Nonlinear susceptibility in glassy systems: A probe for cooperative dynamical length scales

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We argue that for generic systems close to a critical point, an extended fluctuation-dissipation relation connects the low frequency nonlinear (cubic) susceptibility to the four-point correlation function. In glassy systems, the latter contains interesting information on the heterogeneity and cooperativity of the dynamics. Our result suggests that if the abrupt slowing down of glassy materials is indeed accompanied by the growth of a cooperative length \( \ell \), then the nonlinear, \( 3\omega \) response to an oscillating field (at frequency \( \omega \)) should substantially increase and give direct information on the temperature (or density) dependence of \( \ell \). The analysis of the nonlinear compressibility or the dielectric susceptibility in supercooled liquids, or the nonlinear magnetic susceptibility in spin-glasses, should give access to a cooperative length scale, that grows as the temperature is decreased or as the age of the system increases. Our theoretical analysis holds exactly within the mode-coupling theory of glasses.

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I. INTRODUCTION

A yet unexplained property of fragile glasses is the extremely fast rise of their relaxation time (or viscosity) as the temperature is lowered, much faster than predicted by a simple thermal activation formula.\(^1\) If interpreted in terms of an effective activation energy, the latter increases by a factor of 5–10 between 1.5\( T_g \) and the glass transition temperature \( T_g \). The basic mechanism for this increase is not well understood, but it is reasonable to think that it is intimately related to cooperative effects\(^2,3\) and possibly to the presence of an underlying critical point.\(^4–11\) The dynamics becomes sluggish and the activation energy increases because larger and larger regions of the material have to move in a correlated way to allow for a substantial motion of individual particles. Long time scales must be somehow associated with large length scales. Although the idea of a cooperative length has been discussed in the context of glasses for many years,\(^2,12\) it is only recently that proper measures of cooperativity (and of the size of the rearranging regions) were proposed theoretically\(^8\) (see Ref. 13 for earlier insights) and measured in numerical simulations\(^13–16\) (see also Refs. 12, 17, and 18 for related experimental work). The idea is to measure how the dynamics is correlated in space; technically, this involves a four-point correlation function which measures the spatial correlations of the temporal correlation [see Eq. (9) below for a more precise definition]. Recent extensive numerical evaluations of this four-point correlation function in Lennard-Jones systems have confirmed the existence of a growing length scale as temperature is decreased,\(^11,15,16\) and have shown that different observables, such as the relaxation time or the diffusion constant, scale as powers of this length, emphasizing its crucial importance as far as the physics is concerned. In the framework of granular systems, diverging length scales near the jamming transition have also been reported in numerical studies of model systems.\(^19\)

Although many different theoretical approaches to the glass transition\(^4–11\) can potentially explain the existence of such a growing dynamical correlation length, these theories lead to rather different quantitative predictions for the behavior of the four-point correlation function (see the detailed discussion in Ref. 20). Thus, experiments measuring directly this four-point function would be extremely valuable to refine our understanding of the glass phenomenon and prune down the number of candidate models. Up to now, unfortunately, only indirect experimental indications of a cooperative length scale associated to heterogeneous dynamics have been reported.\(^12,17,21\)

On a different front, that of spin-glasses, length scale ideas have also been expressed in recent years to account for nonequilibrium phenomena such as aging, memory, and rejuvenation effects.\(^22–27\) Although spin-glass order is not easy to define nor to detect, the idea is that some kind of domain growth occurs, whereby spin-glass correlations establish on larger and larger length scales as the age of the system increases. The growth of this “coherence length” has been established numerically by comparing two replicas of the same system.\(^28–32\) This trick is obviously inaccessible to experimentalists, who have nevertheless provided indirect evidence of a growing length scale, and some indications on its rate of growth with time and temperature.\(^23,33–35\) Again, a direct measure of this length scale is lacking—finding a clear-cut experimental signal of a cooperative length in disordered, amorphous systems would certainly be a major breakthrough.\(^12\)

The aim of this paper is to point out that in slow glassy systems at equilibrium, the nonlinear (cubic) response to an external field (electric, magnetic, pressure, etc.) in fact probes directly the four-point correlation function mentioned above, and therefore the cooperative length it may contain. Our main prediction, detailed below, is that the \( 3\omega \) harmonic response to an ac field of frequency \( \omega \) and amplitude \( h \) is given by \( \chi_3(\omega,t)h^3 \), where the nonlinear susceptibility \( \chi_3 \) behaves at low frequency as

\[ T_g \]
\[ \chi_3(\omega, T) = \frac{\chi_0^2}{k_B T} \ell^2 \bar{H}(\omega \tau). \]  

In the above relation, \( \chi_0 \) is the static linear susceptibility, \( \bar{H} \) a certain complex function that depends weakly on temperature, and \( \tau \) is the temperature dependent relaxation time of the system, which can be directly measured using the linear susceptibility. The cooperative length \( \ell \) (measured in units of the microscopic length \( \xi \) obtained from the two point correlation function) is expected to grow as the temperature is reduced, and \( \bar{H} \) an exponent related to the spatial structure of the four-point correlation function.\(^{36}\) Our central result, Eq. (1), that we will motivate below, states that (a) the nonlinear susceptibility has the same frequency scaling as the linear susceptibility, which is not surprising and (b) it grows as the cooperative length increases, which should allow a direct experimental test of the relationship between length and time scales in glassy systems.

