Anomalous non-linear response of glassy liquids: general arguments and a Mode-Coupling approach

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Abstract

We study theoretically the non-linear response properties of glass formers. We establish several general results which, together with the assumption of Time-Temperature Superposition, lead to a relation between the non-linear response and the derivative of the linear response with respect to temperature. Using results from Mode-Coupling Theory (MCT) and scaling arguments valid close to the glass transition, we obtain the frequency and temperature dependence of the non-linear response in the $\alpha$ and $\beta$-regimes. Our results demonstrate that supercooled liquids are characterized by responses to external perturbations that become increasingly non-linear as the glass transition is approached. These results are extended to the case of inhomogeneous perturbing fields.
I. INTRODUCTION AND MOTIVATIONS

Physical systems become very susceptible to external perturbations close to a phase transition. In several theoretical approaches the huge increase of the relaxation time of super-cooled liquid is traced back to the proximity to a phase transition [41]. Therefore, it would be natural to expect that responses to external fields become singular also approaching the glass transition. However, standard linear responses (as well as correlation functions) are known to remain quite featureless. In this work, following up [1], we show using general arguments that instead non-linear responses do increase. Furthermore, we work out detailed predictions within the Mode Coupling Theory of glasses and we show what is the relation between the growth of non-linear responses and the one of previously introduced probes of dynamic correlations.

In order to grasp why only non-linear responses may grow approaching the glass transition, it is instructive to recall the situation of standard critical phenomena and contrast it to the one of spin glasses. In standard critical phenomena there is a spontaneous symmetry breaking toward an ordered phase. The main consequence of the broken symmetry is that there are different but thermodynamically equivalent states in which the system can be found: they are all related by the symmetry at hand. For example, below the ferromagnetic transition the state with a given magnetization $M$ and the one characterized by the magnetization $-M$ are equivalent and the system will be in one or the other depending on boundary conditions, residual fields, etc. Switching on an external field that couples to the order parameter allows one to select one given state, e.g. a positive magnetic field selects the state with positive magnetization in ferromagnetic systems. As a consequence, it is easy to understand that just before the transition, where the system is at the brink of developing long range order, the response to an external field is huge and actually becomes infinite at the critical point. The situation is more subtle for systems characterized by the appearance and growth of amorphous long range order, as it is the case in spin glasses and is conjectured to be the case for glasses [2, 3, 4]. The only diverging linear susceptibility would be the staggered one: the response obtained by using a small field with spatial modulation correlated to the one of the amorphous state. Of course, this is not doable in experiments and not even in simulations since it is impossible to guess the external field which would impose a given amorphous long-range ordered state because it is amorphous as the state it pins (an
external field with an uncorrelated spatial modulation, e.g. an homogenous field, does not allow to select one state from the others and so it does not lead to singular responses). For spin glasses, the square of the staggered linear response can nevertheless be probed, since it is related to the static third order non-linear susceptibility $\chi_3$, which was shown to diverge at the transition. Similar arguments [1] (see also below) adapted to supercooled liquids - where the disorder is not quenched but self-induced - suggest that linear responses will be featureless but non-linear susceptibilities should instead increase approaching the glass transition. The main difference between spin glasses and structural glasses is that in the latter case one has to focus on dynamical non-linear responses. It was argued in [1], on the basis of physical and heuristic arguments, that the non-linear dielectric susceptibility $\chi_3(\omega)$ should exhibit a growing peak around $\omega \tau_\alpha = 1$, while $\chi_3(\omega = 0)$ should remain trivial, in contrast with the case of spin-glasses ($\tau_\alpha$ is the standard notation for the relaxation time of super-cooled liquids). However, the detailed shape of $\chi_3(\omega)$ in the glassy region is beyond the grasp of those heuristic arguments. Since the corresponding experiments are currently being performed [8, 9], it is quite important to get more precise predictions on the expected shape of $\chi_3(\omega)$. This is the primary aim of the present study, where we obtain for the first time, using general arguments made more precise in the context of the Mode Coupling Theory (MCT) [10] of the glass transition, some precise information on the non-linear susceptibility, in particular concerning both its frequency and temperature dependence. Our results can be generalized to other non-linear responses such as non-linear compressibility and non-linear rheological responses. These should be measurable for colloids approaching the glass transition.

It is important to relate the results on non-linear responses to the ones obtained recently on dynamical correlations. This is the second aim of our work. For purpose of self-consistency, we recall below some definitions and results that we will use in the following sections.

It was established in the last decade that glass-forming liquids become more and more dynamically correlated approaching the glass transition [11]. This phenomenon, related to an increasing heterogeneity in the dynamics, is remarkable since, for the first time, some type of spatial correlation has been clearly connected to the slowing down of the dynamics of supercooled liquids. In order to unveil the existence of dynamical correlations, one has to focus on some local probe of the relaxation dynamics - typically a two point function
\( \mathcal{O}(x, t) = \phi(x, t)\phi(x, 0) \) where \( \phi(x, t) \) could be the density fluctuation, \( \delta \rho(x, t) \), at position \( x \) and time \( t \), or the mobility field \( \phi \). A measure of dynamical spatial correlations is obtained by considering the four point correlator \( G_4(x - y; t) = \langle \mathcal{O}(x, t)\mathcal{O}(y, t) \rangle \), where the bracket denotes the usual connected average over dynamical histories. By analogy with standard critical phenomena, a 'susceptibility' \( \chi_4 \) may be naturally defined by spatially integrating \( G_4 \): \( \chi_4(t) = \int dx G_4(x, t) \). This 'dynamical susceptibility' \( \chi_4 \) has been intensively studied in the past few years, both theoretically and numerically \( [13, 14, 15, 16, 17, 18, 19, 20, 21] \).

One finds that \( \chi_4 \) reaches a peak value for time scales of the order of the relaxation time of the system \( \tau_\alpha \), and the height of this peak increases as the temperature is reduced, as a clear sign of the growth of some dynamical correlation length as the glass transition is approached. From an experimental point of view, however, four-point correlation functions are very difficult to measure directly, except in cases where one can monitor the trajectory of individual particles - for example granular and colloidal systems where \( \chi_4 \) can be measured directly and again shows interesting features as the system jams \( [22, 23, 24, 25] \).

Another interesting quantity, extensively studied in the context of dynamic heterogeneity in the past few years, is the derivative of the standard two-body correlation \( C(\tau) \) (or susceptibility \( \chi_1(\omega) \)) with respect to the temperature (or the density) - a quantity called \( \chi_T = T\partial C(\tau)/\partial T \) (or \( \chi_\rho = \rho \partial C(\tau)/\partial \rho \)) in \( [26] \). This is a non-standard linear dynamical response and is clearly an easily accessible quantity, which also shows a peak at times of the order of \( \tau_\alpha \) and whose height grows as the temperature is lowered \( [26, 27] \). This has lead to direct estimates of the size of the dynamical correlation length in supercooled liquids and glasses \( [26, 27, 28] \). The relation between \( \chi_4 \) and \( \chi_T \) is however highly non-trivial and has been investigated thoroughly in \( [19, 20] \). It was realized in these papers that the existence of conserved quantities (energy, density) crucially affects the properties of \( \chi_4 \), which depends both on the thermodynamic ensemble (NVE vs. NPT for example) and on the dynamics (Brownian vs. Newtonian for example). The true glassy correlation length, on the other hand, does not depend on these choices, and therefore the direct interpretation of \( \chi_4(t) \) in terms of a correlation volume is somewhat obscured. At a deeper level, the basic ingredient leading to the critical behaviour of \( \chi_4 \) turns out to be entirely contained in the response function \( \chi_T \) itself, as the field theoretical analysis of \( [19] \) explicitly demonstrates and the numerical results presented there fully confirm. For example, for Brownian dynamics or for Newtonian dynamics in the NVE ensemble, \( \chi_4 \approx \chi_T \), whereas for Newtonian dynamics in
the NVT ensemble, one rather finds $\chi_4 \approx \chi_T^2$, see [19, 20] for a detailed discussion.

