Evidence of Growing Spatial Correlations at the Glass Transition from Nonlinear Response Experiments

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The ac nonlinear dielectric response $\chi_3(\omega, T)$ of glycerol was measured close to its glass transition temperature T_g to investigate the prediction that supercooled liquids respond in an increasingly nonlinear way as the dynamics slows down (as spin glasses do). We find that $\chi_3(\omega, T)$ indeed displays several nontrivial features. It is peaked as a function of the frequency ω and obeys scaling as a function of $\omega\tau(T)$, with $\tau(T)$ the relaxation time of the liquid. The height of the peak, proportional to the number of dynamically correlated molecules $N_{\text{corr}}(T)$, increases as the system becomes glassy, and χ_3 decays as a power law of ω over several decades beyond the peak. These findings confirm the collective nature of the glassy dynamics and provide the first direct estimate of the T dependence of N_{corr}.

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Most liquids undergo a transition to an amorphous solid state, the glass, when the temperature T decreases to their glass transition temperature T_g. This transition is similar for a vast variety of systems such as polymeric, colloidal, and molecular liquids. This ubiquity echoes the universality of critical phenomena, where the emergence of long range order makes most of the microscopic details irrelevant, yielding the same critical behavior in various systems. This is why it has been argued for a long time that some collective effects should be associated to the glass transition, ultimately related to the proximity of a phase transition [1]. An immediate problem with this idea is that standard equilibrium correlation and response functions remain those of a normal liquid when $T \to T_g$ [2]. In the two past decades, however, the heterogeneous nature of the dynamics close to T_g was established [3,4], and a length scale associated to these dynamic heterogeneities was estimated [5]. The increase of the number of correlated molecules N_{corr} when T decreases towards T_g is expected to explain the main aspect of the glass transition, i.e., the huge increase of the relaxation time; $N_{\text{corr}}(T)$ has therefore become a central concern in the field. The first estimate of this dependence [6–8] relied on the temperature derivative of a two-point correlation function. Its relation with the number of dynamically correlated molecules $N_{\text{corr}}(T)$ is however ambiguous because it involves a temperature dependent prefactor difficult to estimate and control [7,9]. Furthermore, this estimator leads to a low-temperature divergence of $N_{\text{corr}}(T)$ for a purely Arrhenius system, for which no collective behavior is expected, at least at first sight [7]. An indisputable experimental estimate of the T dependence of the dynamical correlation volume is thus still lacking. In this work, we fill this gap by measuring the anomalous increase of a physical susceptibility. It leads to a *direct* estimate of $N_{\text{corr}}(T)$, up to a numerical prefactor that is now temperature independent. Our findings show that supercooled liquids respond in an increasingly nonlinear way approaching the glass transition. For many systems, e.g., spin glasses, such an increase is related to criticality. In the present case, it suggests that an underlying phase transition could possibly be present as well, although it does not necessarily imply it.

The spin glass transition taught us that two-point functions can be blind to the amorphous long range order and that this critical behavior is revealed, in particular, by the third order nonlinear magnetic susceptibility [10,11]. It was recently argued [12,13] that the frequency and temperature dependent nonlinear dielectric susceptibility $\chi_3(\omega, T)$ in supercooled liquids plays a role similar to the nonlinear magnetic susceptibility in spin glasses and that its increase when T decreases would be a signature of the incipient long range amorphous order. Accordingly, $\chi_3(\omega, T)$ should display a peak for $\omega\tau(T) \sim 1$ whose height grows as one approaches T_g. Here $\tau(T)$ is the relaxation time of the supercooled liquid which increases rapidly as T decreases toward T_g. Contrary to spin glasses, however, $\chi_3(\omega = 0, T)$ should remain trivial since at long times glasses still behave as disordered liquids [13]. One expects that when $\tau(T)$ is large, χ_3 takes the following scaling form:

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

where $N_{\text{corr}}(T)$ is the T-dependent average number of dynamically correlated molecules, $\Delta\chi_1 = \chi_1(\omega = 0) - \chi_1(\omega \to \infty)$ 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 certain complex scaling function that goes to zero both for small and large arguments. The humped shape of $|\mathcal{H}(\omega\tau)|$ is a distinctive feature of the glassy correlations. Indeed, in the "no correlation case" [14,15], $\chi_3(\omega, T)$ is given by the prefactor of Eq. (1) times a function that, for all T, reaches its maximum value at $\omega = 0$. Furthermore, $N_{\text{corr}}(T)$ does not show any temperature dependence in that case.

