PHYSICAL REVIEW B **84**, 104204 (2011)

Nonlinear dielectric susceptibilities: Accurate determination of the growing correlation volume in a supercooled liquid

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(Received 13 May 2011; revised manuscript received 15 July 2011; published 12 September 2011)

The nonlinear dielectric susceptibilities $\chi_3^{(1)}(\omega,T)$ and $\chi_3^{(3)}(\omega,T)$, corresponding respectively to the first- and third-harmonic responses, have been measured in supercooled glycerol close to the glass transition temperature T_g. By analyzing the two contributions to the nonlinear response, saturation of the polarization and glassy correlations, we show that the first one is dominant at low frequencies and verify the scaling prediction of Bouchaud and Biroli [Phys. Rev. B **72**, 064204 (2005)] in what concerns the second one. Such a detailed investigation allows an accurate determination of the temperature dependence of the average number of correlated molecules $N_{\text{corr}}(T)$.

DOI: 10.1103/PhysRevB.84.104204 PACS number(s): 64.70.kj, 77.22.−d, 89.75.Da

I. INTRODUCTION

The glass transition remains a topic of strong interest because it is characterized by an increase of the viscosity when the temperature decreases that is yet unexplained.[1] A picture which could account for this liquid-solid transition is that of growing dynamical heterogeneities (DH's):[2,3] The extremely fast rise of the relaxation time when the temperature T is lowered would be related to an increase of the DH's sizes. For this reason, the temperature dependence of the average number $N_{\text{corr}}(T)$ of correlated molecules in a DH when T decreases toward the glass transition temperature T_g recently has become a major issue of the field.[4–6] Two methods for evaluating $N_{\text{corr}}(T)$ from experimental data have been put forward in the past several years. The first one uses the temperature derivative of a two-point correlation function $\phi(t,T)$ and yields $N_{\text{corr}}(T) \propto T\chi_T$, with $\chi_T = \partial\phi(t,T)/\partial T$.[4,6] The second one is based on the alternative current (a.c.) nonlinear susceptibility χ_3,[7,8] which describes the a.c. response of the fluid at a frequency 3 times that of the excitation (the latter can be of any nature, e.g., dielectric as it is the case in practice[8]). It has been shown[7] that χ_3 is related to $N_{\text{corr}}(T)$ through

$$\chi_3(\omega,T) \approx \frac{\epsilon_0(\Delta\chi_1)^2 a^3}{k_B T} N_{\text{corr}}(T)\,\mathcal{H}(\omega\tau_\alpha)\,, \tag{1}$$

where ω is the angular frequency, $\Delta\chi_1 = \chi_{\text{lin}}(\omega = 0) - \chi_{\text{lin}}(\omega \to \infty)$ is the part of the static linear susceptibility corresponding to the slow relaxation process we consider, a^3 the volume occupied by one molecule, and $\mathcal{H}$ a complex scaling function going to zero both for small and large arguments, the humped shape of $|\mathcal{H}(\omega\tau_\alpha)|$ being a distinctive feature of the glassy correlations. $\tau_\alpha(T)$ is the typical relaxation time at temperature T. As mentioned in Refs. 8 and 9, the method using the nonlinear susceptibility has the advantage over that based on $T\chi_T$ to be free of some assumptions that are not well under control. In addition, being inspired by the spin glass phase transition physics,[10] the method using χ_3 can be considered as an indicator of the possible existence of an underlying phase transition for structural glasses.

Recently, we have measured the third-harmonic nonlinear susceptibility in supercooled glycerol close to T_g, using a specially dedicated experiment based on a two-capacitors bridge.[11] Our data verified the scaling prediction of Ref. 7 given by Eq. (1), and the dependence of $N_{\text{corr}}(T)$ could be determined experimentally from them. In practice, investigating the scaling predicted by Eq. (1) consists in verifying that the complex quantity $\chi_3(\omega,T)$ depends only on the product $\omega\tau_\alpha(T)$, except that the modulus of $\chi_3(\omega,T)$ should depend on T for a given value of $\omega\tau_\alpha(T)$. However, in doing so, it appears that one of the main limitations to this study of the scaling is the fact that *two* physical mechanisms contribute to the nonlinear susceptibility. The first one stems from the dynamical correlations among the molecules and is given by Eq. (1). In what follows, this contribution to the nonlinear susceptibility will be called singular. It was theoretically shown in Ref. 7 that on quite general grounds this is related to dynamical correlations that emerge when decreasing T. Several physical mechanisms aimed at explaining the growth of dynamical correlations have been put forward in the literature (see, e.g., the book quoted in Ref. 9). The second contribution is due to the standard well-known saturation of the microscopic polarization of the dipoles.[12,13] In what follows, this contribution to the nonlinear susceptibility will be called "trivial," as it should be present whatever the system under study. On general grounds, one expects $\chi_{3,\text{trivial}}$ to be negligible with respect to $\chi_{3,\text{singular}}$ only in the case where N_{corr} becomes infinite. This is not the case of the glass transition, since the various estimates yield N_{corr} of a few tens close to T_g.[2,6,14] In this paper, we investigate the consequences of this double contribution for the study of the scaling predicted in Ref. 7 and given by Eq. (1) and for the extraction of the $N_{\text{corr}}(T)$ dependence from experimental data. We present the results of our measurements of two distinct nonlinear susceptibilities on supercooled glycerol: $\chi_3^{(1)}$ and χ_3 (that will be called $\chi_3^{(3)}$ below) corresponding respectively to the first- and the third-harmonic responses. We show how they can be used to disentangle the trivial and singular contributions to the nonlinear response, thus allowing an accurate verification of the scaling predicted by Eqs. (1) and (6) and a precise determination of the $N_{\text{corr}}(T)$ dependence. The $\chi_3^{(1)}$ results we give in this paper are presented for