A. Summary of results

One of the two main results of this work consists in obtaining the precise relation between non-linear responses and probes of dynamical correlations introduced previously in the literature. In particular, we shall focus on the third-order non-linear dielectric response $\chi_3(\omega)$ and work out its relationship with the dielectric dynamical susceptibility $\chi_T$. The latter is known to be related to $\chi_4$, see [19] for a detailed discussion. We will establish simple identities between $\chi_3$ and $\chi_T$ which hold whenever Time-Temperature Superposition (TTS) holds, i.e. whenever all dependence of the linear response of the system on external parameters (temperature, density, electric field, ...) comes through the dependence of the relaxation time on these parameters. This is a strict statement within MCT, where a true dynamical phase transition takes place at a finite temperature $T_c$ [10]. More precisely, we will show that at low enough frequency (in fact much smaller than the inverse of the relaxation time), the following relation holds:

$$\Im (\chi_3(\omega)) \approx \frac{\kappa \omega}{T^2} \chi_T(2\omega),$$  

(1)

where $\kappa$ is a slow varying function of the temperature, see the following sections for a precise definition. This relation is actually a consequence of a more general one relating $\chi_3(\omega)$ to the standard linear response $\chi_1(\omega)$, which is also valid only at low frequency and reads:

$$\chi_3(\omega) \approx \kappa \frac{\partial \chi_1(2\omega)}{\partial T},$$  

(2)

These simple relations do not extend over the whole frequency domain, however one could argue that they should do so in a scaling sense (as long as the TTS is valid). A general proof based on field theory along the lines of [19] is left for the future. In this work, we have checked that within MCT this is indeed what happens. Furthermore, within MCT, we have also worked out the complete critical behavior of $\chi_3$, which is sketched in Fig. 1.

- In the $\alpha$-regime, i.e. $\omega \sim 1/\tau_\alpha \sim \epsilon^{1/2a+1/2b}/\tau_0$, $\chi_3(\omega)$ grows and reaches its maximum, of height of order $1/\epsilon$, after which it decreases as $\omega^{-b/\tau_0}$ at large $\omega$. In this regime, one has the scaling form: $\chi_3(\omega) = \frac{1}{\epsilon} G(\omega \tau_\alpha)$.
- At the crossover between the early $\alpha$-regime and late $\beta$-regime $\chi_3(\omega)$ is of order $1/\sqrt{\epsilon}$. 

\[ \log |\chi_3(\omega)| \]

\[ \sim 1/\epsilon \]

\[ \sim 1/\sqrt{\epsilon} \]

\[ \log \omega \]

\[ \alpha \text{-regime} \quad (late) \quad \beta \text{-regime} \quad (early) \]

**FIG. 1**: Sketch of \( \log |\chi_3(\omega)| \) as a function of \( \log \omega \), showing five different frequency regimes:

\[ \omega \tau_\alpha \ll 1, \quad \omega \tau_\alpha \sim 1, \quad \omega \tau_\beta / \tau_\alpha \ll 1 \quad (\epsilon = T - T_c), \quad \omega \tau_\beta \gg 1, \quad \omega \tau_0 \sim 1. \]

Note that the low frequency limit is non zero but much smaller than the peak value for \( T \) close to \( T_c \).

- In the \( \beta \)-regime, i.e. \( \omega \sim 1/\tau_\beta \sim \epsilon^{1/2a}/\tau_0 \), \( \chi_3(\omega) \) decreases as \( \omega^{-b}\tau_\beta \) at small \( \omega \) and as \( \omega^{-a}\tau_\beta \) at large \( \omega \), with scaling form \( \chi_3(\omega) = \frac{1}{\sqrt{\epsilon}} F(\omega \tau_\beta) \)

Exponents \( a \) and \( b \) are well known critical exponents of MCT, which characterize respectively how the correlators decay and exit of the plateau; \( \tau_0 \) is a microscopic relaxation time. All along this paper, \( \epsilon = T - T_c \), the distance from the Mode Coupling critical temperature \( T_c \), will be our control parameter. We remark that the existence of the peak and the decrease at low frequency is a non trivial prediction since it is in contrast to what happens for the (trivial) non-linear response of uncorrelated Brownian dipoles \[29\] and for spin glasses (the decrease with an exponent three at high frequency sketched in Fig. 1 is instead trivial and
will be discussed later).

For symmetry reasons, the quadratic non-linear susceptibility $\chi_2(\omega)$ is zero for unpolarized systems. This would not be the case for example for polarized systems, or when considering the response to a density perturbation. Indeed, the non-linear response to a density perturbation contains a quadratic term. The arguments presented below make it clear that in that case $\chi_2(\omega)$ itself is directly related to $\chi_T$. We therefore expect that all the results presented below can be straightforwardly generalized to describe the long-wavelength ($q \to 0$) non-linear compressibility (or more general non-linear rheological responses) of supercooled liquids and colloids. Moreover, by adapting these arguments to the explicit results obtained for Inhomogenous Mode Coupling Theory $^{[30]}$ we will also extend these results to finite wavevectors $q$ and find that whenever TTS holds, $\chi_3(\omega)$ takes in the $\alpha$-region the scaling form conjectured in $^{[1]}$:

$$\chi_3(\omega) \sim \xi_\alpha^{2-\eta} G(\omega \tau_\alpha),$$

where $\xi_\alpha$ is the dynamical correlation length which also appears in $\chi_T$, and $\eta$ a certain critical exponent that within MCT is equal to minus 2.

### B. Organisation of the article

The organisation of the paper is as follows. We first introduce the theoretical framework needed to deal with non-linear responses to an external field and establish some general relations between different quantities that naturally appear (Section II). We then exploit - when they exist - the Time-Temperature superposition (TTS) properties of the correlation function of glassy systems to establish in Section III general relations, valid at low frequency, between $\chi_3$ and the temperature derivative of the linear response. The critical behavior of $\chi_3(\omega)$ is obtained in Section IV using scaling arguments and within MCT. We finally discuss the extension of these results to spatially inhomogeneous perturbing fields and beyond MCT. We end by a conclusion with open problems, possible extensions and experimental suggestions.
II. NON-LINEAR SUSCEPTIBILITY: GENERAL FRAMEWORK

In this Section, we introduce the formalism needed to deal with non-linear response and establish a general relation between the non-linear susceptibility and a dynamical response function recently introduced in the literature, which was argued to capture the critical spatio-temporal correlations of the dynamics in the glassy region. In order to remain close to recent and ongoing experiments on glycerol, we use below the language of dielectric susceptibility. However, as mentioned in the Introduction, our arguments and results can be extended to more general non-linear susceptibilities (mechanical, magnetic, etc.).

