) \chi_j(t, t_w) \\ = & \frac{1}{4} \left[\langle \sigma_i(t) \sigma_i(t) \sigma_j(t) \sigma_j(t) \rangle - \langle \sigma_i(t) \sigma_i(t) \sigma_j(t) \sigma_j(t_w) \rangle \right. \\ & - \int_{t_w}^t dt_1 \langle \sigma_i(t) \sigma_i(t) \sigma_j(t) B_i(t_1) \rangle - \langle \sigma_i(t) \sigma_j(t) \sigma_j(t) \sigma_i(t_w) \rangle \\ & + \langle \sigma_i(t) \sigma_i(t_w) \sigma_j(t) \sigma_j(t_w) \rangle + \int_{t_w}^t dt_1 \langle \sigma_i(t) \sigma_j(t) B_j(t_1) \sigma_i(t_w) \rangle \\ & - \int_{t_w}^t dt_1 \langle \sigma_i(t) \sigma_j(t) \sigma_j(t) B_i(t_1) \rangle + \int_{t_w}^t dt_1 \langle \sigma_i(t) \sigma_j(t) B_i(t_1) \sigma_j(t_w) \rangle \\ & \left. + \int_{t_w}^t dt_1 \int_{t_w}^t dt_2 \langle \sigma_i(t) \sigma_j(t) B_i(t_1) B_j(t_2) \rangle \right] - \chi_i(t, t_w) \chi_j(t, t_w). \end{aligned} \quad (\text{A.17})$$

This shows once again that in the case $i \neq j$

$$V_{ij}^X(t, t_w) = \mathcal{V}_{ij}^X(t, t_w). \quad (\text{A.18})$$

For equal sites, on the other hand, one obtains from equations (A.16) and (A.17) the following relation:

$$V_{ii}^X(t, t_w) = \mathcal{V}_{ii}^X(t, t_w) + K_i^X(t, t_w) \delta_{ij}, \quad (\text{A.19})$$

where

$$\mathcal{V}_{ij}^X(t, t_w) = -\chi_i^2(t, t_w) - \Delta_i(t, t_w), \quad (\text{A.20})$$

(with Δ_i defined below equation (14)) and

$$K_i^X(t, t_w) = -\frac{1}{4} \int_{t_w}^t dt_1 \langle \sigma_i(t)^2 \tilde{B}_i(t_1) \rangle. \quad (\text{A.21})$$

This quantity has been studied for specific models in [30] and it is found to be positive and to diverge as $t - t_w$ increases. Finally, let us consider the equal site variance V_{ii}^X in the case where the perturbed definition (A.3) is used. By forming products of $\hat{\chi}_i(t, t_w)$ one has

$$V_{ii}^X(t, t_w) = \lim_{h \rightarrow 0} \left\langle \left[\widehat{\delta \chi}_i(t, t_w) \right]^2 \right\rangle = \tilde{K}_i^X, \quad (\text{A.22})$$

with

$$\tilde{K}_i^X(t, t_w) = T^2 \lim_{h \rightarrow 0} h^{-2} - \chi_i^2(t, t_w). \quad (\text{A.23})$$

This term diverges in the vanishing field limit. Since V_{ii}^X is finite, this implies that V_{ii}^X and V_{ii}^{χ} are necessarily different.

In conclusion, with every definition of the fluctuating part the variances and \mathcal{V}_{ij}^X turn out to be the same, with the exception of V_{ii}^X which takes different values.

Appendix B

In this appendix we derive the equilibrium relation (13) among the variances, for $i \neq j$. First, let us write explicitly the variances defined in equations (4) and (6) with the help of equation (7):

$$V_{ij}^C(t, t_w) = \langle \hat{C}_i(t, t_w) \hat{C}_j(t, t_w) \rangle - C_i(t, t_w) C_j(t, t_w) \quad (\text{B.1})$$

$$\begin{aligned} V_{ij}^{C\chi}(t, t_w) = & \frac{1}{2} \left[\langle \sigma_i(t) \sigma_i(t_w) \sigma_j(t) \sigma_j(t_w) \rangle - \langle \sigma_i(t) \sigma_i(t_w) \sigma_j(t) \sigma_j(t_w) \rangle \right. \\ & \left. - \int_{t_w}^t dt_1 \langle \sigma_i(t) \sigma_j(t) B_j(t_1) \sigma_i(t_w) \rangle \right] - \langle \sigma_i(t) \rangle \langle \sigma_i(t_w) \rangle \chi_j(t, t_w) \\ & - C_i(t, t_w) \chi_j(t, t_w). \end{aligned} \quad (\text{B.2})$$

The variance V^X can be read from equation (A.17).