1098-0121/2011/84(10)/104204(7)

the first time by us: Our previous results concerned $\chi_3^{(3)}$ only. Measurements to which $\chi_3^{(1)}$ can be related have been presented by the R. Richert group:[13,15] The variation of the imaginary part of the dielectric susceptibility when the field is increased should be proportional to the imaginary part of $\chi_3^{(1)}$. We checked that this is indeed the case, even if the comparison is not so straightforward since the temperature and field ranges are not the same in our work and in Refs. 13 and 15; this will be addressed in detail in the forthcoming paper in which we shall also compare our $\chi_3^{(1)}$ data with the model put forward by the R. Richert group in a series of recent papers.[13,15,16]

II. EXPERIMENT

A. From measurements to nonlinear susceptibilities

We now turn to the detailed definition of the a.c. nonlinear susceptibility and to the two related quantities that can be reached experimentally, $\chi_3^{(3)}(\omega)$ and $\chi_3^{(1)}(\omega)$, which govern respectively the contribution of the nonlinear susceptibility to the third- and first-harmonic responses. We consider the case where the excitation is an a.c. electric field at angular frequency ω and first write the response [polarization $P(t)$] to the excitation $E(t)$ as a series expansion in $E(t)$ [note that no even terms are allowed because of the symmetry with respect to field reversal $E(t) \to -E(t)$]:

$$\begin{aligned}\frac{P(t)}{\epsilon_0} = {} & \int_{-\infty}^{\infty} \chi_1(t-t')E(t')dt' \\ & + \iiint_{-\infty}^{\infty} \chi_3(t-t_1',t-t_2',t-t_3') \\ & \times E(t_1')E(t_2')E(t_3')dt_1'dt_2'dt_3' + \cdots, \qquad (2)\end{aligned}$$

where ϵ_0 is the dielectric constant of vacuum, χ_1 the linear susceptibility, and χ_3 the cubic nonlinear susceptibility in the time domain. The dots in Eq. (2) correspond to an infinite sum involving higher-order nonlinear susceptibilities χ_5, and so on. The Fourier transform of Eq. (2) for a purely a.c. field $E(t) = E_0\cos(\omega t)$ gives

$$\begin{aligned}\frac{P(\omega')}{\epsilon_0} = {} & \frac{E_0}{2}\left[\chi_1(\omega) + \frac{3E_0^2}{4}\chi_3(-\omega,\omega,\omega) + \cdots\right]\delta(\omega'-\omega) \\ & + \frac{E_0}{2}\left[\chi_1(-\omega) + \frac{3E_0^2}{4}\chi_3(\omega,-\omega,-\omega) + \cdots\right] \\ & \times\delta(\omega'+\omega) + \frac{E_0^3}{8}\chi_3(\omega,\omega,\omega)\delta(\omega'-3\omega) \\ & + \frac{E_0^3}{8}\chi_3(-\omega,-\omega,-\omega)\delta(\omega'+3\omega) + \cdots, \qquad (3)\end{aligned}$$

where the polarization P and the susceptibilities χ_i are now written in the frequency domain and the dots indicate again infinite sums involving higher-order terms. The response $P(t)$ to $E(t)$ can thus be written

$$\begin{aligned}P(t)/\epsilon_0 = {} & \mathrm{Re}\left[\left(E_0\chi_1(\omega) + 3/4E_0^3\chi_3^{(1)}(\omega) + \cdots\right)e^{-i\omega t}\right] \\ & + \mathrm{Re}\left[1/4E_0^3\chi_3^{(3)}(\omega)e^{-i3\omega t} + \cdots\right] + \cdots. \qquad (4)\end{aligned}$$

We have used the fact that because χ_1 and χ_3 are real in the time domain, their Fourier transform verifies $\chi_1^*(\omega) = \chi_1(-\omega)$ and $\chi_3^*(\omega_1,\omega_2,\omega_3) = \chi_3(-\omega_1,-\omega_2,-\omega_3)$ (the star denotes the complex conjugate) and the invariance of χ_3 by permutation of its arguments. For simplicity, we write $\chi_3^{(3)}(\omega) = \chi_3(\omega) = \chi_3(\omega,\omega,\omega)$ and $\chi_3^{(1)}(\omega) = \chi_3(-\omega,\omega,\omega)$. Equation (4) can be written:

$$\begin{aligned}P(t)/\epsilon_0 = {} & E_0\,|\chi_1|\cos(\omega t-\delta_1) + 3/4E_0^3\left|\chi_3^{(1)}\right|\cos\left(\omega t-\delta_3^{(1)}\right) \\ & + \cdots + 1/4E_0^3\left|\chi_3^{(3)}\right|\cos\left(3\omega t-\delta_3^{(3)}\right) + \cdots, \qquad (5)\end{aligned}$$

where the susceptibilities $\chi_i^{(j)}$ are written as $|\chi_i^{(j)}|e^{i\delta_i^{(j)}}$ and where $-\delta_3^{(3)}$ and $-\delta_3^{(1)}$ are the corresponding phases (reported below in this work).

Thus, experimentally, the third-order nonlinear susceptibility is given by two quantities, $\chi_3^{(3)}(\omega)$ and $\chi_3^{(1)}(\omega)$, which are the Fourier transforms of $\chi_3(t_1,t_2,t_3)$ at points (ω,ω,ω) and $(-\omega,\omega,\omega)$, respectively. They govern the third- and the first-harmonic contributions to the nonlinear response. Both correspond to contributions to P which are proportional to the third power of the exciting electric field magnitude E_0. As a consequence, in a dielectric spectroscopy experiment using a capacitor with the supercooled liquid as dielectric layer, they can be obtained by performing the difference between the responses obtained at two different values of the exciting voltage.[13,15] With the bridge technique that we use,[8,11] each of them can be obtained in a single experiment, just by selecting the measurement harmonics. We verified that the magnitude of the measured signal was indeed proportional to the third power of the excitation voltage. An equation relating N_{corr} to $\chi_3^{(1)}$, similar to Eq. (1), holds:

$$\chi_3^{(1)}(\omega,T) \approx \frac{\epsilon_0(\Delta\chi_1)^2a^3}{k_BT}N_{\mathrm{corr}}(T)\,\mathcal{G}\left(\omega\tau_\alpha\right). \qquad (6)$$

Where $\mathcal{G}$ is a complex scaling function going to zero both for small and large arguments, with the humped shape of $|\mathcal{G}(\omega\tau_\alpha)|$ being a distinctive feature of the glassy correlations.