A. Linear and non-linear response: small field expansion

Let us consider a dipolar molecular liquid in presence of a small external electric field oscillating at frequency $\omega$ in the $z$-direction. We denote it as:

$$E(t) = ze(t) \equiv z E \cos(\omega t),$$

where $z$ is the unit vector in the $z$ direction and $E(t) = E \cos(\omega t)$ is its $z$-component with peak field amplitude $E$.

When the external field is sufficiently small, the polarization vector (per particle) $P(t, E)$ can be expanded in powers of $E$. In the following we will denote $P(t, E)$ its $z$-component. Due to the rotational symmetry in the $x$-$y$ plane the other components are identically zero. Furthermore, because of the up-down symmetry in the $z$ direction, the polarization must be an odd function of $E$, i.e., $P(t, -E) = -P(t, E)$. As a consequence, the expansion of $P$ in powers of $E$ contains only odd terms:

$$P(t, E) = P_1(t)E + P_3(t)E^3 + O(E^5),$$

where $P_1(t)$ and $P_3(t)$ can be expressed as functional derivatives of the polarization with respect to the external field:

$$P_1(t) = \int_{t_1 < t} dt_1 \left. \frac{\delta P(t)}{\delta E(t_1)} \right|_{E=0} \cos(\omega t_1)$$

$$P_3(t) = \frac{1}{6} \int_{t_1, t_2, t_3 < t} dt_1 dt_2 dt_3 \left. \frac{\delta^3 P(t)}{\delta E(t_1) \delta E(t_2) \delta E(t_3)} \right|_{E=0} \cos(\omega t_1) \cos(\omega t_2) \cos(\omega t_3).$$

It is important to remark that the linear and non-linear response kernels in the above integrals are time translation invariant (TTI), i.e. they do not change if all time variables...
are shifted by the same amount. This comes from the fact that they are equilibrium response functions, measured in absence of the external field. Using this result and the specific form of the external field, Eq. (4), one finds:

\[ P(t, E) = E \Re (\chi_1(\omega) e^{i\omega t}) + \frac{E^3}{4} \Re (\chi_{1,2}(\omega) e^{i\omega t} + \chi_3(\omega) e^{3i\omega t}) + O(E^5). \]  

which defines the usual frequency dependent linear susceptibility, \( \chi_1(\omega) \), and the frequency dependent non-linear susceptibility, \( \chi_3(\omega) \), while \( \chi_{1,2}(\omega) \) is the \( E^2 \) correction to the first harmonic susceptibility \( \chi_1(\omega) \). The non-linear susceptibility \( \chi_3(\omega) \), which is the quantity will focus on throughout this paper, can be accessed experimentaly by filtering \( O(E^3) \) terms at frequency \( 3\omega \).

Following the same procedure, one can expand in powers of the electric field the (z-component) polarization correlation and linear response functions of the system driven by the electric field \( E(t) \). The up-down symmetry in the \( z \) direction implies that they both are even functions of \( E \). Therefore their expansion in power of \( E \) contains only even terms:

\[ C(t, t') = C_0(t, t') + C_2(t, t') E^2 + O(E^4) \]
\[ R(t, t') = R_0(t, t') + R_2(t, t') E^2 + O(E^4). \]  

\( C_0 \) and \( R_0 \) are the unperturbed correlation and response functions in absence of the external field. At equilibrium, they are functions only of the time difference \( \tau = t - t' \geq 0 \): \( C_0(t, t') = C_0(t - t') \) and \( R_0(t, t') = R_0(t - t') \). Moreover, the Fluctuation-Dissipation theorem (FDT) holds for the unperturbed correlation and response functions:

\[ R_0(\tau) = -\frac{1}{T} \frac{\partial C_0(\tau)}{\partial \tau}. \]  

The second-order correlation and response functions appearing in Eq. (8) are defined as:

\[ C_2(t, t') = \frac{1}{2} \int_{t_1, t_2 < t} dt_1 dt_2 \frac{\delta^2 C(t, t')}{\delta E(t_1) \delta E(t_2)} \bigg|_{E=0} \cos(\omega t_1) \cos(\omega t_2). \]  

\[ R_2(t, t') = \frac{1}{2} \int_{t_1, t_2 < t} dt_1 dt_2 \frac{\delta^2 R(t, t')}{\delta E(t_1) \delta E(t_2)} \bigg|_{E=0} \cos(\omega t_1) \cos(\omega t_2). \]  

The second order correlation function, \( C_2(t, t') \), was introduced in the context of spin-glasses by Huse in the static limit, and more recently studied in details in [31, 32]. Neither TTI nor FDT holds for \( C_2(t, t') \) and \( R_2(t, t') \), which are explicit functions of both \( t \) and
However, the response kernels appearing inside the above integrals are TTI. Using this property and developing the product of cosines in complex exponentials one finds easily that:

\[ C_2(t, t') = c_0^{(\omega)}(t - t') + \left( e^{i\omega(t + t')} c_1^{(\omega)}(t - t') + c.c. \right) \]
\[ R_2(t, t') = r_0^{(\omega)}(t - t') + \left( e^{i\omega(t + t')} r_1^{(\omega)}(t - t') + c.c. \right). \]  \hspace{1cm} (12)

**B. Relation between non-linear susceptibility and second-order response**

In the following we aim at establishing a relation between the second order response function defined above and the non-linear susceptibility. By definition, the electric polarization is given by the convolution of the response function with the external field:

\[ P(t) = \int_{-\infty}^{t} dt' R(t, t') E(t'). \]  \hspace{1cm} (13)

Therefore, using Eqs. (5) and (8), we simply get that:

\[ EP_1(t) = \int_{-\infty}^{t} dt' R_0(t - t') E(t'), \]  \hspace{1cm} (14)

and

\[ EP_3(t) = \int_{-\infty}^{t} dt' R_2(t, t') E(t'). \]  \hspace{1cm} (15)

Thus, the component of order \( E^3 \) of the polarization (related to \( \chi_3 \)) turns out to be just the convolution of the field with the function \( R_2(t, t') \) defined in Eq. (10). As a consequence, using the above expression, together with Eq. (12), we find, for an oscillating field at frequency \( \omega' \):

\[ P_3(t) = \Re \left\{ e^{i\omega t} \left( \tilde{r}_0^{(\omega)}(0) + \tilde{r}_1^{(\omega)}(0) \right) + e^{3i\omega t} \tilde{r}_1^{(\omega)}(2\omega) \right\}, \]  \hspace{1cm} (16)

where we denoted \( \tilde{r}_0^{(\omega)}(\omega') \) and \( \tilde{r}_1^{(\omega)}(\omega') \) the semi-Fourier transform (with respect to \( \tau \)) at frequency \( \omega' \) of the coefficients appearing in the Fourier expansion, \( r_0^{(\omega)}(\tau) \) and \( r_1^{(\omega)}(\tau) \). The previous equation allows us to establish a general relation between \( \chi_3^{(\omega)} \) and the Fourier transform of \( r_n^{(\omega)}(\tau) \):

\[ \chi_3^{(\omega)} = 4 \tilde{r}_1^{(\omega)}(2\omega) = 4 \int_{0}^{\infty} d\tau e^{-2i\omega\tau} r_1^{(\omega)}(\tau). \]  \hspace{1cm} (17)