The above prediction holds for equilibrium systems; we will however see below that in the case of glasses and spin-glasses in a field, \( \bar{H}(0) = 0 \). Below the glass transition temperature, on the other hand, the system by definition falls out of equilibrium. Its dynamics becomes nonstationary and exhibits aging, which means that the effective relaxation time of the system increases with the age \( t_w \) of the system.\(^{37,38}\)

This increase of the relaxation time is again most probably related to the growth of a coherence length in the system, \( \ell_w = \ell(t_w) \). On very general grounds,\(^{38}\) one expects that the generalization of the equilibrium result (1) to the aging case will read, for a large class of systems:

\[ \chi_3(\omega, t_w) = \frac{\chi_0^2}{k_B T} \ell_w^2 \bar{H}(\omega \tau), \]  

where \( h \) is a certain increasing function, which in simple domain growth models is the typical size of the domains. From experimental results,\(^{39}\) a plausible guess is that simple aging will hold in spin-glasses, i.e., \( h(t_w) = t_w \). (Of course, more complicated scaling forms, with an infinite number of time domains, may hold in some cases, such as models with full replica symmetry breaking.\(^{38}\)) In the above equation, \( \bar{H} \) is another scaling function, which also contains possible violations of the standard fluctuation dissipation theorem and the appearance of a nontrivial, \( t_w \) dependent, effective temperature.\(^{39}\) Equation (2) should in any case allow one to extract from nonlinear aging susceptibilities a nonequilibrium coherence length, in a much more direct way than previous attempts.

As for comparison with previous works, the divergence of the static nonlinear susceptibility at the spin-glass (in zero field) or dipolar-glass transition, displayed by Eq. (1) at \( \omega = 0 \), is of course well documented, both theoretically and experimentally.\(^{40-42}\) The generalization to the dynamical nonlinear susceptibility in the critical region was also discussed\(^{22,43,44}\) but not, to the best of our knowledge, its generalization to the nonequilibrium, aging regime, Eq. (2). The situation for glassforming liquids is quite different, since no static phase transition with a diverging static susceptibility has ever been identified, neither in experiments nor in simulations. Purely based on an analogy with spin-glasses, it was suggested in Ref. 45 that the nonlinear dielectric constant of molecular glasses might grow as the glass phase is approached (although this was not borne out by the experiments done at that time\(^{45}\)). A similar suggestion was made in Ref. 46 concerning the nonlinear compressibility of soft sphere binary mixtures, with numerical results that are not incompatible with a substantial increase of \( \chi_3(\omega \rightarrow 0) \) as the temperature is lowered. We will show below that such a growth is indeed expected, although the theoretical situation for glass formers is much less clear than for spin-glasses—in particular, although \( \chi_3 \) is growing may never diverge in glass formers. Different scenarios for the glass transition can be envisaged and lead to quite different predictions, for example on the value of \( \bar{H} \) and on the relationship between \( \ell \) and \( \tau \) (or \( t_w \)).

In the following section we will give some physical arguments that motivate our results, and muster the predictions of different theoretical models for glass formers. A more detailed and technical discussion is then presented in Sec. III. Finally our conclusions are presented in Sec. IV.

II. PHYSICAL ARGUMENTS AND RESULTS

A. Spin-glasses

1. Order parameter and nonlinear susceptibility

Let us first focus on spin-glasses in zero external magnetic field, \( H = 0 \). These systems are thought, both theoretically and experimentally, to have a nonzero transition temperature below which the magnetization profile, \( \langle s \rangle \), freezes into one (or more) amorphous configurations. The ordered state is characterized by a nonzero Edwards-Anderson (EA) parameter \( q = \langle s^2 \rangle \), where \( \langle \cdot \cdot \rangle \) indicates thermal averaging and the brackets a spatial (or disorder) average. These systems display an unusual type of long-range order, which cannot be detected using either one body or two-body spin-spin correlations: because the ordering pattern is random, the average magnetization \( \langle s^2 \rangle \) remains zero and the spin-spin correlation \( \langle s s' \rangle \) short-ranged, even in the spin-glass phase. Correspondingly, the linear susceptibility, related by a fluctuation dissipation theorem (FDT) to the integral of the spin-spin correlation function, does not diverge as \( T_g \) is approached, even if some long-ranged correlations appear in the system. The way to get rid of the spurious cancellation between strongly correlated and strongly anticorrelated spins is well known: exactly as one should square \( \langle s \rangle \) to obtain a nonzero Edwards-Anderson parameter, one should also square \( \langle s s' \rangle \) before averaging over disorder. The integral over space of that quantity now diverges as \( T_g \) is approached, and in fact has two interesting physical interpretations.

(1) The first one is the susceptibility of the spin-glass order parameter to small random ordering fields. Imagine one adds small random magnetic fields \( h_y \) on every site. Using linear response, one can write, for a given sample at \( T > T_g \) and \( H = 0 \):

\[ \delta \langle s_x \rangle = \frac{1}{k_B T} \sum_y \langle s_x s_y \rangle h_y, \]  

where the subscript 0 means that the correlation functions are evaluated at zero external field. Squaring this relation, sum-
ming over $x$ and averaging over the random fields gives the sensitivity of the EA order parameter to a random pinning field:

$$\chi_{SG} = \frac{\partial q}{\partial (h^2)} = \frac{1}{N(k_B T)^2} \sum_{x,y} [\langle s_x s_y \rangle_0]^2. \quad (4)$$

Clearly, the divergence of $\chi_{SG}$ signals an incipient instability towards an ordering pattern favored by the small pinning fields, exactly as the divergence of the usual two-body susceptibility signals an instability to ferromagnetic order, triggered by a small (uniform) magnetic field.