B. Experimental setup

The liquid used in this experiment is ultrapure (99.5%) glycerol ($T_g \simeq 190$ K) purchased from VWR (BDH Prolabo). Special care was taken to avoid water absorption during sample preparation. Two samples were prepared between metallic electrodes 2 cm in diameter, with polymer spacers ensuring interelectrode distances of 12 and 26 μm or of 8 and 27 μm. The samples were placed in a cryogenerator, and their temperature T was regulated with a precision much better than 100 mK in an interval $T_g + 4$ K to $T_g + 35$ K. A low-harmonic-distortion voltage source yielded a field $E_0 \leqslant 3\times10^6$ V/m (rms) in the thinnest capacitor. $\chi_3^{(3)}(\omega,T)$ and $\chi_3^{(1)}(\omega,T)$ were respectively obtained from the third- and first-harmonic currents. For the third-harmonic measurements, our high-sensitivity method based on a bridge containing the two glycerol capacitors[11] allows us to get rid of the harmonic distortion of our electronic apparatus. For the first-harmonic measurements, a very careful equilibration of the bridge at low voltage source allowed us to make the effect of χ_1 negligible with respect to that of $\chi_3^{(1)}$ [see Eq. (5)] for E_0 in the range 1.5–3 × 10^6 V/m.

C. Getting rid of possible artifacts: Heating and mechanical effects

We briefly explain how we managed to avoid any distortion of the data reported here by heating or mechanical effects. Heating effects come from the dissipated electrical power ρ that raises the temperature T of the liquid by an amount δT. For a field $E(t) = E_0 \cos(\omega t)$, one finds that $\rho \sim E_0^2$ contains a constant term and a term oscillating at frequency 2ω; see Ref. 17. As a result, $\delta T(t) = \delta T_{\mathrm{dc}} + \delta T_2(t)$, where $\delta T_{\mathrm{dc}} \sim E_0^2$ is a constant and $\delta T_2(t) \sim E_0^2$ oscillates at 2ω. The heating affects the polarization by an amount given, as a first-order estimate, by $\delta P(t) \simeq [\partial P_{\mathrm{lin}}(t)/\partial T]\delta T(t) \propto E_0^3$, where $P_{\mathrm{lin}}(t)$ is the linear part of the polarization. Thus, one sees that $\delta T_2(t)$ enters in products of two terms oscillating at ω and 2ω, yielding a heating contribution to the third harmonics. This contribution was carefully studied in Ref. 17 where it was shown that it only plays a minor role at high frequencies and high temperatures. In the range of parameters reported here, this heating contribution to the third harmonics can be safely neglected. The smallness of the heating effect on third harmonics comes mainly from the "skin effect," i.e., from the fact that the oscillating part of heating is exponentially damped in the thick metallic electrodes of the samples. This contrasts with δT_{dc} that is not damped in the electrodes and yields the main contribution of heating to the nonlinear part of the first harmonics. Fortunately, the thermal time constant $\tau_{\mathrm{dc}} \sim 300$ s associated with the settlement of δT_{dc} is really long since it corresponds to heat transfer across the whole experimental cell. Thus, the effect of δT_{dc} can be avoided by carrying out the measurements of the nonlinear part of the first harmonics over a time scale τ_1 much smaller than τ_{dc}. As in Refs. 13,15, and 16 we checked that different values of τ_1 did not change the measured $\chi_3^{(1)}$ noticeably, provided that the condition $\tau_1 \ll \tau_{\mathrm{dc}}$ was obeyed. We note here that the heating effects we consider must not be confused with those studied in the box model framework[13,15,16,18] because the latter are a possible description of the physics of the connection between the nonlinear susceptibilities and the DH's.

Mechanical effects would come from a time dependence of the thickness e of the capacitance due to electrical forces between the electrodes that would yield a nonlinear component in the response. We considered this possibility by calculating its contribution to $\chi_3^{(1)}$ and $\chi_3^{(3)}$. The oscillations of the capacitance can be rather easily obtained by taking into account the electric attractive force ($\sim E_0^2$) between the electrodes and the elasticity of the spacers and glycerol layer. As for heating effects of Ref. 17 evoked above, one finds that the variation $\delta e(t)$ of the thickness contains a constant term and a term oscillating at angular frequency 2ω, i.e., $\delta e(t) = \delta e_{\mathrm{dc}} + \delta e_2(t)$, where both terms are proportional to E_0^2. The result of our calculation is that such an effect can safely be neglected since it gives a contribution that is less than 1.5% of the values of $|X_3^{(i)}|$ reported here. In addition, we note that, in our experiments, we checked [for $X_3^{(3)}$] that the measured values are the same whatever the surface or shape of the spacers. As their size and shape contribute to the possible spurious nonlinear response, we consider this experimental result as an important clue that the contribution of the attractive force between the electrodes to the nonlinear response can be neglected. Note that a similar calculation has been performed by the authors of Ref. 13. Their result confirms that electrode attraction can be disregarded as a significant source of nonlinearity.