In the following, we will use two properties involving the quantity B_i [16, 26, 36]:

$$\langle B_i(t)\mathcal{O}(t_1) \rangle = \frac{\partial}{\partial t} \langle \sigma_i(t)\mathcal{O}(t_1) \rangle \quad t > t_1, \quad (\text{B.3})$$

$$\langle [B_i(t)\sigma_j(t) + B_j(t)\sigma_i(t)]\mathcal{O}(t_1) \rangle = \frac{\partial}{\partial t} \langle \sigma_i(t)\sigma_j(t)\mathcal{O}(t_1) \rangle \quad t > t_1, \quad (\text{B.4})$$

where $\mathcal{O}(t)$ is a generic observable. In particular, at equilibrium, using time translation and time inversion invariance, from equation (B.3) one has

$$\langle \mathcal{O}(t)B_i(t_1) \rangle_{\text{eq}} = -\frac{\partial}{\partial t_1} \langle \mathcal{O}(t)\sigma_i(t_1) \rangle_{\text{eq}} \quad t > t_1, \quad (\text{B.5})$$

where we have introduced the notation $\langle \cdots \rangle_{\text{eq}}$ to indicate the equilibrium dynamics. This relation allows us to perform the integrals $\int_{t_w}^t dt_1 \langle \sigma_i(t)\sigma_i(t)\sigma_j(t)B_i(t_1) \rangle$ and $\int_{t_w}^t dt_1 \langle \sigma_i(t)\sigma_j(t)\sigma_j(t)B_i(t_1) \rangle$ appearing in equation (A.17). This yields

$$\begin{aligned} V_{ij}^X(t, t_w) = & \frac{1}{4} \left[3\langle \sigma_i(t)\sigma_i(t)\sigma_j(t)\sigma_j(t) \rangle_{\text{eq}} - 2\langle \sigma_i(t)\sigma_i(t)\sigma_j(t)\sigma_j(t_w) \rangle_{\text{eq}} \right. \\ & - 2\langle \sigma_i(t)\sigma_j(t)\sigma_j(t)\sigma_i(t_w) \rangle_{\text{eq}} + \langle \sigma_i(t)\sigma_i(t_w)\sigma_j(t)\sigma_j(t_w) \rangle_{\text{eq}} \\ & + \int_{t_w}^t dt_1 \langle \sigma_i(t)\sigma_j(t)B_j(t_1)\sigma_i(t_w) \rangle_{\text{eq}} + \int_{t_w}^t dt_1 \langle \sigma_i(t)\sigma_j(t)B_i(t_1)\sigma_j(t_w) \rangle_{\text{eq}} \\ & \left. + \int_{t_w}^t dt_1 \int_{t_w}^t dt_2 \langle \sigma_i(t)\sigma_j(t)B_i(t_1)B_j(t_2) \rangle_{\text{eq}} \right] - \chi_i(t, t_w)\chi_j(t, t_w). \end{aligned} \quad (\text{B.6})$$

Moreover, exploiting again the relation (B.5), the double integral appearing in equation (B.6) can be rewritten as