(2) As defined above, $\chi_{SG}$ has a clear theoretical interpretation but seems hard to access experimentally. Fortunately, $\chi_{SG}$ has another interpretation in terms of a nonlinear susceptibility, which can be directly measured. The intuitive idea is that the nonlinear susceptibility is actually a measure of the (quadratic) dependence of the linear susceptibility on the external field. Using again FDT the change of the connected correlation function between two spins (and hence of the linear susceptibility) induced by the field contains the term:

$$\delta \langle s_x(s_y) \rangle = \sum_{z,z'} \langle s_x s_z \rangle_0 \langle s_z s_{z'} \rangle_0 \frac{h^2}{(k_B T)^2}. \quad (5)$$

Averaging over space (or over disorder), only the terms ($z_0=x,z'=x,y$) survive, the first one giving $[\langle s_x s_y \rangle_0]^2$ as in $\chi_{SG}$. A more precise treatment for Ising spins at zero field leads to the exact relation $\chi_3(\omega=0) = -3(\chi_{SG} - 2)/(k_B T)^2$.

Therefore, the static nonlinear susceptibility of spin-glasses diverges as the spin-glass transition temperature $T_G$ is approached, a well-known effect that allows one to measure some of the critical exponents experimentally.\(^{40,41}\) The physics behind the correlation induced amplification of $\chi_3$ is clear: the influence of the polarization of spin $s_x$ on $s_y$ may be either positive or negative, but it has the same sign as the reverse influence of $s_y$ on $s_x$. Therefore, the quadratic effect of an external field $h$ on the dynamical correlation between any pair of spins has a well defined sign, in turn leading to a diverging nonlinear susceptibility as the size of correlated regions increases, even if the linear susceptibility remains small.

2. Nonzero external field and $T<T_G$

The case where a nonzero external field $H$ is present is more subtle. In mean-field, the spin-glass phase survives in a whole region of the $T,H$ plane, below the de Almeida-Thouless (AT) line. The spin-spin correlation function $[\langle s_x s_y \rangle - \langle s_x \rangle \langle s_y \rangle]^2$ is long-ranged in the whole spin-glass phase but is no longer directly related to the static nonlinear susceptibility. Some exact compensation mechanism\(^{47,48}\) actually cancels the divergence in the combination of four-spin correlations appearing in $\chi_3(\omega=0)$. Therefore, the nonlinear susceptibility is finite in the whole spin-glass phase (including $H=0$ in strict mean-field). There is in particular no divergence of $\chi_3(\omega=0)$ on the AT line, except at $H=0$; rather, the nonlinear susceptibility is discontinuous across the AT phase transition.\(^{49}\)

Within the droplet theory, on the other hand, the spin-glass is destroyed by any nonzero field in finite dimensions.

Both the spin-glass and nonlinear susceptibilities are therefore finite when $H \neq 0.22,50$ For $H=0$, a compensation mechanism similar to that of mean-field glasses is also at play, but does not prevent the nonlinear susceptibility to diverge for all $T < T_G$.\(^{22}\) The replica field theory of spin-glasses in finite dimensions seems also compatible with a diverging nonlinear susceptibility for $T<T_G$ at zero field.\(^{51}\)

3. Dynamical nonlinear susceptibility

The above qualitative arguments for the static nonlinear susceptibility can be extended to the dynamical case as well. As will be recalled below, the dynamical FDT gives

$$\langle s_x(t) \rangle = \frac{1}{k_B T} \sum_\gamma \int dt_3 \frac{d}{dt_3} \langle s_x(t_1) s_y(t_3) \rangle_0 \delta(t_3) h_y(t_3). \quad (6)$$

Therefore, the change in the connected dynamical correlations between $s_x(t_1)$ and $s_y(t_2)$, induced by a uniform, but time dependent external field, will contain a term like

$$\sum_\gamma \int dt_3 dt_4 \frac{d}{dt_3} \langle s_x(t_1) s_y(t_3) \rangle_0 \frac{d}{dt_4} \langle s_y(t_2) s_z(t_4) \rangle_0 h_y(t_3) \delta(t_4). \quad (7)$$

Repeating the same argument developed in the static case, i.e., averaging over space (or disorder) and using FDT to relate the connected correlation function to the dynamical linear susceptibility leads to a nonlinear response function that reads

$$\chi_3(t_1,t_2,t_3,t_4) = \sum_\gamma \int dt_3 dt_4 \frac{d}{dt_3} [\langle s_x(t_1) s_y(t_3) \rangle_0 \langle s_y(t_4) s_y(t_2) \rangle_0]. \quad (8)$$

Taking $t_1,t_2,t_3,t_4$ all within an interval of the order of the relaxation time $\tau$ of the system, we see that the correlation function entering $\chi_3$ above defines a cooperative length scale $\ell$, such that the dynamics of $s_x$ and $s_y$ within this time interval is dominated by common events. This in turn leads to our scaling prediction, Eq. (1), near the transition temperature. The exact result for the dynamical $\chi_3(t_1,t_2,t_3,t_4)$ needs to be worked out carefully (see Sec. III), since FDT for higher order correlations is more involved than for two point functions.\(^{52}\) Although different from the above naive expression, it indeed contains four-spin correlation functions that capture the cooperativity of the dynamics. Intuitively, again, the nonlinear response is strong if on the scale of the relaxation time, two spins feedback on each other’s dynamics—this cross correlation is squared and survives averaging, even if the correlation itself is of random sign.