We have devised an experiment to measure, for the first time, $\chi_3(\omega, T)$ of a classic glass former (glycerol), via third harmonics measurements. Our findings are in good agreement with the predictions of Eq. (1): the scaling, the growth of the number of dynamically correlated molecules with decreasing T, the humped shape of $|\mathcal{H}|$ and its power-law dependence for $\omega\tau \gg 1$ are all confirmed experimentally. The anomalous increase of χ_3 is compatible with the existence of incipient critical fluctuations when $T \to T_g$, even if our measurements are too far from the possible critical point to be a clue of criticality.

Our measurements were performed at temperatures between $T_g + 4$ K and $T_g + 35$ K, with $T_g \approx 190$ K. The linear susceptibility $\chi_1(\omega) = \chi_1'(\omega) + i\chi_1''(\omega)$ quantifies the first harmonic response of polar molecules to a periodic excitation field $Ee^{-i\omega t}$. The polarization, $P(\omega)e^{-i\omega t}$, of the system is given to first order by $P(\omega) = \epsilon_0\chi_1(\omega)E$. We define the relaxation time $\tau(T)$ as the inverse of the frequency f_α where χ_1'' is maximum. The nonlinear response is dominated by $\chi_3(\omega)$ which gives to first order the magnitude of the third harmonics response to the field at pulsation ω [14,16], $P(3\omega)e^{-3i\omega t} = \epsilon_0\chi_3(\omega)[Ee^{-i\omega t}]^3$ (the second harmonics is zero because of the $E \to -E$ symmetry). While $\chi_1(\omega, T)$ has been widely studied in supercooled liquids [17–19], the T and ω dependence of χ_3 has not been measured so far, for any liquid, glassy or not [20].

In a closed cell, two high purity glycerol samples were prepared between gold plated copper electrodes 2 cm in diameter, with Mylar® spacers ensuring interelectrode distances of 19 μm and 41 μm [14,16]. The cell was placed in a cryogenerator, and the temperature T of the samples was regulated with a precision of 50 mK. A low harmonic distortion voltage source yielded a field $E \sim 7 \times 10^5$ V/m (rms) in the thinnest capacitor, and $\chi_3(\omega, T)$ was obtained from the measured third harmonics current $I(3\omega)$. This nonlinear signal was 10^{-7} to 10^{-5} of the linear one, well below the harmonic distortion of electronic devices. To get rid of them, we used a high sensitivity method based on a bridge containing the two glycerol capacitors [16].

Figure 1 shows, for five temperatures, the ω dependence of $X(\omega, T) = |\chi_3(\omega, T)| \times k_BT/[(\Delta\chi_1)^2a^3\epsilon_0]$. According to Eq. (1), this quantity should be $N_{\text{corr}}(T)|\mathcal{H}(\omega\tau)|$. Two striking results, confirming the predictions of Eq. (1), can be seen in Fig. 1. First, $X(\omega, T)$ is actually peaked at a frequency f^* of the order of $1/\tau(T)$; more precisely $f^* \simeq 0.21/\tau(T)$. Second, the height of the peak, which should be proportional to $N_{\text{corr}}(T)$, increases significantly as T decreases. The small value of $X(\omega, T)$ can be understood from calculations of $\chi_3(\omega, T)$ for molecules undergoing independent rotational Brownian motion [14,15], which should be accurate for simple supercooled liquids at high T. They indicate that for the "no correlation" case, $X(\omega, T) \leq 0.2$.

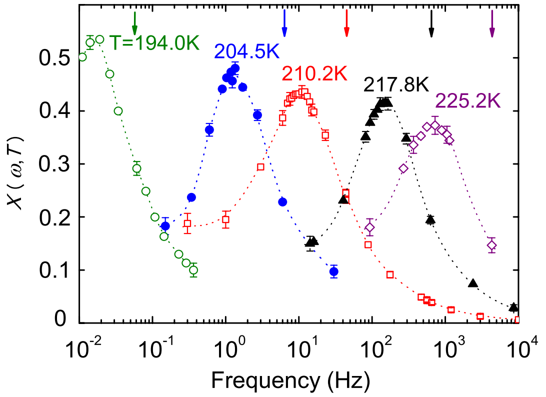

FIG. 1 (color online). For each of the five temperatures labelling the curves, $X(\omega, T) = |\chi_3(\omega, T)| \times k_BT/[\epsilon_0(\Delta\chi_1)^2a^3]$ is given as a function of frequency $f = \omega/2\pi$. The arrows indicate the five relaxation frequencies $f_\alpha(T)$, for which $\chi_1''(\omega)$ is maximum. The dashed lines are a guide to the eye.