$$\begin{aligned} & \int_{t_w}^t dt_1 \int_{t_w}^t dt_2 \langle \sigma_i(t)\sigma_j(t)B_i(t_1)B_j(t_2) \rangle_{\text{eq}} \\ &= \int_{t_w}^t dt_1 \int_{t_w}^{t_1} dt_2 \left(-\frac{\partial}{\partial t_2} \right) \langle \sigma_i(t)\sigma_j(t)B_i(t_1)\sigma_j(t_2) \rangle_{\text{eq}} \\ &+ \int_{t_w}^t dt_2 \int_{t_w}^{t_2} dt_1 \left(-\frac{\partial}{\partial t_1} \right) \langle \sigma_i(t)\sigma_j(t)B_j(t_2)\sigma_i(t_1) \rangle_{\text{eq}} \\ &= -\int_{t_w}^t dt_1 \langle \sigma_i(t)\sigma_j(t)B_i(t_1)\sigma_j(t_1) \rangle_{\text{eq}} + \int_{t_w}^t dt_1 \langle \sigma_i(t)\sigma_j(t)B_i(t_1)\sigma_j(t_w) \rangle_{\text{eq}} \\ &- \int_{t_w}^t dt_2 \langle \sigma_i(t)\sigma_j(t)B_j(t_2)\sigma_i(t_2) \rangle_{\text{eq}} + \int_{t_w}^t dt_2 \langle \sigma_i(t)\sigma_j(t)B_j(t_2)\sigma_i(t_w) \rangle_{\text{eq}} \\ &= \int_{t_w}^t dt_1 \langle \sigma_i(t)\sigma_j(t)B_i(t_1)\sigma_j(t_w) \rangle_{\text{eq}} + \int_{t_w}^t dt_1 \langle \sigma_i(t)\sigma_j(t)B_j(t_1)\sigma_i(t_w) \rangle_{\text{eq}} \\ &+ \int_{t_w}^t dt_1 \frac{\partial}{\partial t_1} \langle \sigma_i(t)\sigma_j(t)\sigma_j(t_1)\sigma_i(t_1) \rangle_{\text{eq}} \\ &= \int_{t_w}^t dt_1 \langle \sigma_i(t)\sigma_j(t)B_i(t_1)\sigma_j(t_w) \rangle_{\text{eq}} + \int_{t_w}^t dt_1 \langle \sigma_i(t)\sigma_j(t)B_j(t_1)\sigma_i(t_w) \rangle_{\text{eq}} \\ &+ \langle \sigma_i(t)\sigma_i(t)\sigma_j(t)\sigma_j(t) \rangle_{\text{eq}} - \langle \sigma_i(t)\sigma_j(t)\sigma_i(t_w)\sigma_j(t_w) \rangle_{\text{eq}}, \end{aligned} \quad (\text{B.7})$$

where we have used the relation (B.4) to obtain the third equality. Substituting this result into equation (B.6), one finally obtains

$$\begin{aligned} V_{ij}^{\chi}(t, t_w) = \frac{1}{4} & \left[4 \langle \sigma_i(t) \sigma_i(t) \sigma_j(t) \sigma_j(t) \rangle_{\text{eq}} - 2 \langle \sigma_i(t) \sigma_i(t) \sigma_j(t) \sigma_j(t_w) \rangle_{\text{eq}} \right. \\ & - 2 \langle \sigma_j(t) \sigma_j(t) \sigma_i(t) \sigma_i(t_w) \rangle_{\text{eq}} + 2 \int_{t_w}^t dt_1 \langle \sigma_i(t) \sigma_j(t) B_j(t_1) \sigma_i(t_w) \rangle_{\text{eq}} \\ & \left. + 2 \int_{t_w}^t dt_1 \langle \sigma_i(t) \sigma_j(t) B_i(t_1) \sigma_j(t_w) \rangle_{\text{eq}} \right] - \chi_i(t, t_w) \chi_j(t, t_w). \end{aligned} \quad (\text{B.8})$$

Now, using the FDT $\chi_i(t, t_w) = C_i(t, t) - C_i(t, t_w)$ and assuming space translation invariance $C_i(t, t_w) = C_j(t, t_w)$ and $\langle \sigma_i(t) \sigma_j(t) B_j(t_1) \sigma_i(t_w) \rangle_{\text{eq}} = \langle \sigma_i(t) \sigma_j(t) B_i(t_1) \sigma_j(t_w) \rangle_{\text{eq}}$, from equations (B.1), (B.2) and (B.8) one obtains

$$V_{ij}^C(t, t_w) + 2V_{ij}^{C\chi}(t, t_w) + V_{ij}^{\chi}(t, t_w) = \langle \hat{C}_i(t, t) \hat{C}_j(t, t) \rangle_{\text{eq}} - C_i(t, t) C_j(t, t), \quad (\text{B.9})$$

which is the equilibrium relation (13).