4. The aging regime

In the low temperature, spin-glass phase, the relaxation time $\tau$ is infinite and the age of the system $t_\mu$ plays a crucial role—all time dependent correlation functions depend explicitly on $t_\mu$, which sets the time scale for the relaxation of the system,\(^{53}\) and also for higher order correlation functions, such as the four-point correlation. Intuitively, exciting the
system with a field of frequency $1/t_w$ will give the nonlinear response of a spin-glass equilibrated only up to a certain length scale $\ell \approx \ell(t_w)$.$^{53}$

Interestingly, and contrarily to standard ordering transitions, spin-glasses are thought to be critical throughout their low temperature phase, in the sense that the space integral of the connected correlation function $\langle s_x s_y \rangle^2$ diverges for all $T<T_g$. In the special case of mean-field spin-glasses, the static nonlinear susceptibility within one phase is, as mentioned above, finite (except for $T=T_g$ and $H=0$).$^{57}$ Except if some further cancellations operate at finite frequencies, an equation similar to Eq. (2) should hold in the aging phase of mean-field spin-glasses, but with an infinite number of time domains rather than a simple scaling variable such as $\omega t_w$. The explicit calculation of $\tilde{H}$ in the context of a spherical $p$-spin model would be extremely interesting; in particular one may ask whether the effective temperature appearing in the nonlinear response is the same as that appearing in the linear response.$^{54}$

In the droplet picture,$^{22,50}$ and for the replica theory in finite dimensions,$^{51}$ the static nonlinear susceptibility diverges for all $T<T_g$ (at least for $H=0$), and one should certainly observe a nonlinear susceptibility increasing as in Eq. (2). In the original droplet model with activated dynamics one predicts a function $\tilde{H}$ of $\ln \omega / \ln t_w$ associated with the logarithmic growth of $\ell(t_w)$. The peak value $\chi^c(t_w, \omega=1/t_w)$ should grow as $\ell(t_w)^{2-\eta}$. The numerical value of $2-\eta$ is yet unknown, but following Fisher and Huse,$^{22}$ one may expect $d-3 < 2-\eta < d$ with $\theta = 0.2$ in three dimensions.

B. Structural glasses

1. Four-point density functions

Let us now discuss structural glasses. The important lesson we learn from spin-glasses is that a nontrivial amorphous type of long-range order can set in. In the case of glasses, the subtlety comes from the absence of quenched disorder; however, there has now been many papers exploring the idea of self-induced disorder which could drive a similar transition in homogeneous, frustrated systems (see, e.g., Ref. 38, and references therein). This has led, in particular, to the “Random First Order Transition” scenario,$^{4}$ where a glass transition of the same nature as the spin-glass transition in mean-field $p$-spin models takes place (see Ref. 7 for recent quantitative results). Whether a true transition of this type can exist in real systems with finite range interactions is still an actively debated issue; it is nevertheless extremely fruitful to explore the properties of systems for which this transition is, in some sense, nearly present. The order parameter in the would-be glass phase is the amplitude of the frozen in (random) density fluctuations $\delta \rho_x$. As for spin-glasses, the average of this quantity is zero, but $\langle (\delta \rho)^2 \rangle$ is not, and plays the role of the Edwards-Anderson parameter. (The square brackets above now means an average over times longer than the relaxation time of the system, see Sec. II B 3.) Similarly, one expects $\langle (\delta \rho_x \delta \rho_y) \rangle$ not to show any interesting features (beyond that typical of a liquid structure factor), whereas its square may reveal long-range cooperative dynamics. The analog of the spin-glass and nonlinear susceptibilities discussed previously can be easily found in the case of glasses: the former can be seen as the susceptibility to a random external pinning field$^{55}$ that triggers the appearance of one particular type of frozen density fluctuation, whereas the latter is directly related to the nonlinear compressibility, i.e., the response to a pressure field that couples to the density. Other nonlinear responses to a field that couples to the degrees of freedom undergoing a glass transition are also relevant (for example, the dielectric response when the dipoles are strongly coupled to the translational degrees of freedom, such as in glycerol, OTP, etc.). Let us directly focus on the dynamical susceptibility and postpone the discussion of its static limit to Sec. II B 3. Indeed, the analogy with spin-glasses has to be taken with a grain of salt (see Sec. II B 3). The dynamical four-point density function is defined as

$$G_{2}(r,t) = \langle (\delta \rho_x(t=0) \delta \rho_x(t) \delta \rho_{x+y}(t=0) \delta \rho_{x+y}(t)) \rangle - C^2(t), \quad C(t) = \langle \delta \rho_x(t=0) \delta \rho_x(t) \rangle. \quad (9)$$