III. RESULTS AND DISCUSSIONS

In Fig. 1, the dimensionless value $X_3^{(3)}(\omega,T) = \chi_3^{(3)}(\omega,T) \times k_B T/[(\Delta\chi_1)^2 a^3 \epsilon_0]$ is plotted as a function of the frequency $f = \omega/(2\pi)$ for six temperatures.[19] The definition of $X_3^{(3)}$ is chosen in order that according to Eq. (1), $|X_3^{(3)}|$ is $N_{\mathrm{corr}}(T)\,|\mathcal{H}(\omega\tau_\alpha)|$. Indeed, we find that for each temperature, the frequency dependence exhibits the expected humped shape, while the overall magnitude of the curves increases when T decreases as expected from Eq. (1) since this magnitude[7] should be proportional to $N_{\mathrm{corr}}(T)$. Figure 2 shows, for two temperatures, the dimensionless value $X_3^{(1)}(\omega,T) = \chi_3^{(1)}(\omega,T) \times k_B T/[(\Delta\chi_1)^2 a^3 \epsilon_0]$ as a function of the frequency. As for $X_3^{(3)}$, a humped shape is found and the magnitude of $|X_3^{(1)}(\omega,T)|$ increases as T decreases, as expected from Eq. (6). We now investigate the possible scaling behavior of $X_3^{(3)}(\omega,T)$ and $X_3^{(1)}(\omega,T)$.

A. Scaling of $X_3^{(3)}$

The main part of Fig. 3 shows the same results as Fig. 1 but plotted as a function of the ratio f/f_α, where $f_\alpha(T) = 1/[2\pi\tau_\alpha(T)]$ is the relaxation frequency at temperature T, obtained as the frequency for which χ_1'' is maximum. As found in Ref. 8, for each temperature, the maximum value of $|X_3^{(3)}(\omega,T)|$ is obtained for $f/f_\alpha \simeq 0.21$. In the inset of Fig. 3, for each temperature, the values of $|X_3^{(3)}(\omega,T)|$ have been divided by their maximum value over frequency to test the scaling predicted by Eq. (1). It can be seen that around the peak of $|X_3^{(3)}|$ the predicted scaling is well obeyed. The phase

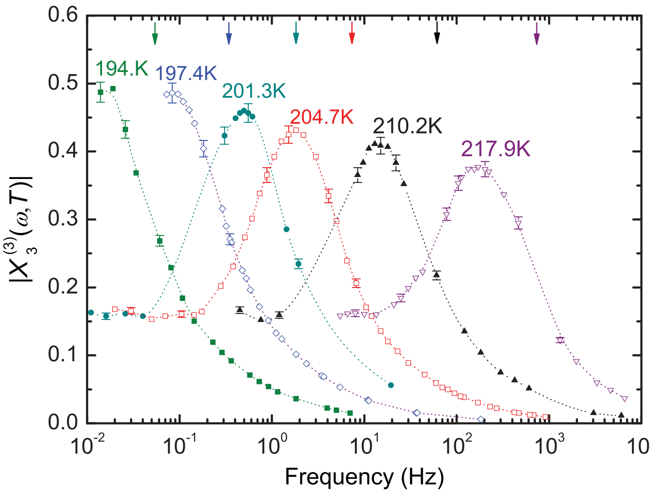

FIG. 1. (Color online) $|X_3^{(3)}(\omega,T)|$, the modulus of the dimensionless third-harmonic nonlinear susceptibility $\chi_3^{(3)}(\omega,T)$ measured in supercooled glycerol, is plotted as a function of the frequency for six temperatures labeling the curves. The arrows indicate the relaxation frequency f_α for each temperature, f_α being the frequency for which $\chi_1''(\omega,T)$ is maximum.

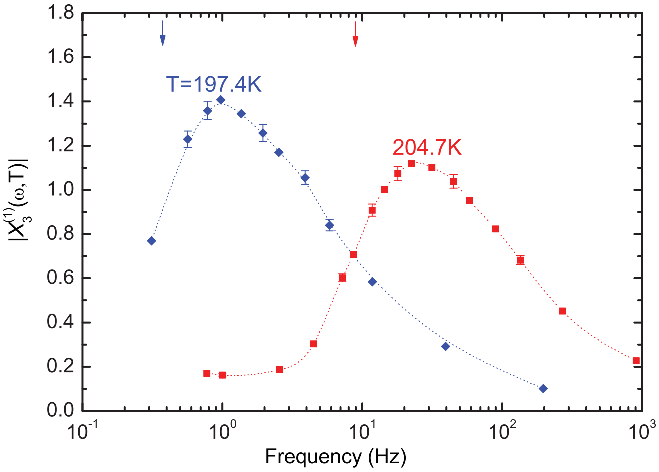

FIG. 2. (Color online) $|X_3^{(1)}(\omega,T)|$, the modulus of the dimensionless first-harmonic nonlinear susceptibility $\chi_3^{(1)}(\omega,T)$ measured in supercooled glycerol, is plotted as a function of the frequency for two temperatures labeling the curves. The arrows indicate the relaxation frequency f_α for each temperature.

of $X_3^{(3)}$ (see Fig. 4) confirms this scaling, since, as found in Ref. 8, the phases measured at different temperatures depend only on f/f_α.

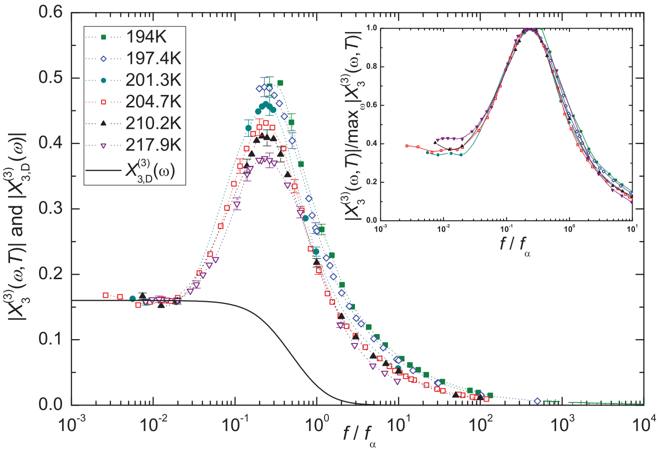

FIG. 3. (Color online) $|X_3^{(3)}(\omega,T)|$ is plotted as a function of f/f_α for six temperatures, where f_α is the relaxation frequency at the considered temperature. The data (and the temperatures) are the same as those shown in Fig. 1. The continuous line is $X^{(3)}_{3,D}(\omega)$, an estimate of the "trivial" contribution to the nonlinear susceptibility. (Inset) The same data, normalized to test the scaling predicted by Eq. (1): $|X_3^{(3)}(\omega,T)|/\max_\omega|X_3^{(3)}(\omega,T)|$ is plotted as a function of f/f_α (trivial estimate not shown).