Appendix C

In this appendix we show that the quantity $\mathcal{V}_{ij}^{\chi}(t, t_w)$ at equal sites verifies the relation (18). In the case of Ising spins, since $R_{ij;ij}^{(2,2)}$ vanishes for $i = j$ by definition, one immediately obtains $\mathcal{V}_{ii}^{\chi} = -\chi_i^2$, and, using the definitions (B.1) and (B.2) and the property $\sigma(t)^2 \equiv 1$, one can easily check that equation (18) holds. In the case of continuous variables, in equilibrium, using the property (B.5), from equation (A.16) one has

$$\begin{aligned} \mathcal{V}_{ii}^{\chi}(t, t_w) = \frac{1}{4} & \left\{ 3 \langle \sigma_i(t)^4 \rangle_{\text{eq}} + \langle \sigma_i(t)^2 \sigma_i(t_w)^2 \rangle_{\text{eq}} - 4 \langle \sigma_i(t)^3 \sigma_i(t_w) \rangle_{\text{eq}} \right. \\ & + 4 \int_{t_w}^t dt_1 \langle \sigma_i(t)^2 B_i(t_1) \sigma_i(t_w) \rangle_{\text{eq}} - 2 \int_{t_w}^t dt_1 \langle \sigma_i(t)^2 B_i(t_1) \sigma_i(t_1) \rangle_{\text{eq}} \\ & \left. + \int_{t_w}^t dt_1 \langle \sigma_i(t)^2 \tilde{B}_i(t_1) \rangle_{\text{eq}} \right\} - \chi_i(t, t_w)^2. \end{aligned} \quad (\text{C.1})$$

The quantities appearing in the last two terms in the braces at time t_1 can be rewritten as

$$\begin{aligned} -2B_i \sigma_i + \tilde{B}_i &= -2 \sum_{\sigma'} [\sigma'_i - \sigma_i] \sigma'_i w(\sigma' | \sigma) + \sum_{\sigma'} [\sigma'^2_i + \sigma_i^2 - 2\sigma'_i \sigma_i] w(\sigma' | \sigma) \\ &= \sum_{\sigma'} [-\sigma'^2_i + \sigma_i^2] w(\sigma' | \sigma) \end{aligned} \quad (\text{C.2})$$

yielding

$$\begin{aligned} \int_{t_w}^t dt_1 \langle \sigma_i(t)^2 [-2B_i(t_1) \sigma_i(t_1) + \tilde{B}_i(t_1)] \rangle_{\text{eq}} &= \int_{t_w}^t dt_1 \frac{\partial}{\partial t_1} \langle \sigma_i(t)^2 \sigma_i(t_1)^2 \rangle_{\text{eq}} \\ &= \langle \sigma_i(t)^4 \rangle_{\text{eq}} - \langle \sigma_i(t)^2 \sigma_i(t_w)^2 \rangle_{\text{eq}}. \end{aligned} \quad (\text{C.3})$$

Substituting this result into equation (C.1), one finds

$$\mathcal{V}_{ii}^x(t, t_w) = \langle \sigma_i(t)^4 \rangle_{\text{eq}} - \langle \sigma_i(t)^3 \sigma_i(t_w) \rangle_{\text{eq}} + \int_{t_w}^t dt_1 \langle \sigma_i(t)^2 B_i(t_1) \sigma_i(t_w) \rangle_{\text{eq}} - \chi_i(t, t_w)^2 \quad (\text{C.4})$$

which coincides with equation (18), as can easily be checked recalling the definitions (B.1) and (B.2).

Appendix D

In this appendix we compute the large time limit of V^C , $V^{C\chi}$ and \mathcal{V}^x , starting from an equilibrium state ($t_w > t_{\text{eq}}$) and taking the limit $t - t_w \rightarrow \infty$. For the variance of the autocorrelation function one has

$$\begin{aligned} \lim_{t-t_w \rightarrow \infty} V_{ij}^C(t, t_w) &= \lim_{t-t_w \rightarrow \infty} [\langle \hat{C}_i(t, t_w) \hat{C}_j(t, t_w) \rangle_{\text{eq}} - C_i(t - t_w) C_j(t - t_w)] \\ &= C_{ij, \text{eq}} (C_{ij, \text{eq}} + 2m^2), \end{aligned} \quad (\text{D.1})$$

where factorization at large $t - t_w$ has been used, and $m = \langle \sigma_i \rangle_{\text{eq}}$ is the equilibrium magnetization.