This relation will be very useful. Using scaling arguments we will now obtain the critical behavior of \( r_1^{(\omega)}(\tau) \) within MCT. The relation above will then allow us to obtain straightforwardly the scaling behaviour of \( \chi_3^{(\omega)} \).
III. LOW FREQUENCY LIMIT AND RELATIONSHIP TO DYNAMICAL LINEAR RESPONSES

A. Low frequency limit

In the following we focus on the evolution of the correlation and response function when the period of oscillation of the external field is much smaller than the relaxation time, in other words in the low-frequency limit $\omega \tau_\alpha \ll 1$. By definition all degrees of freedom relevant for this time-sector of the response or correlation relax on timescales much smaller than $\omega^{-1}$. As a consequence the correlation/response functions are expected to be given by their equilibrium expression in the presence of a quasi-constant external field $E \cos(\omega t)$. Therefore, in this regime:

$$C(t, t') = C_{eq}(t - t', E \cos(\omega t)) \quad (18)$$
$$R(t, t') = R_{eq}(t - t', E \cos(\omega t)).$$

Since we are interested in the small $E$ behavior, we can expand the above expression up to second order in $E$. For the response function, for instance, this yields:

$$R_{eq}(\tau, E \cos(\omega t)) \approx R_0(\tau) + \frac{E^2 \cos^2(\omega t)}{2} \frac{\partial^2 R_{eq}(\tau, E)}{\partial E^2} \bigg|_{E=0}, \quad (19)$$

where $R_0(\tau)$ is the unperturbed equilibrium response function, and the derivative is computed with respect to a constant external field. Comparing the last equation with Eq. (12) in the stationary regime ($t, t' \to \infty$ with $\tau = t - t'$ finite) we find a very simple expression for the $n = 1$ component of the expansion $r_1^{(\omega)}(\tau)$ in the regime $\omega \tau, \omega \tau_\alpha \ll 1$:

$$r_1^{(\omega)}(\tau) = \frac{1}{8} \frac{\partial^2 R_{eq}(\tau, E)}{\partial E^2} \bigg|_{E=0}, \quad (20)$$

An analogous relation holds for the correlation function:

$$c_1^{(\omega)}(\tau) = \frac{1}{8} \frac{\partial^2 C_{eq}(\tau, E)}{\partial E^2} \bigg|_{E=0}. \quad (21)$$

These general results provide important insights to understand the behaviour of the non-linear susceptibility. First of all, since the correlation and response functions appearing in Eq. (18) are defined in equilibrium in presence of a constant field, they must obey FDT. Therefore one can establish a sort of generalized Fluctuation-Dissipation relation between
the second order correlation and response functions, which reads:

\[ r_1^{(\omega)}(\tau) = -\frac{1}{T} \frac{\partial c_1^{(\omega)}(\tau)}{\partial \tau}, \quad (22) \]

which is however only valid in the low frequency domain \( \omega \tau, \omega \tau_\alpha \ll 1 \).

**B. Relationship with dynamical linear responses**

The results of the previous Section allow us to establish an interesting relation between the second order correlation and response functions and the dynamical response \( \chi_T(\tau) \equiv T \frac{\partial C_{eq}(\tau)}{\partial T} \) that was recently introduced and extensively studied in \[19, 20, 26, 27, 28, 30\], in particular in relation with the behaviour of the four-point dynamical correlation function.

The key idea is that in the glassy dynamics regime, the equilibrium correlation function \( C_{eq}(\tau) \) satisfies to a good approximation the time-temperature superposition (TTS) principle. This means that the correlation function for different temperatures, densities, external fields, etc., can be written as a function of \( \tau / \tau_\alpha(T, \rho, E) \), and the whole \( T, \rho, E \) dependence is captured by the structural relaxation time \( \tau_\alpha(T, \rho, E) \). This becomes actually an exact statement within the \( \alpha \)-regime of MCT, when the system approaches the dynamical critical point. In this case, the dynamical critical temperature is expected to show a quadratic dependence on the external field (for small fields) of the form:

\[ T_{MCT}(E) \approx T_{MCT}(E = 0) + \kappa E^2. \quad (23) \]

Close to the critical point, a small field changes slightly the critical temperature. Since the only thing that matters for the critical behaviour is the distance from the critical point, one finds that applying a small field is equivalent to a small change in temperature. Note that this implies that the relations found below carry over, within MCT, to the \( \beta \)-regime as well.

More generally, since \( \tau_\alpha(T, \rho, E) \) is expected to be an even function of \( E \) because of the up-down symmetry, it should rather be written as \( \tau_\alpha(T, \rho, \Theta) \), with \( \Theta = E^2 \). Then approximate TTS immediately leads to:

\[ \frac{\partial C_{eq}(\tau)}{\partial \Theta} \approx \frac{\partial \tau_\alpha / \partial \Theta}{\partial \tau_\alpha / \partial T} \frac{\partial C_{eq}(\tau)}{\partial T}. \quad (24) \]

Around \( E = 0 \) one has \( \partial^2 C_{eq}/\partial E^2 = 2 \partial C_{eq}/\partial \Theta \); using the above results one finds the very interesting relation (valid for \( \omega \tau \ll 1 \)):

\[ c_1^{(\omega)}(\tau) \approx \frac{\kappa}{4} \frac{\partial C_{eq}(\tau)}{\partial T} = \frac{\kappa}{4T} \chi_T(\tau), \quad (25) \]
where \( \kappa = \frac{\partial \tau}{\partial \Theta} / \frac{\partial \tau}{\partial T} \). Analogously one finds for the response function (using the FDT relation (22)):

\[
\tau^{(\omega)}(\tau) = -\frac{\kappa}{4T^2} \frac{\partial \chi_T(\tau)}{\partial \tau}.
\]

Using Eq. (17) one directly finds the relation between \( \chi_3 \) and \( \tilde{\chi}_T \) given in Eq. (1).

One can in fact obtain a slightly more general relation provided the Fourier transform of Eq. (17) is dominated by the region \( \omega \tau \ll 1 \). One then finds with some degree of generality that:

\[
\chi_3(\omega) \approx \frac{\partial \chi_1(2\omega)}{\partial \Theta},
\]

and finally, using TTS, Eq. (2). This result is important because it establish a firm link with the linear dynamical responses that are often used to evaluate dynamical correlations.

More generally, the amplitude of the correlation function also depends on temperature and electric field:

\[
C_{eq}(\tau) = A(T, E, ...) c_{eq}(\frac{t}{\tau_\alpha}),
\]

and the derivative of \( A \) brings extra contributions that affect the above equalities. In glassy systems, the relaxation time \( \tau_\alpha \) is usually most sensitive to external parameters, and it is reasonable to discard these corrections, except at zero frequencies where the above contribution is in fact zero. The case in spin-glasses is very different, because the correlation amplitude itself depends critically on temperature.