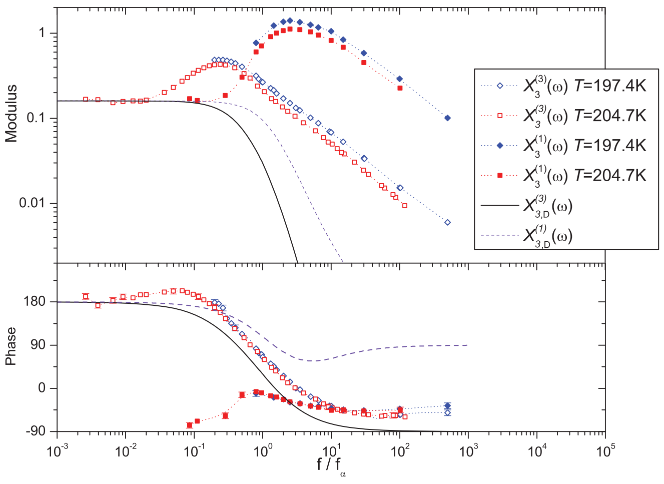

FIG. 4. (Color online) (Upper graph) $|X_3^{(3)}(\omega,T)|$ and $|X_3^{(1)}(\omega,T)|$, the moduli of the dimensionless measured nonlinear susceptibilities $\chi_3^{(3)}(\omega,T)$ and $\chi_3^{(1)}(\omega,T)$, are plotted as a function of f/f_α for two temperatures. The lines without symbols $X^{(3)}_{3,D}(\omega)$ (black solid) and $X^{(1)}_{3,D}(\omega)$ (purple dashed) are estimates of the "trivial" contributions to the nonlinear susceptibilities. (Lower graph) Phases (in degrees) corresponding to the moduli of the upper graph (same symbols).

In Fig. 3, the most important departure from scaling arises for $f/f_\alpha < 3 \times 10^{-2}$ where the $|X_3^{(3)}(\omega,T)|$ curves fall on the same plateau value ~0.16 at low frequency. We explain this deviation to complete scaling by the fact that at low frequency $\chi_3^{(3)}(\omega)$ is dominated by the trivial contribution $\chi^{(3)}_{3,\mathrm{trivial}}$ (due to the saturation of the polarization of the dipoles). To confirm this explanation, we evaluate $\chi^{(3)}_{3,\mathrm{trivial}}$ by using the analytic calculation of Ref. 12. In this calculation that is free of any glassy correlations, the nonlinear response $\chi^{(3)}_{3,D}(\omega,T)$ is calculated for a system made of independent rigid polar molecules with a Brownian rotational motion in a viscous medium. To the best of our knowledge, Ref. 12 is the only framework yielding the frequency dependence of the nonlinear effects for polar molecules under rotational Brownian motion. This is, of course, a very simplified view of the trivial contribution of glycerol where each molecule contains several dipoles.

Following Ref. 12, we calculate $\chi^{(3)}_{3,D}(\omega,T)$. $\chi^{(3)}_{3,D}$ yields, as for $\chi_3^{(3)}$, the dimensionless nonlinear susceptibility $X^{(3)}_{3,D}(\omega,T) = |\chi^{(3)}_{3,D}(\omega,T)| \times k_B T/[(\Delta\chi_1)^2 a^3 \epsilon_0]$. We find that $X^{(3)}_{3,D}(\omega,T)$ depends only on the ratio f/f_α and that the magnitude of $X^{(3)}_{3,D}(\omega,T)$ is independent of the temperature. The continuous line in Fig. 3 shows the frequency dependence of $|X^{(3)}_{3,D}|$: $|X^{(3)}_{3,D}|$ has no peak at finite frequency. This confirms that the humped shape of the measured $|X_3^{(3)}|$ is a distinctive feature of glassy correlations, as predicted by Bouchaud and Biroli in Ref. 7. Besides, $X^{(3)}_{3,D}$ reaches its maximum plateau value for $f/f_\alpha < 10^{-1}$ and decreases to zero for $f/f_\alpha > 10^{-1}$, becoming negligible with respect to the measured $|X_3^{(3)}(\omega,T)|$ of glycerol at $f/f_\alpha > 1$. Let us emphasize that the values of $|X^{(3)}_{3,D}(\omega,T)|$ reported in Fig. 3 are those calculated in Ref. 12 times a factor 0.8. This factor was chosen to enforce the agreement between our model of trivial effects and the experimental measurements in the plateau regime occuring for $f/f_\alpha < 3 \times 10^{-2}$. Due to the fact that the analytic calculation of Ref. 12 is only a first crude model of the trivial nonlinear effects of glycerol, the use of an adjustable factor close to unity is reasonable. Thus, the fact that $\chi_3^{(3)}$ results from both the contributions of $\chi^{(3)}_{3,\mathrm{singular}}$ (due to glassy correlations[7]) that should be dominant for $f/f_\alpha > 0.1$ and of $\chi^{(3)}_{3,\mathrm{trivial}}$ that is dominant for $f/f_\alpha < 5 \times 10^{-2}$ can well explain that the scaling predicted by Eq. (1) is verified only for $f/f_\alpha > 0.05$, as found in our previous paper.[8]