To what extent is the scaling predicted by Eq. (1) verified by $\chi_3(\omega, T)$? Figure 2 shows the same data as in Fig. 1 but plotted as a function of $\log(f/f_\alpha)$ with $f_\alpha = \tau(T)^{-1}$, and normalized by their maximum at each T. We also show the phase of χ_3. Both the moduli and the phases collapse fairly well on a single master curve, as predicted by Eq. (1). A weak departure from scaling occurs at low ω for the highest T. This is not surprising: scaling should not hold far above T_g, where the dynamical correlations become short-ranged [12,13]. Furthermore, the nonlinear response results both from trivial dielectric saturation effects [15,21,22] (always present for $\omega\tau < 1$), and from the nontrivial dynamical correlations contribution. As the latter vanishes when $\omega \to 0$ ([12,13]), the contribution of the trivial saturation effect should dominate at high T and low ω. The observed departure from scaling can thus be explained by the different T and ω dependencies of the two contributions.

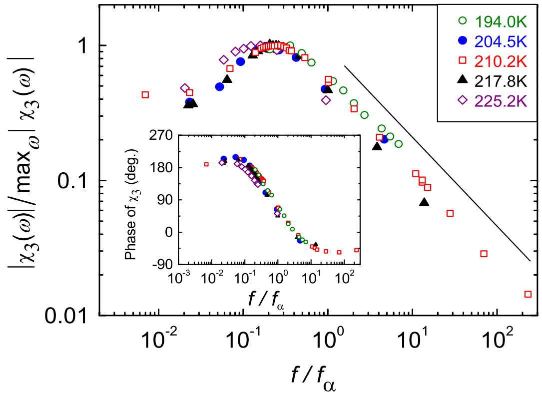

FIG. 2 (color online). The quantity $|\chi_3(\omega, T)|$ at five temperatures (same data and symbols as in Fig. 1), normalized to its maximum value at each T, plotted as a function of the ratio $f/f_\alpha(T)$. The straight line is a power law with an exponent -0.65. Inset: corresponding phase of $\chi_3(\omega, T)$.

Figure 3 gives the T dependence of the maximum value of $X(\omega, T)$, reached for $\omega = \omega^* = 2\pi f^*$. Since scaling is well obeyed, Eq. (1) tells us that this maximum value is proportional to $N_{\rm corr}(T)$. A clear increase of this quantity as T decreases toward T_g is visible in Fig. 3. This is one of the main results of our study, and strong experimental evidence of growth of the dynamical correlation length close to T_g. We now investigate how our results are related to another estimate of the size of the dynamical heterogeneities, using the temperature derivative of $\chi_1(\omega)$.

In [7,8], the T derivative of the two-body correlation $C(t)$ (or of $\chi_1(\omega)$) was introduced as a new response function $\chi_T(t) = \partial C(t)/\partial T$. It turns out that $T\chi_T(t)$ is also proportional to a dynamical correlation volume, but with an unknown, and possibly T-dependent prefactor [7,9]. The line in Fig. 3 is the number of correlated molecules estimated from $\max_\omega[T\partial(\chi_1'(\omega)/\Delta\chi_1)/\partial T]$ where, due to the unknown value of $\mathcal{H}$, the normalization was chosen such that it coincides with $X(\omega^*, T = 202\text{ K})$. We see that the T dependencies of these two quantities are close. However, whereas the increase of $X(\omega^*, T)$ is a proof of a growing correlation length, one needs some extra assumptions to infer this from χ_T [7]. That χ_3 and χ_T lead to a similar T dependence for $N_{\rm corr}(T)$ suggests that these assumptions are indeed warranted (at least for glycerol) and validates the simpler procedure advocated in [6], and used extensively in [8], to extract $N_{\rm corr}(T)$.