**IV. CRITICAL BEHAVIOUR OF THE NON-LINEAR SUSCEPTIBILITY WITHIN MCT: SCALING ARGUMENTS**

In this section we analyze the behaviour of the non-linear susceptibility using general physical and scaling arguments. These results can be confirmed by an exact analysis of the schematic Mode Coupling (p-spin) equations. For sake of clarity of this paper, the technical aspects related to the derivation of the schematic MCT equations in presence of an external oscillating field and their analysis will presented in a separate publication [33].

**A. Technical preliminaries**

The results above establish a clear connection between the dynamical response \( \chi_T \) and the non-linear susceptibility \( \chi_3 \). In the following, we will exploit the consequences of this
connection within the MCT framework, using scaling arguments. Note that we will implicitly assume, as previously done in the literature, that the results obtained within MCT for density correlation functions carry out to polarization fluctuations. In fact, experimentally, it has been established that the dielectric susceptibility probes the glassy dynamics as well as the density correlation functions, see e.g. [34]. A quantitative theory of dielectric polarization fluctuations and their coupling to density fluctuations in the slow dynamics regime would be certainly very involved due to the presence of Onsager cavity fields [35].

Let us now recall the behaviour of $\chi_T(\tau)$ within MCT [20, 30], where two critical relaxation regimes occur close to the MCT transition: the $\beta$-regime, with relaxation time $\tau_\beta \sim \tau_0 \epsilon^{-1/2}$, and the $\alpha$-regime, with relaxation time $\tau_\alpha \sim \tau_\beta \epsilon^{-1/2} \gg \tau_\beta$.

The critical properties of $\chi_T(\tau)$ have been derived in terms of scaling functions both in the $\alpha$ and $\beta$-regimes [20]. Using these results, the relations established above and the FDT of Eq. (22), one can obtain the scaling behaviour of $c_1^{(\omega)}(\tau)$ and $r_1^{(\omega)}(\tau)$ close to the MCT transition in the different time regimes. The strategy is the following: we start with very low frequencies, where we know the scaling behaviour from the relation with $\chi_T$, and extend it to the whole regimes assuming that critical scaling holds. Finally, from the scaling behavior of $c_1^{(\omega)}(\tau)$ and $r_1^{(\omega)}(\tau)$ we will obtain the one of $\chi_3(\omega)$. We will first analyse the $\beta$-regime and afterwards the $\alpha$-regime.

1. The $\beta$-regime

Let us first analyze the regime $\omega \tau \ll 1$. In this case, one can use the results (25,26) valid in the regime $\tau_0 \ll \tau \sim \tau_\beta \ll \tau_\alpha$ and the known behavior of $\chi_T$ [20, 30] to find:

$$c_1^{(\omega)}(\tau) \approx \frac{1}{\sqrt{\epsilon}} c_\beta \left( \frac{\tau}{\tau_\beta} \right)$$

$$r_1^{(\omega)}(\tau) \approx \frac{1}{\sqrt{\epsilon}} \frac{1}{\tau_\beta} r_\beta \left( \frac{\tau}{\tau_\beta} \right),$$

where the scaling function $c_\beta(x)$ behaves asymptotically as $x^a$ for $x \ll 1$ and as $x^b$ for $x \gg 1$, whereas $r_\beta(x)$ behaves as $x^{a-1}$ for $x \ll 1$ and as $x^{b-1}$ for $x \gg 1$.

On the other hand, for very large frequencies, such that $\omega \tau \gg 1$, the field oscillates so fast that the system has no time to respond and one expects vanishing (for $\omega \tau \to \infty$) small second order correlation and response functions.
Finally, for $\omega \tau$ of the order of one, the most general scaling behavior in the $\beta$-regime generalizing the one above reads:

$$c_1^{(\omega)}(\tau) \approx \frac{1}{\sqrt{\epsilon}} \hat{f}_\beta \left( \frac{\tau}{\tau_\beta}, \omega \tau \right)$$

(30)

$$r_1^{(\omega)}(\tau) \approx \frac{1}{\sqrt{\epsilon}} \frac{1}{\tau_\beta} \hat{g}_\beta \left( \frac{\tau}{\tau_\beta}, \omega \tau \right).$$

(31)

The most general assumption compatible with previous results is a factorized form for $\hat{f}_\beta$ and $\hat{g}_\beta$ in both regimes $\tau \gg \tau_\beta$ and $\tau \ll \tau_\beta$. In the late $\beta$-regime, one has (with $L$ for ‘late’):

$$c_1^{(\omega)}(\tau) \approx \frac{1}{\sqrt{\epsilon}} \left( \frac{\tau}{\tau_\beta} \right)^{b} f_\beta^L(\omega \tau)$$

(32)

$$r_1^{(\omega)}(\tau) \approx \frac{1}{\sqrt{\epsilon}} \frac{1}{\tau_\beta} \left( \frac{\tau}{\tau_\beta} \right)^{b-1} g_\beta^L(\omega \tau).$$

(33)

where both functions $f_\beta^L, g_\beta^L$ tend to a constant when their argument $\omega \tau$ is small, and tend to zero when $\omega \tau$ is large. In the early $\beta$-regime, a similar result holds, with a priori different scaling functions $f_\beta^E, g_\beta^E$ ($E$ for ‘early’):

$$c_1^{(\omega)}(\tau) \approx \frac{1}{\sqrt{\epsilon}} \left( \frac{\tau}{\tau_\beta} \right)^{a} f_\beta^E(\omega \tau)$$

(34)

$$r_1^{(\omega)}(\tau) \approx \frac{1}{\sqrt{\epsilon}} \frac{1}{\tau_\beta} \left( \frac{\tau}{\tau_\beta} \right)^{a-1} g_\beta^E(\omega \tau).$$

(35)

These new functions $f_\beta^E, g_\beta^E$ again tend to a constant when their argument $\omega \tau$ is small, and tend to zero when $\omega \tau$ is large.

In this regime, the explicit dependence with $\tau$ and $\omega$ occurs only through the rescaled time and frequency $\tau/\tau_\beta$ and $\omega \tau_\beta$. In the rest of the text, we will frequently use the variables $\hat{\tau} = \tau/\tau_\beta$, $\hat{\omega} = \omega \tau_\beta$ and $x = \omega \tau$.

2. The $\alpha$-regime

The behaviour of $c_1^{(\omega)}, r_1^{(\omega)}$ in the $\alpha$-regime follows similar scaling laws. When $\omega \tau \ll 1$, the results of [20, 30] allow one to obtain:

$$c_1^{(\omega)}(\tau) \approx \frac{1}{\epsilon} c_\alpha \left( \frac{\tau}{\tau_\alpha} \right)$$

(36)

$$r_1^{(\omega)}(\tau) \approx \frac{1}{\epsilon} \frac{1}{\tau_\alpha} r_\alpha \left( \frac{\tau}{\tau_\alpha} \right),$$
The matching between the late $\beta$-regime and the $\alpha$-regime determine the asymptotic behaviour of the scaling functions defined above. One finds that $c_\alpha(x \ll 1)$ behaves as $x^b$ and $r_\alpha(x \ll 1)$ as $x^{b-1}$, whereas both functions tend exponentially fast to zero for $x \gg 1$.