The point of this paper is that this correlation function is related to the dynamical nonlinear response of the system to an external excitation that couples to the density.$^{56}$ Once again, the idea is that the change of the two point correlation between $x$ and $y$ induced by the external field of frequency $\omega \sim \tau^{-1}$ will be large if on that time scale, the dynamics at these two points is strongly correlated, which is true precisely if $G_{2}(x-y, \tau)$ is large. The extended, nonlinear FDT discussed in the next section makes this statement more precise and finally leads to our central results, Eq. (1) and Eq. (26) below. Now, recent numerical$^{13-16}$ and theoretical work$^{8,9,11,20,57}$ have focused on the above choice of four point density function. Its integral over space $\chi_{4}(x) = \int d^d r G_{2}(r,t)$ (divided by $V$) gives the variance of the correlation function $C(t)$ for a system of finite volume $V$.$^{58}$ and is therefore a good quantitative measure for dynamical heterogeneities. This quantity was unambiguously shown to display a peak at $t=\tau$, of increasing amplitude as the temperature is decreased and the glass temperature is approached.$^{13-16}$ Signaling increased cooperativity in the dynamics and the growth of a length scale $\ell$, which should in turn show up in the nonlinear response of the system.

2. Different scenarios for the glass transition: Qualitative predictions

We therefore expect, on very general grounds, the nonlinear response to a field that couples to degrees of freedom undergoing a collective freezing phenomenon, to increase substantially (as $\ell^{2-\eta}$) as the glass phase is approached. However, as we discuss now, the details of this increase do depend on the specific scenario at play. Most important in that respect is the quantitative relation between the cooperative length scale $\ell$ and the relaxation time $\tau$, which is often a power-law $\tau \sim \ell^z$ where $z$ is the dynamical exponent.

One scenario for the glass state is based on the idea that some mobility defects are needed to trigger the dynamics, which slows down at low temperatures because these defects become rare.$^{57,59,60}$ Kinetically constrained models provide
nonlinear susceptibility in glassy...
Even the spin-glass case turns out to be tricky since, as mentioned above, the scaling function $\mathcal{H}(x \to 0)$ in fact also goes to zero for $H \neq 0$ in the context of the full replica symmetry breaking solution.\textsuperscript{47,48} Nevertheless, our dynamical result Eq. (26) suggests this sum rule will generically not hold at finite frequency whenever the four-point correlation function has a nontrivial time dependence. This statement should of course be checked explicitly for mean-field models with continuous replica symmetry breaking.\textsuperscript{54} If indeed $\mathcal{H}(x \to 1)$ is found to be nonzero close to the $\Delta T$ line, the experimental study of the dynamical nonlinear susceptibility, predicted to diverge for $\omega \tau \to 1$, would offer a direct way to prove or disprove the existence of an $\Delta T$ line in real systems (see Ref. \textsuperscript{67} for a recent discussion).

### III. THEORETICAL ANALYSIS

In the rest of this paper, we give some theoretical justifications of our central result, Eq. (1). These arguments also suggest that in the nonequilibrium phase, Eq. (2) will hold. We will use the Langevin equation formalism for continuous spins,\textsuperscript{52} but our result are expected to hold more generally (for example, if the continuous spins are replaced by interacting particles with Newtonian dynamics).

#### A. Linear response

We assume that the equation of motion of spin $s_i$ is given by

$$\partial_t x_i = - \partial_x H + \eta(t),$$

where $H$ is the Hamiltonian of the system, which we do not specify explicitly. In the case of spin glasses it contains quenched disorder and possibly one body terms ensuring an Ising-type character to the spins $s_i$. The coupling to an external, site dependent field $h_i(t)$, amounts to add to $H$ the sum over spins of $h_i(t)s_i$. The Gaussian noise $\eta$ is as usual of zero mean, white in time and decorrelated from spin to spin,

$$\langle \eta(t_1) \eta(t_2) \rangle = 2k_BT \delta(t_1 - t_2) \delta_{ij}. \tag{13}$$

Since the noise is Gaussian, one can establish the following identity:

$$\langle s_j(t_1) \eta(t_2) \rangle = k_BT \frac{\partial s_j(t_1)}{\partial h_i(t_2)}. \tag{14}$$

Let us first quickly re-establish the standard linear FDT. From the above equation and the equation of motion, the response of a spin to an earlier field is

$$\chi_0(t_1,t_2) = \left\langle \frac{\partial s_j(t_1)}{\partial h_i(t_2)} \right\rangle = \frac{1}{k_BT} \left\langle s_j(t_1) \left[ \partial_t s_j + \partial_x H(t_2) \right] \right\rangle. \tag{15}$$

The averaging above assumes the system to be in equilibrium: we average over all histories with initial conditions appearing with the equilibrium Boltzmann weight. The second term in the right-hand side is zero since, for an arbitrary observable $\mathcal{O}(\{s_{\alpha}\})$ that depends on times $t_{\alpha}$, all posterior to $t_2$, one has

$$\langle O(\{t_{\alpha}\}) \partial_x \mathcal{H}(t_2) \rangle = -k_BT \int \prod_{\alpha} ds(t_{\alpha}) P[\{s(t_\alpha)\}] s_2 O(\{s(t_{\alpha})\})$$

$$\times \delta(s_2 - s(t_2)) \exp[-H(s_2)/k_BT] = 0, \tag{16}$$

where $s_2 = s(t_2)$ and the last equality holds because the last term is a total derivative. Therefore, one finds the usual FDT relation,

$$\chi_0(t_1,t_2) = \left\langle \frac{d}{dt_2} \langle s(t_1) s(t_2) \rangle \right\rangle. \tag{17}$$

Integrating this quantity over $t_2$ with a constant field $h(t_2) = h$ gives the static susceptibility $\chi_0$, which, as is well known, is found to be the integral over space of the two-body correlation function. In the case of a static critical point where the correlation length $\xi$ diverges, one would have $\chi_0 \sim \mu^2 \xi^{-\eta}/k_BT$, where $\eta$ is the standard critical exponent of the static transition and $\mu$ the elementary magnetic moment. However, in the case of glassy systems, the two point function is not critical and one rather expects $\chi_0 \sim \mu^2 \xi^2/k_BT$ where $\xi$ remains microscopic and does not grow appreciably lowering the temperature (or increasing the density). As emphasized in Sec. II, one should in the case of amorphous systems rather focus on nonlinear effects to observe some nontrivial behavior.