B. Scaling of $X_3^{(1)}$

In what concerns $X_3^{(1)}$, similar results are obtained: in Fig. 4 (closed symbols), we can see that for two different temperatures, the curves $|X_3^{(1)}(f/f_\alpha)|$ have the same shape but not the same magnitude. In addition, the phases depend only on f/f_α as can be seen in Fig. 4. Thus the scaling predicted by Eq. (6) holds for $X_3^{(1)}$. Comparing the measured $|X_3^{(1)}|$ and $|X_3^{(3)}|$ in Fig. 4 reveals that (i) the former is peaked at a value of f/f_α larger than the latter and (ii) both quantities decrease at large frequencies with similar power laws whose exponent is -0.61 ± 0.04. These two features can be accounted for by using (and extending) the considerations of Ref. 20 where $\chi_3^{(3)}$ and $\chi_3^{(1)}$ were computed analytically within the mode coupling theory (MCT) framework. As MCT is valid at temperatures much higher than those of our experiments,[21] the fact that some of the features predicted within MCT are still observed close to T_g might come from the dynamical amorphous order that emerges in supercooled liquids as the temperature is decreased. Comparisons with theoretical models, in particular the one developed by the R. Richert group,[13,15,16] was thoroughly done very recently in Ref. 18 for $X_3^{(3)}$ and will be done in a forthcoming publication for $X_3^{(1)}$.

As for $\chi_3^{(3)}$, we have evaluated the contribution to $\chi_3^{(1)}$ due to the polarization saturation $\chi_{3,\text{trivial}}^{(1)}$ by calculating $\chi_{3,D}^{(1)}$ in the model of Ref. 12. The resulting dimensionless nonlinear susceptibility $X_{3,D}^{(1)}$, multiplied by the same factor 0.8 as in Fig. 3, is shown in Fig. 4 (purple dashed line). As for $|X_{3,D}^{(3)}|$, its modulus has no peak and reaches a maximum plateau value at low frequencies, which does not depend on T, and decreases to negligible values at high frequencies. Even if, in Fig. 4, the measured $|X_3^{(1)}|$ is close to the trivial estimate $|X_{3,D}^{(1)}|$ for frequencies as high as $f/f_\alpha = 0.3$, the phase of the measured $X_3^{(1)}$ is still well above the value of $\pm180°$ which is expected, on general grounds, for the trivial contribution. Thus, the trivial contribution does not fully dominate the measured $X_{3,D}^{(1)}$ in the range $f/f_\alpha = 0.1$–0.3 and we hypothesize that this happens at lower frequencies, say $f/f_\alpha \leqslant 0.05$, just as for $\chi_3^{(3)}$.

Finally, from Fig. 4 we conclude that concerning the scaling and the extraction of $N_{\text{corr}}(T)$ from the magnitude of the dimensionless nonlinear susceptibility, $\chi_3^{(1)}$ is a better candidate than $\chi_3^{(3)}$ because, at the peak frequency [$f/f_\alpha \simeq 0.21$ for $\chi_3^{(3)}$ and $f/f_\alpha \simeq 2.5$ for $\chi_3^{(1)}$], the value of the estimated trivial relative contribution is much smaller for $\chi_3^{(1)}$ than for $\chi_3^{(3)}$.

C. Extraction of $N_{\text{corr}}(T)$

Considering the results and discussions presented above, we can now look for the best way to estimate the $N_{\text{corr}}(T)$ dependence from the $\chi_3^{(1)}$ and $\chi_3^{(3)}$ data, taking into account the fact that the glassy correlations contribution to the nonlinear susceptibility is dominant only at "large" frequencies.

1. Subtraction of $X_{3,D}^{(3)}$

Figure 5 shows the maximum values reached by $|X_3^{(3)}(\omega)|$ and $|X_3^{(1)}(\omega)|$ when ω varies as a function of the temperature. According to Eqs. (1) and (6), those quantities are proportional to N_{corr}, the average number of correlated molecules in a DH. The comparison of the rates of increase of $\max_\omega[|X_3^{(3)}(\omega,T)|]$ and $\max_\omega[|X_3^{(1)}(\omega,T)|]$ when T decreases below 205 K confirms our previous discussion on the two contributions. Indeed, as at the peak frequency the relative contribution of the trivial component is weaker for $X_3^{(1)}$ than for $X_3^{(3)}$, the maximum of $|X_3^{(1)}|$ increases faster than the maximum of $|X_3^{(3)}|$. Figure 5 shows the quantity $\max_\omega[|X_3'(\omega,T)|]$, where X_3' is the dimensionless nonlinear susceptibility from which the estimate of the trivial contribution has been subtracted:

$$X_3'(\omega,T) = X_3^{(3)} - X_{3,D}^{(3)}. \tag{7}$$

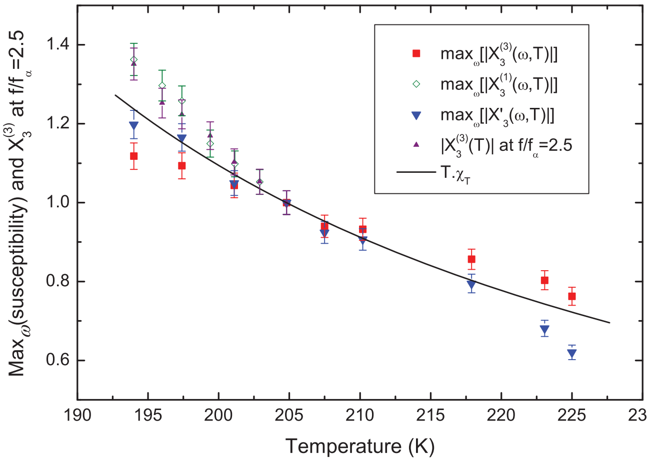

FIG. 5. (Color online) Estimated $N_{\text{corr}}(T)$ dependence obtained from the maximum of $|X_3^{(3)}(\omega,T)|$, according to Eq. (1) (filled squares) and from the maximum of $|X_3^{(1)}(\omega,T)|$, according to Eq. (6) (open lozenges). The triangles pointing down correspond to the maximum of $X_3'(\omega,T)$ that is obtained from $X_3^{(3)}(\omega,T)$ by subtracting an estimated trivial contribution. The filled triangles correspond to $|X_3^{(3)}(f/f_\alpha = 2.5,T)|$, which should be free of any trivial contribution (see text). The continuous line is a *simplified* estimator of the number of correlated molecules estimated from $T \times \chi_T$ (see Ref. 6 and text). All the data are normalized to 1 at $T = 204.7$ K to allow an accurate comparison of their relative evolution with temperature.