When $\omega\tau$ is not small, the scaling behaviour in the $\alpha$-regime reads:

$$c_1^{(\omega)}(\tau) \approx \frac{1}{\epsilon} f_\alpha\left(\frac{\tau}{\tau_\alpha}, \omega\tau\right)$$

(37)

$$r_1^{(\omega)}(\tau) \approx \frac{1}{\epsilon} g_\alpha\left(\frac{\tau}{\tau_\alpha}, \omega\tau\right).$$

(38)

In the early $\alpha$-regime, that is when $\tau \ll \tau_\alpha$, one finds:

$$c_1^{(\omega)}(\tau) \approx \frac{1}{\epsilon} \left(\frac{\tau}{\tau_\alpha}\right)^b f_\alpha(\omega\tau)$$

(39)

$$r_1^{(\omega)}(\tau) \approx \frac{1}{\epsilon} \left(\frac{\tau}{\tau_\alpha}\right)^{b-1} g_\alpha(\omega\tau).$$

(40)

Furthermore, by requiring the matching between the two regimes of large $\tau/\tau_\beta$ and small $\tau/\tau_\alpha$, one finds that the scaling functions $f_\alpha^E(x)$ and $g_\alpha^E(x)$ are the same as $f_\beta^L(x)$ and $g_\beta^L(x)$.

As in the $\beta$-regime, the explicit dependence with $\tau$ and $\omega$ occurs only through the rescaled time and frequency $\tau/\tau_\alpha$ and $\omega\tau_\alpha$. In the rest of the text, we will frequently use the variables $\tau = \tau/\tau_\alpha$, $\omega = \omega\tau_\alpha$ (and also $x = \omega\tau$).

In Fig. 2 we show a sketch of the behavior of $|c_1^{(\omega)}(\tau)|$ that summarizes all our previous findings.

**B. Scaling behavior of $\chi_3(\omega)$**

In the previous section we have determined the scaling forms governing the time and temperature dependence of $r_1^{(\omega)}(\tau)$ and $c_1^{(\omega)}(\tau)$. Using these results we can now easily analyze the critical behaviour of the non-linear susceptibility, by computing its Fourier transform at frequency $2\omega$, according to Eq. (17). We again focus in turn on the $\beta$-regime and then on the $\alpha$-regime, before commenting on the zero and infinite frequency limits.

1. The $\beta$-regime

Let us first consider probing frequencies of the order of the inverse of the $\beta$-relaxation time. We set $\hat{\omega} = \omega\tau_\beta$ and assume that only the $\beta$-regime of $r_1^{(\omega)}(\tau)$ contributes to Eq. (17).
FIG. 2: Sketch of log $|c_1^{(ω)}(τ)|$ as a function of log $τ$. In the $ω \to 0$ limit $c_1^{(ω)}(τ)$, behaves as $χ_τ(τ)$, i.e., it scales as $1/\sqrt{\varepsilon}(τ/τ_β)^a$ in the early $β$-regime and as $1/\sqrt{\varepsilon}(τ/τ_β)^b$ in the late $β$-regime (or, equivalently, as $1/ε(τ/τ_α)^b$ in the early $α$-regime). In the $α$-regime $|c_1^{(ω)}(τ)|$ reaches a maximum of order $1/ε$. At finite frequency $ω$, $|c_1^{(ω)}(τ)|$ drops to values of $O(1)$ as $τ \gtrsim 1/ω$ (red curves).

This assumption can be fully justified by the exact analysis of the schematic Mode Coupling equations [33]. Indeed one can show that $r_1^{(ω)}(τ \sim τ_α)$ is small due to the fact that the scaling function $g_α^E(x)$, introduced in Eq. (40), vanishes as $1/x^{1+b}$ at large $x$. Therefore, for probing frequencies of the order of the inverse of the $β$-relaxation time, the contribution to the non-linear susceptibility coming from the time integral in the $α$-regime is negligible in Eq. (17).

One then finds that:

$$χ_3(ω) \simeq \frac{1}{\sqrt{ε}} F(ω)$$ (41)
where the function $\mathcal{F}(x)$ is defined as:

$$
\mathcal{F}(\hat{\omega}) = \frac{4}{\hat{\omega}} \int_0^\infty du \, e^{-2i\hat{\omega}u} \hat{g}_\beta \left( \frac{u}{\hat{\omega}}, u \right)
$$

The asymptotic behaviour of the scaling function $\mathcal{F}$ can easily be obtained from the results of the previous section. One finds:

$$
\mathcal{F}(\hat{\omega}) \simeq 4\hat{\omega}^{-b} \int_0^\infty du \, u^{b-1} e^{-2i\hat{\omega}u} \hat{g}_\beta^L(u) \quad \omega \tau_\beta \ll 1 
$$

$$
\simeq 4\hat{\omega}^{-a} \int_0^\infty du \, u^{a-1} e^{-2i\hat{\omega}u} \hat{g}_\beta^E(u) \quad \omega \tau_\beta \gg 1.
$$

Using the asymptotic properties of $g_\beta^L(u), g_\beta^E(u)$ and the fact that $a, b$ are between zero and one insures the convergence of the integrals appearing in the above equation, at both small and large $u$. This confirms that the scaling behaviour of $\chi_3(\omega)$ in this region is indeed dominated by the $\beta$-regime of $r_1^{(\omega)}(\tau)$. Note that in the high frequency region the $\epsilon$ dependence of $\chi_3(\omega)$ drops out, as it should in order to match the non critical $\tau_0^{-1}$ frequency regime.

2. The $\alpha$-regime

We now consider the $\alpha$-regime, where we set $\overline{\omega} = \omega \tau_\alpha$, and again assume that only the scaling form of $r_1^{(\omega)}(\tau)$ in this same regime, Eq. (38), contributes significantly to Eq. (17). Indeed, the contribution due to the time integral in the $\beta$-regime is at least a factor $\sqrt{\epsilon}$ smaller than the one coming from the $\alpha$-regime, and yields a subleading contribution to the critical behavior of $\chi_3(\omega)$. We then find that the non-linear susceptibility scales as:

$$
\chi_3(\omega) \simeq \frac{1}{\epsilon} \mathcal{G}(\overline{\omega})
$$

where the function $\mathcal{G}(x)$ is defined as:

$$
\mathcal{G}(\overline{\omega}) = \frac{4}{\overline{\omega}} \int_0^\infty du \, e^{-2i\overline{\omega}u} \overline{g}_\alpha \left( \frac{u}{\overline{\omega}}, u \right)
$$

Clearly, because of the matching of $\overline{g}_\alpha$ for small first arguments with $\hat{g}_\beta$ at large first arguments, we find that the scaling of the early $\alpha$-regime ($\omega \tau_\alpha \gg 1$) of the non-linear susceptibility matches with that of the late $\beta$-regime ($\omega \tau_\beta \ll 1$), with:

$$
\chi_3(\omega) \propto \epsilon^{(b-a)/2a} \omega^{-b}.
$$
3. Low frequency limit

In the low frequency limit, one finds that $\chi_3(\omega)$ decreases from its peak value $\epsilon^{-1}$ reached for $\omega \sim 1/2\tau_\alpha$ to a non critical, finite value given by Eq. (27). As discussed in [1], contrary to the case of spin-glasses, the non-linear susceptibility is critical only for small but non zero values of the frequencies. Zero frequency corresponds to a static equilibrium response (or correlation, via FDT). In glasses, these are not expected to have any critical behavior.