For the covariance $V_{ij}^{C\chi}(t, t_w)$ one has

$$\begin{aligned} \lim_{t-t_w \rightarrow \infty} V_{ij}^{C\chi}(t, t_w) &= \lim_{t-t_w \rightarrow \infty} \left\{ \frac{1}{2} \left[C_i(t - t_w) - \langle \sigma_i(t) \sigma_i(t_w) \sigma_j(t) \sigma_j(t_w) \rangle_{\text{eq}} \right. \right. \\ &\quad \left. \left. - \int_{t_w}^t dt_1 \langle \sigma_i(t) \sigma_j(t) B_j(t_1) \sigma_i(t_w) \rangle_{\text{eq}} \right] - m^2 \chi_j(t, t_w) - C_i(t - t_w) \chi_j(t - t_w) \right\} \\ &= \frac{1}{2} \left[m^2 - \langle \sigma_i \sigma_j \rangle_{\text{eq}}^2 - 2m^2 (1 - \langle \sigma_i \sigma_j \rangle_{\text{eq}}^2) \right. \\ &\quad \left. - \lim_{t-t_w \rightarrow \infty} \int_{t_w}^t dt_1 \langle \sigma_i(t) \sigma_j(t) B_j(t_1) \sigma_i(t_w) \rangle_{\text{eq}} \right] \\ &\quad - m^2 (1 - m^2). \end{aligned} \quad (\text{D.2})$$

The integral can be computed in the following way. Introduce an intermediate time t^* between t and t_w and take t_w , t^* and t sufficiently far apart. Then one can write

$$\begin{aligned} \int_{t_w}^t dt_1 \langle \sigma_i(t) \sigma_j(t) B_j(t_1) \sigma_i(t_w) \rangle_{\text{eq}} &= \int_{t_w}^{t^*} dt_1 \langle \sigma_i(t) \sigma_j(t) \rangle_{\text{eq}} \langle B_j(t_1) \sigma_i(t_w) \rangle_{\text{eq}} \\ &\quad + \int_{t^*}^t dt_1 \langle \sigma_i(t) \sigma_j(t) B_j(t_1) \rangle_{\text{eq}} \langle \sigma_i(t_w) \rangle_{\text{eq}}. \end{aligned} \quad (\text{D.3})$$

Using the property (B.3), the integral in the first term of the rhs can be rewritten as

$$\begin{aligned} \int_{t_w}^{t^*} dt_1 \langle \sigma_i(t) \sigma_j(t) \rangle_{\text{eq}} \langle B_j(t_1) \sigma_i(t_w) \rangle_{\text{eq}} &= \langle \sigma_i(t) \sigma_j(t) \rangle_{\text{eq}} \int_{t_w}^{t^*} dt_1 \frac{\partial}{\partial t_1} \langle \sigma_j(t_1) \sigma_i(t_w) \rangle_{\text{eq}} \\ &= \langle \sigma_i(t) \sigma_j(t) \rangle_{\text{eq}} [\langle \sigma_j(t^*) \sigma_i(t_w) \rangle_{\text{eq}} - \langle \sigma_j(t_w) \sigma_i(t_w) \rangle_{\text{eq}}] \\ &\rightarrow m^2 \langle \sigma_i \sigma_j \rangle_{\text{eq}} - \langle \sigma_i \sigma_j \rangle_{\text{eq}}^2, \end{aligned} \quad (\text{D.4})$$

where in the last line the limit $t^* \rightarrow \infty$ has been taken. Analogously, using the property (B.5), the second term on the rhs of equation (D.3) can be computed, yielding

$$-m(m - \langle \sigma_i \sigma_j \rangle_{\text{eq}} m). \quad (\text{D.5})$$

Thus, replacing the integral appearing in equation (D.2) with equations (D.4) and (D.5) one finds

$$\lim_{t-t_w \rightarrow \infty} V_{ij}^{C\chi}(t, t_w) = -m^2 C_{ij,eq}. \quad (D.6)$$

From equation (10), by means of analogous computations, one can easily check that

$$\lim_{t-t_w \rightarrow \infty} \mathcal{V}_{ij}^{\chi}(t, t_w) = -C_{ij,eq}^2. \quad (D.7)$$

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