#### B. Nonlinear response: The static limit

As a consequence we want to extend the above calculation to the response of the system at time $t_1 > t_2$ to three field “kicks” at times $t_2 > t_3 > t_4$. This is given by

$$\chi_{3,ijk}(t_1,t_2,t_3,t_4) = \left\langle \frac{\partial^3 s_j(t_1)}{\partial h_i(t_2) \partial h_k(t_3) \partial h_l(t_4)} \right\rangle = (k_BT)^{-3} \left\langle s_j(t_1) \eta_j(t_2) \eta_j(t_3) \eta_j(t_4) \right\rangle. \tag{18}$$

Using three times the Langevin equation of motion, and once the above trick to get rid of the final $\partial_x H(t_2)$, we find the following general relation, involving four terms:

$$(k_BT)^3 \chi_{3,ijk}(t_1,t_2,t_3,t_4) = \frac{d^3}{dt_2 dt_3 dt_4} \langle s_j(t_1) s_j(t_2) s_j(t_3) s_j(t_4) \rangle$$

$$+ \frac{d^2}{dt_2 dt_4} \langle s_j(t_1) \partial_j H(t_2) s_j(t_3) s_j(t_4) \rangle$$

$$+ \frac{d^2}{dt_3 dt_4} \langle s_j(t_1) s_j(t_2) \partial_j H(t_3) s_j(t_4) \rangle$$

$$+ \frac{d}{dt_4} \langle s_j(t_1) s_j(t_2) s_j(t_3) \partial_j H(t_4) \rangle. \tag{19}$$

Let us first analyze the static limit of this expression. From the above result, one can show in full generality that the static nonlinear susceptibility $\chi_{3,ij} = \chi_{3,ij}(\omega = 0, T)$, obtained by integrating over all $t_2 > t_3 > t_4$ with a constant field $h(t) = h$ on all sites, is given by
where the subscript \( c \) means that one takes the connected part of the correlation and \( N \) the total number of sites. This result is exact and can be obtained directly using equilibrium statistical mechanics. In the present context, the first term in expression Eq. (19) for \( \chi_{3x} = \langle s_i(t_1)s_j(t_2)s_k(t_3)s_l(t_4) \rangle \), contributes to \( \omega=0 \). As discussed in Sec. II, the long range order setting in spin-glasses is unveiled not by the two-body correlation that oscillates in sign and averages to zero, but by the square of this two-body correlation. Therefore, the leading dominant term in the above sum corresponds to the square of the two-body correlation obtained pairing \( i, j, k, l \), say, \( i \) with \( j \) and \( k \) with \( l \) within the two-body correlation length \( \xi \) (which typically remains small at all temperatures):

\[
(k_B T)^3 \chi_{3x} = \frac{3}{N} \sum_{ijkl} (s_i(t_1)s_j(t_2)s_k(t_3)s_l(t_4))c. 
\]  

(20)

If one now assumes that \( G_{ik} \) scales as in usual critical phenomena\(^{22,47} \):

\[
G_{ik} = \frac{1}{|r_i - r_k|^{d-2\eta}} \left( \frac{r_i - r_k}{\ell} \right),
\]

(22)

then the sum over \( i, k \) behaves as \( N \epsilon^{2\eta} \), finally leading to a static nonlinear susceptibility given by

\[
\chi_{3x} = \frac{C \mu^2 \epsilon^{2d}}{(k_B T)^3} \xi^{2-\eta} \sim \frac{\xi^2}{k_B T} \epsilon^{2-\eta},
\]

(23)

where \( C \) is a constant, and \( \ell \) is counted in units of the static correlation length \( \xi \). This is the zero frequency result given in Eq. (1).

C. Nonlinear response: Dynamics

1. Some general arguments

The extension to nonzero frequency of the above result can proceed in different ways. Our result Eq. (1) can be simply seen as a standard dynamical scaling assumption close to a critical point, as is indeed correct for spin-glasses.\(^{43,44} \) This result is expected to hold whenever a critical point is responsible for the simultaneous increase of the relaxation time and the cooperative length. This is true of the mode-coupling theory of glasses,\(^{8,9} \) and also of other scenarios discussed in the introduction and in Sec. II, which rely on the existence of an underlying critical point.\(^{4-7,10,11} \) From a more technical point of view we want to justify that the behavior of the nonlinear cubic response is the same as of the first term on the right-hand side of Eq. (19), whereas the three other terms are either negligible or of the same order of magnitude (on frequencies of the order of \( \tau^{-1} \)), but not more divergent.