In particular, in the low frequency limit, one can expand Eq. (17) up to second order in $\omega \tau$. Using Eq. (19) we have:

$$\chi_3(\omega) \approx \kappa \int_0^\infty d\tau \left( 1 - 2i\omega \tau - 2\omega^2 \tau^2 \right) \frac{\partial R_{eq}(\tau)}{dT} \left. \right|_{T=0}$$

where

$$\kappa \int_0^\infty d\tau \left\{ \chi_1(0) \left( 1 - 2i\omega A_1 \tau_\alpha - 4\omega^2 A_2 \tau_\alpha^2 \right) \right\},$$

and the zero frequency limit of the linear susceptibility, $\chi_1(0)$, equals the static polarization fluctuations (along the z-axis) divided by temperature, $N\langle P^2 \rangle / T$. $A_1$ and $A_2$ are two temperature-independent constants defined as $A_i = \int_0^\infty ds s^i \chi_eq(s)$ (here we have used again the time-temperature superposition principle, writing $R_{eq}(\tau) = \chi_1(0) r_{eq}(\tau/\tau_\alpha)/\tau_\alpha$). The last equation allows us to determine the low frequency behavior of the real and imaginary part of the non-linear susceptibility:

$$\Re (\chi_3(\omega)) \approx \kappa \frac{d\chi_1(0)}{dT} + B_1\omega^2 + O((\omega \tau_\alpha)^4)$$

$$\Im (\chi_3(\omega)) \approx B_2\omega + O((\omega \tau_\alpha)^3),$$

with $B_1 = -4\kappa A_2 \omega^2 d(\chi_1(0)\tau_\alpha^2)/dT > 0$ and $B_2 = -2\kappa A_1 \omega d(\chi_1(0)\tau_\alpha)/dT > 0$.

4. Large frequency limit

At very large frequencies (very small timescales) the non-linear susceptibility is vanishing because the system has not enough time to respond to the oscillating field. One could argue that the analysis of Eq. (6) at very large frequencies yields:

$$P_3(t) \sim \frac{\delta^3 P}{\delta E^3(0)} \left. \right|_{E=0} \left[ \int_0^t dt_1 \left( e^{i\omega t_1} + e^{-i\omega t_1} \right) \right]^3. \tag{47}$$

As a result, at very large frequency the non-linear susceptibility behaves as:

$$\chi_3(\omega \rightarrow \infty) \sim \frac{1}{(i\omega)^3} \frac{\delta^3 P}{\delta E^3(0)} \left. \right|_{E=0}. \tag{48}$$
This analysis is oversimplified and assumes analytic properties of the function \( \frac{\delta^3 P}{\delta E(t_1) \delta E(t_2) \delta E(t_3)} \) that are not granted and may depend strongly on the microscopic dynamics. For instance, in the case of Ising spins with a Monte Carlo heat bath dynamics one can easily verify that the previous arguments do not apply and the large frequency behavior is proportional to \( 1/(i\omega) \). The conclusion is that the high frequency behavior depends on the underlying microscopic dynamics and, likely, on the type of the non-linear response considered. In the case of non-linear dielectric susceptibility the underlying microscopic dynamics should be provided by Langevin equations for dipoles in a non-polar solvent (this is an approximation since at extremely high frequency inertia effects will play a role). To work out the high frequency behavior one can neglect interactions with other dipoles and the coupling to structural relaxation. Thus, the analysis of the non-linear response of a single dipole in a non-polar solvent worked out in \[36\] should apply. The outcome is the \( 1/(i\omega)^3 \) behavior discussed above.

C. Beyond schematic Mode Coupling: general considerations and non-linear responses to time and space inhomogeneous fields

The previous scaling arguments are rather general. We emphasis here that they can be fully derived from a rigorous analysis of schematic Mode Coupling equations, in the framework of the spherical p-spin model in presence of an oscillating external field. Analysing the equations up to second order in the external field, it is possible to determine the critical behaviour obtained using scaling arguments in the previous sections.

Beyond the schematic approach, one may wonder about specific but important details such as the role of conserved variables like energy or density on the above results. As recalled in the introduction, we know that these conserved variables can dramatically change the scaling behaviour of \( \chi_4 \) for example, which also diverges as \( (T - T_c)^{-1} \) within a p-spin framework with Langevin dynamics, but diverges as \( (T - T_c)^{-2} \) when the contribution of conserved variables is taken into account \[19, 20\]. From a diagrammatic point of view, this is due to the presence of ‘squared ladder’ diagrams which gives the dominant contribution to \( \chi_4 \). One can check that due to the causality of the response functions, these diagrams in fact are absent when one computes the non-linear susceptibility and the above results are
expected to hold for a *bona fide* MCT theory of liquids. Thus, the result \[ \chi_3(\omega) \simeq \xi^{2-\eta} G(\omega \tau_\alpha), \] (49)
is expected to hold even beyond schematic MCT ($\xi$ is the dynamical correlation length which also appears in $\chi_T$). A complete proof could be obtained generalizing the Inhomogeneous MCT calculation of [30] to account for a space and time dependent source term, that would describe the non-linear response to an oscillating field with wave-vector $q$ and frequency $\omega$. In a first attempt, we adapt the previous scaling arguments to the explicit results of [30] on the wavevector-dependent dynamical response. This allow us to obtain the critical behavior of $\chi_3(\omega, q)$. In the $\beta$-regime one finds:

$$\chi_3(\omega, q) = \xi^2 H_\beta(\omega \tau_\beta, q \xi) \quad \xi = \epsilon^{-1/4}, \quad \tau_\beta = \epsilon^{-\frac{1}{2\nu}}$$

where the scaling function $H_\beta(x, y)$ is equal to $F(x)$ for $y = 0$, i.e. for a uniform electric field one finds back Eq. (41). For large $y$ one expects a power law behavior such as $\frac{h_\beta(x)}{y}$. As discussed in [30] this is needed to cancel out the diverging prefactor $\xi^2$ and match the critical behavior to the non-critical one taking place for $q \propto O(1)$. The asymptotic behavior with respect to $x$ is identical to the one already described for homogeneous fields. Very small $x$ correspond to the matching between $\alpha$ and $\beta$ regimes. Since in the $\alpha$ regime $\chi_3$ is expected to diverge as $\xi^4$, the matching imposes the behavior at small $x$: $\frac{h_\alpha(x)}{x^a}$ (where $h_\beta^L(y)$ is another scaling function). For large $x$ values, the field varies so rapidly that the system has not enough time to adjust and to respond to the field. Again, in order to cancel the diverging prefactor and match the non-critical behavior one expects a large $x$ behavior such as $\frac{h_\alpha^E(y)}{x^b}$ (where $h_\beta^E(y)$ is a third scaling function). It would be interesting to specify in more details the shape of the scaling functions $h_\beta, h_\beta^L, h_\beta^E$.