We can see in Fig. 5 that when T decreases, the increase of $\max_\omega[|X_3'(\omega,T)|]$ is steeper than that of $\max_\omega[|X_3^{(3)}(\omega,T)|]$, which again confirms the importance of getting rid of the trivial contribution to $\chi_3^{(3)}$ for estimating the $N_{\text{corr}}(T)$ dependence from the nonlinear susceptibility. The difference between the rates of increase of $\max_\omega[|X_3'(\omega,T)|]$ and of $\max_\omega[|X_3^{(1)}(\omega,T)|]$ is yet unexplained. This suggests that we should clarify our two assumptions. First, the estimate of the trivial contribution could be refined, since the detailed shapes of the $X_3^{(3)}(\omega)$ and $X_3^{(1)}(\omega)$ functions compared to that of the $X_{3,\text{trivial}}^{(i)} \simeq X_{3,D}^{(i)}$ play a major role in the comparison of Fig. 5. Second, our assumption that the trivial contribution simply adds to the singular one is questionable, especially when the two contributions are of the same order of magnitude. A refined theoretical analysis would be needed on that point.

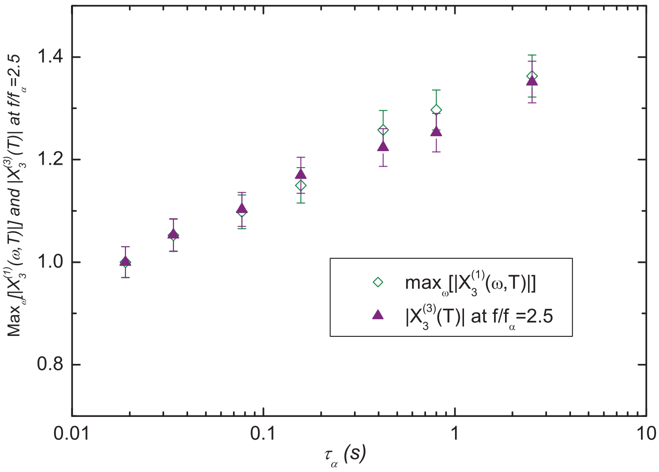

FIG. 6. (Color online) Estimated $N_{\rm corr}(\tau_\alpha)$ dependence obtained from the maximum of $|X_3^{(1)}(\omega,T)|$, according to Eq. (6) (open lozenges). τ_α is defined as $\tau_\alpha(T) = 1/[2\pi f_\alpha(T)]$. The filled triangles correspond to $|X_3^{(3)}(f/f_\alpha = 2.5,T)|$, which should be free of any trivial contribution (see text). As in Fig. 5, all the data are normalized to 1 at $T = 204.7$ K.

2. *The best estimate of the T dependence of $N_{\rm corr}(T)$*

We see in Fig. 5 that $|X_3^{(1)}(f/f_\alpha = 2.5)|$ has the same temperature dependence as $|X_3^{(3)}(f/f_\alpha = 2.5)|$. This confirms that, in the range where the trivial contribution is fully negligible, both $|\chi_3^{(1)}|$ and $|\chi_3^{(3)}|$ have the same temperature evolution, as expected from Eqs. (1) and (6). This is why the most precise way to extract the T dependence of $N_{\rm corr}(T)$ is to follow $|X_3^{(1)}(f/f_\alpha = 2.5)|$ or $|X_3^{(3)}(f/f_\alpha = 2.5)|$. This yields a T dependence faster than that of $T\chi_T$: we note here that $T\chi_T$ is defined as $T\chi_T = \max_\omega[T\partial(\chi'_{\rm lin}(\omega)/\Delta\chi_1)/\partial T]$, see Ref. 6, where $\chi'_{\rm lin}(\omega)$ is the real part of the linear dielectric response. Let us emphasize that $T\chi_T$ is an *approximate* estimator of $N_{\rm corr}(T)$. It has the great advantage of being easily obtained from experiments, but its ability to reproduce the T dependence of the "true" $N_{\rm corr}(T)$ is not guaranteed. For example, in the case of strong glasses where one expects $N_{\rm corr}$ to be independent of temperature, one finds instead $T\chi_T \propto 1/T$. For fragile liquids, the T dependencies of $T\chi_T$ and of $N_{\rm corr}(T)$ are only the same provided a prefactor sensitive to microscopic details can be assumed to be temperature independent.[22] Since this assumption is not needed to relate the nonlinear response to the "true" $N_{\rm corr}(T)$, the T dependence extracted from $|X_3^{(3)}(f/f_\alpha = 2.5)|$ and $|X_3^{(1)}(f/f_\alpha = 2.5)|$ is, in our opinion, the most reliable estimate to date of the T dependence of $N_{\rm corr}(T)$.

This increase of $|X_3^{(1)}(f/f_\alpha = 2.5)|$ and of $|X_3^{(3)}(f/f_\alpha = 2.5)|$ when approaching the glass transition is plotted as a function of $\ln \tau_\alpha$ in Fig. 6, exhibiting a linear behavior in the experimentally accessible region (but note that the relative change of $\ln(\tau_\alpha/\tau_0)$ is only 20%, assuming $\tau_0 = 10^{-13}$ s. This means that a nonlinear dependence, if any, is hard to detect). Plotting the corresponding quantities for other supercooled liquids on such a plot would be interesting as it would allow us to compare directly the rate of increase of $N_{\rm corr}(T)$ for glasses with different fragilities and possibly put some experimental constraints onto the microscopic theories aiming at describing the glass transition. Finally, we note that such a logarithmic increase of $N_{\rm corr}(T)$ with τ_α has already been considered, e.g., in Refs. 6 and 23: The relaxation time would be related exponentially to an activation energy or a configurational entropy that would be proportional to a power of $N_{\rm corr}$. This is why it is conceivable that an increase of $N_{\rm corr}(T)$ by 35% corresponds to an increase of τ_α by 2 decades, as in Fig. 6.