A simple case that can be treated in some generality is when the fluctuation of the norm of the spins can be neglected, for example for Ising spins that can be recovered from the Langevin equation in the limit of infinitely sharp double well potential that is zero if \( s^2=1 \) and infinite otherwise. After several integration by parts and using \( s^2=1 \), one can show that the three last terms of Eq. (19) do not contribute to the nonlinear ac susceptibility at low frequencies (much smaller than the microscopic, high frequency scale of the model). One is therefore left with the first term of Eq. (19), that contains three derivatives with respect to time. If one assumes that the four-body correlation \( \langle s_i(t_1)s_j(t_2)s_k(t_3)s_l(t_4) \rangle \) is, for \( |i-k| \sim \ell \), only a function of \( (t_1-t_2)/\tau, (t_2-t_3)/\tau, (t_3-t_4)/\tau \), the integration over \( t_2, t_3, t_4 \) with an oscillating field at frequency \( \omega \) and over space directly leads to Eq. (1), i.e., a nonlinear susceptibility that scales as a certain function \( H \) of \( \omega \tau \). This result is only justified in the low frequency domain; for high frequency, contributions from the short-time \( \beta \)-regime will obviously come into play. Note that very generally, we expect \( H \) to be nontrivial, although it does vanish at zero frequency whenever the static susceptibility is finite, as is the case for glasses and spin-glasses in an external field (see the discussion in Secs. II A 2 and II B 3).

More generally, one can argue both physically and diagrammatically that the three last terms of Eq. (19) give contributions which are at most of the same order of magnitude as the first one. From a physical point of view, these terms contain less time derivatives that the first, but also contain the local “force” acting on the configuration, \( \partial_s H(t) \). Since we are interested in the low frequency response of the system, we can decompose the dynamics of the spins into a fast part \( s' \) and a slow part \( s'' \), that corresponds to the dynamics on a time of order \( \tau \). It is clear that the force acting on the slow modes can only lead to a slow dynamics of these modes, i.e., \( \partial_s H \approx \tau^{-1} \). Therefore, for frequencies \( \sim \tau^{-1} \), one has, for example,

\[
\langle s_i(t_1)\beta_s H(t_2)s_j(t_3)s_k(t_4) \rangle \approx \tau^{-1} F \left( \frac{t_1-t_2}{\tau}, \frac{t_2-t_3}{\tau}, \frac{t_3-t_4}{\tau} \right),
\]

(24)

(where \( F \) is a certain function), which after integration leads again to a result of the form (1).

2. Diagrammatic analysis

One can understand the above result from a different point of view using diagrams for a general Langevin equation, which leads to a dynamical field theory with the spin field \( s \) and the response field \( \chi \).\(^{48} \) The nonlinear cubic response \( \chi_3 \) at time \( t_1 \) to three instantaneous fields at times \( t_2, t_3, t_4 \) can be written in full generality as (see Fig. 1)

\[
\chi_3(t_1; t_2, t_3, t_4) = \int dt_1' dt_2' dt_3' dt_4' \Gamma_{\xi, s, s, s}(t_1' ; t_2', t_3', t_4') \chi(t_1 - t_1') \chi(t_2' - t_2) \chi(t_3' - t_3) \chi(t_4' - t_4'),
\]

(25)

where \( \Gamma_{\xi, s, s, s} \) is the amputated vertex with legs \( s, s, s, s \) (for simplicity we skip here the space indices). Note that the vertex \( \Gamma_{\xi, s, s, s} \) is zero by causality because it contains for sure a closed loop of response functions. The other vertices do not appear because the correlation function \( \langle \tilde{s}s \rangle \) vanishes by causality.
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FIG. 1. General diagrammatic representation of the nonlinear cubic response.

Now let us consider the diagrams contributing to the connected four body correlation function. There is a first contribution $G_4^b$ obtained by plugging three two body correlation functions into $\Gamma_{\hat{s},s,s,s}$, see Fig. 2. It is straightforward to check, using FDT, that this first series of diagrams, $G_4^b$, is directly related to the nonlinear cubic response. If $G_4^b$ was the only contribution, then one would find an extended FDT corresponding to the first term on the right-hand side of Eq. (19) contributes.

There is another contribution, $G_4^c$, that corresponds to constructing ladders with the irreducible vertices $\Gamma_{s,s,s,s}^{irr}$, on the left of $\Gamma_{\hat{s},s,s,s}$ and the irreducible vertices $\Gamma_{s,s,s,s}^{irr}$, on the right of $\Gamma_{\hat{s},s,s,s}$ (see Fig. 3). [We recall that the irreducible vertex $\Gamma_{1,2,3,4}^{irr}$ is the sum of all Feynman diagrams contributing to $\Gamma_{1,2,3,4}$ (the amputated vertex) that has the property that cutting two internal lines does not separate the diagram into two disconnected parts, such that one part contains the lines 1,2 and the other one the lines 3,4.] Finally, the last contribution, $G_4^c$, is formed by plugging together the same irreducible diagrams used in $G_4^b$ but without making use of $\Gamma_{\hat{s},s,s,s}$.