In the $\alpha$ regime one expects:

$$\chi_3(\omega, q) = \xi^4 H_\alpha(\omega \tau_\alpha, q \xi) \quad \xi = \epsilon^{-1/4}, \quad \tau_\alpha = \epsilon^{-\frac{1}{2\nu} - \frac{a}{2}}$$

where the scaling function $H_\alpha(x, y)$ is equal to $G(x)$ for $y = 0$, i.e. for a uniform electric field one finds back eq. (44). The same kind of arguments used above suggests for large $y$ a power law behavior: $H_\alpha(x, y) \simeq \frac{h_\alpha(x)}{y^\eta}$ (where $h_\alpha(x)$ is a scaling function). For very small $x$ the scaling function vanishes in order to match the $x = 0$ value corresponds to the non-critical (non diverging) static non-linear susceptibility. For large $x$ values in order to match the $\beta$ regime one expects a behaviour such as $\frac{h_\alpha^E(x)}{x^a}$ (where $h_\alpha^E(x)$ is another scaling function).
At this point, one may debate about the validity of the power law divergence of the relaxation time described by Mode Coupling Theory and of TTS. However, it is often observed that there are actually regimes, when the dynamics starts slowing down strongly, which are well described by MCT (and thus TTS). In these regimes we expect our predictions for $\chi_3$ to hold, as it seems to be the case for $\chi_4$ [37]. Furthermore, it was recently shown that MCT may be corrected including higher order terms. It was found that these corrections only affect the values of exponents $a$ and $b$, and $T_c$, but do not affect strongly scaling functions [38, 39]. This suggest that the MCT mechanism for describing the slowing down is rather robust and that the MCT regime could in principle being expanded at the price of changing the exponents (in particular the one covering the relaxation time, see e.g. [39]).

V. CONCLUSION

In this work, we have studied in detail the non-linear response of supercooled liquids. Although we are able to provide precise statements within a Mode-Coupling approach, some of our results are in fact more general and only require Time-Temperature Superposition to hold. In particular we expect our results to hold in generalization of Mode Coupling Theory such as [40].

An important theoretical result is the relation (27) between the non-linear response $\chi_3(\omega)$ and the temperature derivative of the usual linear susceptibility, $d\chi_1(2\omega)/dT$, valid at small frequencies (smaller than the inverse relaxation time). This bridges the gap between non-linear responses and probes of dynamic correlations such as three- and four-point correlations and temperature (or density) derivative of standard two-body correlations and response: they are all different facets of the same underlying physical phenomenon.

For larger frequencies - of the order of the inverse of the relaxation time - we have obtained a complete set of scaling predictions concerning the critical behavior of $\chi_3(\omega)$ within MCT. The main results are summarized in Fig. 1. Five different frequency regimes are identified: $\chi_3(\omega)$ exhibits a peak around frequencies of the order of half the inverse of the structural relaxation time of the system $\tau_\alpha$. The height of the peak grows as $(T-T_c)^{-1}$ (or equivalently as $\xi^4$) as the critical temperature is approached. For higher frequencies, $\chi_3(\omega)$ decays as power laws, with an exponent equal to $-b$ in the late $\beta$-regime, to $-a$ in the early $\beta$-regime, and finally to $-3$ at high frequencies.
Our results should be directly applicable to the non-linear dielectric constant of molecular glasses in the weakly supercooled regime where MCT is expected to be relevant, and for describing the non-linear compressibility or more general non-linear rheological responses of hard-sphere colloids close to the glass transition, where MCT does a fair job at describing their relaxation properties. However, it is well known that MCT fails for deeply supercooled liquids, when activated events start playing a major role in the relaxation. The detailed shape of $\chi_3(\omega)$ would require a full theoretical description of the dynamics in this regime, which is unavailable to date. Still, the general low frequency relation between $\chi_3$ and $d\chi_1/dT$, supplemented with the property of Time-Temperature superposition, allows one to give a firmer basis to the scaling relation conjectured in [1], namely that:

$$\chi_3(\omega) \approx \chi_3^* G(\omega \tau_\alpha),$$

where $G$ is a scaling function, and $\chi_3^* \propto d \ln \tau_\alpha / d \ln T$ is the peak value of the temperature derivative of $\chi_1(\omega)$, as measured in [26, 27, 28]. Following [19, 20, 26], we expect $\chi_T^*$ to increase as a power of the dynamical correlation length $\xi(T)$. The detailed shape of $G$ would obviously be worth knowing in order to compare with upcoming experimental results. As a guide, we give the result obtained assuming a Havriliak-Nagami form for the susceptibility and the validity of the relation between $\chi_3$ and $d\chi_1/dT$ at all frequencies, which has no justification apart from suggesting possible fitting functions. One finds:

$$G_{HN}(u) = \frac{(iu)^b}{(1 + (iu)^b)^{1+c}},$$

where $b, c$ are fitting exponents.

Among open problems worth investing is the extension of the present theory to the aging regime of glasses and spin-glasses. From an experimental point of view, a detailed study of the role of the electric field on the glass properties of dipolar liquids (such as glycerol) would be very interesting. For example, the evolution of the glass transition temperature as a function of the field $E$ would allow one to measure the proportionality coefficient $\kappa$ appearing in Eq. [27]. In spin-glasses, a detailed measurement of $\chi_3(\omega)$ would allow to shed light on the existence of spin-glass transition at non zero field, as argued in [1]. The behaviour of $\chi_3(\omega, t_w)$ in the aging phase would furthermore be a very useful probe of the aging process in spin-glasses, in particular during rejuvenation cycles. Numerical simulations of $\chi_3(\omega, t_w)$, using the zero-field techniques developed in [31, 32], would be worth pursuing.
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List of figures

Figure 1 Sketch of log $|\chi_3(\omega)|$ as a function of log $\omega$, showing five different frequency regimes: $\omega \tau_\alpha \ll 1$, $\omega \tau_\alpha \sim 1$, $\tau_\beta/\tau_\alpha \ll \omega \tau_\beta \ll 1$, $\omega \tau_\beta \gg 1$, $\omega \tau_0 \sim 1$. Note that the low frequency limit is non zero but much smaller than the peak value for $T$ close to $T_c$.

Figure 2 Sketch of log $|c_1^{(\omega)}(\tau)|$ as a function of log $\tau$. In the $\omega \to 0$ limit $c_1^{(\omega)}(\tau)$, behaves as $\chi_T(\tau)$, i.e., it scales as $1/\sqrt{\tau/\tau_\beta}$ in the early $\beta$-regime and as $1/\sqrt{\epsilon(\tau/\tau_\beta)}$ in the late $\beta$-regime (or, equivalently, as $1/\epsilon(\tau/\tau_\alpha)$ in the early $\alpha$-regime). In the $\alpha$-regime $|c_1^{(\omega)}(\tau)|$ reaches a maximum of order $1/\epsilon$. At finite frequency $\omega$, $|c_1^{(\omega)}(\tau)|$ drops to values of $O(1)$ as $\tau \gtrsim 1/\omega$ (red curves).

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Whether the transition is avoided or it takes place at finite or zero temperature depends on the approach.

For some technical reasons the function $\chi_4$ was called 'susceptibility' in [15]. This terminology is still used although is a measure of the fluctuation of the dynamics and not a response function.