IV. CONCLUSION

In order to determine experimentally the important physical information provided by the dependence of the number of dynamically correlated molecules $N_{\rm corr}$ on temperature, we have measured the two a.c. nonlinear dielectric susceptibilities $\chi_3^{(3)}$ and $\chi_3^{(1)}$ in supercooled glycerol. According to Ref. 7, those quantities contain a contribution $\chi_{3,\rm singular}^{(i)}$ due to glassy correlations that should have a scaling behavior in its frequency and temperature dependencies and be proportional to $N_{\rm corr}$. By performing a detailed study of the trivial contributions, $\chi_{3,\rm trivial}^{(3)}$ and $\chi_{3,\rm trivial}^{(1)}$, due to standard polarization saturation, we have shown that they indeed affect the scaling, primarily at the lowest frequencies. As a consequence, an accurate determination of the temperature dependence of $N_{\rm corr}$ from the nonlinear susceptibilities needs an appropriate subtraction of the trivial contributions in order to extract the singular part of the nonlinear susceptibility. It seems difficult to have a precise theoretical prediction of the trivial contribution and on its interplay with the glassy contribution to the nonlinear susceptibility. This is why, at present, the most reliable way to get rid of the trivial contribution is to compare the T dependence of $\chi_3^{(3)}$ and of $\chi_3^{(1)}$. This allowed us to conclude that in glycerol the T dependence of $N_{\rm corr}$ is faster than previously determined using the dynamic susceptibility, $T\chi_T$, a method used in many previous publications.[4,6,23]

ACKNOWLEDGMENTS

We thank R. Tourbot for realizing the experimental cell and P. Pari for the cryogenic setup. We acknowledge interesting discussions with C. Alba-Simionesco, A. Lefèvre, and R. Richert and support by ANR grant DynHet.

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[1] See, e.g., P. G. Debenedetti and F. H. Stillinger, Nature **410**, 259 (2001).

[2] M. D. Ediger, Annu. Rev. Phys. Chem. **51**, 99 (2000).

[3] R. Richert, J. Phys. Condens. Matter **14**, R703 (2002).

[4] L. Berthier, G. Biroli, J.-P. Bouchaud, L. Cipelletti, D. El Masri, D. L'Hôte, F. Ladieu, and M. Pierno, Science **310**, 1797 (2005).

[5] L. Berthier, G. Biroli, J.-P. Bouchaud, W. Kob, K. Miyazaki, and D. R. Reichman, J. Chem. Phys. **126**, 184503 (2007).

[6] C. Dalle-Ferrier, C. Thibierge, C. Alba-Simionesco, L. Berthier, G. Biroli, J.-P. Bouchaud, F. Ladieu, D. L'Hôte, and G. Tarjus, Phys. Rev. E **76**, 041510 (2007).

[7] J.-P. Bouchaud and G. Biroli, Phys. Rev. B **72**, 064204 (2005).

[8] C. Crauste-Thibierge, C. Brun, F. Ladieu, D. L'Hôte, G. Biroli, and J.-P. Bouchaud, Phys. Rev. Lett. **104**, 165703 (2010).

[9] See R. Richert, N. Israeloff, C. Alba-Simionesco, F. Ladieu, and D. L'Hôte, in *Dynamical Heterogeneities in Glasses, Colloids and Granular Media* (Oxford University Press, Oxford, UK, 2010).

[10] L. P. Lévy, Phys. Rev. B **38**, 4963 (1988).

[11] C. Thibierge, D. L'Hôte, F. Ladieu, and R. Tourbot, Rev. Sci. Instrum. **79**, 103905 (2008).

[12] J. L. Déjardin and Yu. P. Kalmykov, Phys. Rev. E **61**, 1211 (2000).

[13] S. Weinstein and R. Richert, Phys. Rev. B **75**, 064302 (2007).

[14] U. Tracht, M. Wilhelm, A. Heuer, H. Feng, K. Schmidt-Rohr, and H. W. Spiess, Phys. Rev. Lett. **81**, 2727 (1998).

[15] R. Richert and S. Weinstein, Phys. Rev. Lett. **97**, 095703 (2006).

[16] W. Huang and R. Richert, Eur. Phys. J. B **66**, 217 (2008).

[17] C. Brun, C. Crauste-Thibierge, F. Ladieu, and D. L'Hôte, J. Chem. Phys. **133**, 234901 (2010).

[18] C. Brun, C. Crauste-Thibierge, F. Ladieu, and D. L'Hôte, J. Chem. Phys. **134**, 194507 (2011).

[19] All the values of $X_3^{(3)}$ reported here are 10% smaller than those reported in our Ref. 8, the difference coming mainly from a refined estimate of the thickness of the samples in the present work. Apart from this 10% global change, all the frequencies and temperature dependencies reported here are consistent with those reported previously in Ref. 8.

[20] M. Tarzia, G. Biroli, J.-P. Bouchaud, and A. Lefèvre, J. Chem. Phys. **132**, 054501 (2010).

[21] P. Lunkenheimer, A. Pimenov, M. Dressel, Yu. G. Goncharov, R. Bömer, and A. Loidl, Phys. Rev. Lett. **77**, 318 (1996).

[22] See the discussion about the possible T dependence of the prefactor χ_0 following Eq. (18) in L. Berthier, G. Biroli, J.-P. Bouchaud, W. Kob, K. Miyazaki, and D. R. Reichman, J. Chem. Phys. **126**, 184503 (2007).

[23] S. Capaccioli, G. Ruocco, and F. Zamponi, J. Phys. Chem. B **112**, 10652 (2008).