In the case of the critical equilibrium dynamics of spin-glasses, Eq. (1) is already known\(^{43,44}\) and could have been guessed \textit{a priori} from the general scaling properties of second order phase transitions with a single diverging length (and time) scale. As a consequence in this case $G_4^b$, $G_4^c$, are of the same order or less divergent than $G_4^a$. The case of structural glasses is \textit{a priori} more tricky, since there is no consensus on the effective critical microscopic model that would describe them. However, if we take as an established fact (at least numerically) that the four body correlation is governed by a length scale that increases as the glass is approached, then this effect has to be contained in (at least) one of the three contributions $G_4^b$, $G_4^c$, $G_4^a$. Now, the nonlinear response certainly contains the contribution related to $G_4^a$; therefore both $\chi_3$ and $G_4$ grow (or even diverge) similarly unless another family of (more) diverging diagrams (the ones contributing to $G_4^b$, $G_4^c$) can be constructed. We believe that this is a rather unlikely scenario and instead expect that in general $\Gamma_{\hat{s},s,s}$ contains the leading divergence. As a consequence $G_4^b$ and $G_4^c$, and therefore $\chi_3$ and $G_4$, are of the same order of magnitude whereas $G_4^a$ is subdominant. In this case Eq. (1) holds. Strictly speaking, these arguments only prove that if the nonlinear cubic dynamical response diverges, a similar (or stronger) divergence is expected for the four body correlation function, but not vice versa. Therefore it would be important to check our prediction for specific models of the glass transition, in the spirit of Ref. 20. Although the above general arguments are clearly incomplete, we want to emphasize here they are indeed correct within the mode-coupling theory of the glass transition. This can be seen using the ideas of Ref. 10 which establish the validity of our central result, Eq. (1).

Finally, let us remark that the extension to the nonequilibrium case can be tackled in a similar way. In particular, since the four-body correlation function diverges with $t_\omega$ (Ref. 69) in spin-glasses, and the classification in terms of $G_4^b$, $G_4^c$ carries over to the nonequilibrium case, the above discussion can be generalized to the nonequilibrium case as well.

In summary, we have shown in this section that for glassy systems close to a critical point, where the relaxation time and cooperative length diverge, an extended approximate FDT relates the nonlinear susceptibility to the four-point correlation function in the low frequency domain,

\[ (k_B T)^3 \chi_{3,ijkl}(t_1,t_2,t_3,t_4) \sim \int dt_1 dt_2 dt_3 dt_4 \langle s_j(t_1) s_j(t_2) s_j(t_3) s_j(t_4) \rangle, \]

where $\sim$ means that right and left-hand side have the same critical behavior. The additional terms missing in the above equation are either of the same order of magnitude, or negligible.

**IV. CONCLUSION**

In conclusion, we have shown in this paper that if the abrupt slowing down of glassy materials is accompanied by the growth of a cooperative length $\ell$, then the nonlinear, $3\omega$ response to an oscillating field (at frequency $\omega$) should substantially increase and give precious information on the temperature (or density) dependence of $\ell$. The theoretical moti-
viation is that the nonlinear susceptibility is approximatively related, for glassy systems close to a critical point, to the four-point correlation function that captures dynamical cooperativity. This relation is certainly correct within the context of the mode-coupling theory of glasses, but should hold in other cases as well.

In supercooled liquids, the analysis of the nonlinear compressibility (sound wave harmonics) should allow one to probe directly the existence of a growing cooperative length. This should also be true of the nonlinear dielectric susceptibility, at least in systems where the dipoles are strongly coupled to the glassy degrees of freedom. Although early experiments seemed to show no interesting effects, we believe that more systematic studies should be performed, especially now that numerical simulations have unambiguously shown the growth of a cooperative length in the four-point function. These experiments should also allow one to bridge the gap between the length-scales observed on simulation time scales and the length-scales observed experimentally on much larger time-scales close to the glass transition temperature. The study of nonlinear specific heat effects, although more complex, may be interesting too. From a more general point of view any nonlinear dynamical response (for example, nonlinear rheology in soft glassy materials) should be worth studying if the corresponding linear response can be used as a probe of slow dynamics.

In spin-glasses, nonlinear ac magnetic susceptibility measurements in nonzero field could shed light on the existence of a de Almeida-Thouless line. In the aging phase, such measurements should allow one to test in more details the length scale ideas put forward in Refs. 22–27. Compared to the case of glasses, the experimental situation is particularly encouraging since the nonlinear susceptibility is already known to diverge at the spin-glass transition. There should be a clear trace of this divergence in the aging phase, except if some unlikely cancellation occurs at nonzero frequency (such a cancellation indeed operates in the static limit for spin-glasses in mean-field, but not in finite dimensions). The effect of temperature cycling on the nonlinear susceptibility should then give direct indications of the mechanisms of rejuvenation and memory. We therefore hope that the ideas expressed in this paper will help shed light on the issue of dynamical heterogeneity and cooperativity in disordered, amorphous systems.

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F. Ladieu and D. L’Hote (unpublished).


Note that the ratio of nonlinear effects to linear effects is, in order of magnitude, given by $\chi h^2/\kappa_B T$, i.e., the ratio of the energy of the field to the thermal energy.

Within a field theoretical perspective (Ref. 69) the growing correlation length $\ell_w$ is due to soft-modes, related to the reparametrization invariance of the dynamical action.

71 For practical reasons one has to introduce an overlap function in the definition of $G_4$ or focus on slightly different observables (Refs. 15 and 16).

To derive this result, one should compute $\chi_3$ within one of the states that dominates the partition function at temperature $T < T_{\text{MCT}}$. It is easy to check, using the results of Ref. 72, that the Gaussian fluctuations having a vanishing mass at $T_{\text{MCT}}$ give the same contribution to both the spin-glass and the nonlinear susceptibility. Hence, both diverge as $1/\sqrt{T_{\text{MCT}}-T}$.

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