A precise identity relating χ_T and χ_3 has been obtained in [13]. It holds at low enough ω when the linear response depends only on external parameters (T, density, electric field, ...) via the dependence of $\tau(T)$ on these parameters, a property called time temperature superposition (TTS), and reads:

$$\chi_3(\omega) \approx \kappa\hat{\chi}_T(2\omega) \qquad \omega\tau \ll 1, \tag{2}$$

where κ is independent of ω and $\hat{\chi}_T$ is the Fourier transform of χ_T. Corrections to this relation in the regime $\omega\tau \ll 1$ are due to weak violations of TTS and to the additional term that corresponds to ω independent noncooperative degrees of freedom. The continuous line in Fig. 4 presents $X(\omega, T)$ calculated from the linear susceptibility, according to Eq. (2) with $\kappa = 7.6 \times 10^{-17}\ \text{K}(\text{m}/\text{V})^2$. This value of κ was chosen to be consistent with Fig. 3, i.e., by demanding that the maximum over ω of $\kappa|\hat{\chi}_T(2\omega)|$ corresponds to $X = 0.40$ which is the value of the continuous line of Fig. 3 for $T = 210.2$ K. Although Eq. (2) should only be valid at small ω, we see that it reproduces qualitatively the overall behavior of the data at 210.2 K. At low frequency, $\omega\tau < 0.2$, the discrepancy can be understood by the contribution of the ω independent trivial saturation effect noted above. For $\omega\tau > 1$, our data exhibit a clear power-law behavior with a fitted exponent -0.65 ± 0.04, see also Fig. 2, which is close to that describing the decay of $\hat{\chi}_T(2\omega)$. This behavior is predicted by mode-coupling theory (MCT) [13], and our experimental exponent is compatible with the MCT prediction $-b \simeq -0.6$ for glycerol [23]. Note however that MCT should in fact be relevant only at temperatures much higher than the ones we focused on. Hence, the existence of a power-law regime for large ω with identical exponents for both χ_1 and χ_3 appears to be a generic property, valid outside the MCT regime. We think that this might be related to the possible incipient criticality of the system.

We now address the question of a possible heating contribution to our results. Such effects would come from the fact that applying the field $E(t) = E\cos(\omega t)$ across the glycerol sample leads to a dissipated power per unit volume $p(t) \propto \omega\chi_1''(\omega)E^2[1 + \cos(2\omega t - \phi)]$ (see [14]). The resulting temperature increase is the sum of a constant term and a term $\delta T_{2\omega}(t)$, oscillating at 2ω. This $\delta T_{2\omega}(t)$ oscillation leads to a modulation of the linear susceptibility $\delta\chi_1(\omega)(t) = (\partial\chi_1(\omega)/\partial T)\delta T_{2\omega}(t)$, thus to a 3ω modulation of the polarization $P(t) \propto \chi_1 E$. We calculated precisely this 3ω heating contribution using the heat propagation equation [14]. This calculation gives an *upper limit* to the heating effects contribution, in particular for $f \geq f_\alpha$, because the finite relaxation time τ of the molecules prevents them from following instantaneously the temperature oscillation $\delta T_{2\omega}(t)$ (as already advocated by Richert *et al.* [24]). A representative example of these calculations is given on Fig. 4: the heating effects are negligible in most of the frequency range of interest, in particular, around the $\chi_3(\omega)$ peak. Thus, our estimate of $N_{\rm corr}(T)$ and the power law dependence of $\chi_3(\omega)$ are not affected by heating.

Our results should allow significant progress of models which predict or assume dynamical correlations in supercooled liquids. Such models should not only reproduce the increase of the correlated volume we found as $T \to T_g$ (see Fig. 3), but they should also account for the magnitude and shape of $\chi_3(\omega, T)$, given by the $\mathcal{H}$ function in Eq. (1), which carries important information on the physics of the dynamical correlations [12,13]. Recently, Richert *et al.* put

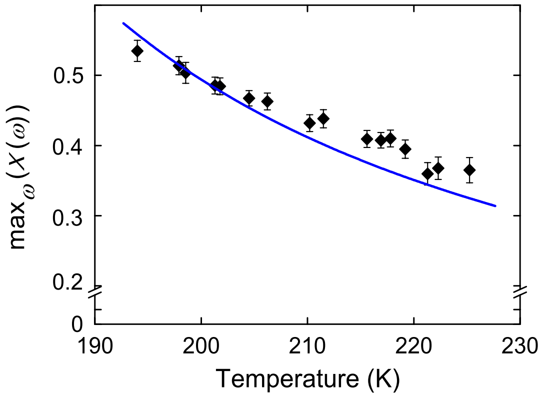

FIG. 3 (color online). The measured quantity $\max_\omega[X(\omega, T)] = \max_\omega(|\chi_3(\omega, T)|) \times k_B T/[\epsilon_0(\Delta\chi_1)^2 a^3]$ plotted vs temperature. The continuous line is the number of correlated molecules estimated from $T\chi_T$ (see [8]) with an arbitrary normalization chosen so that it coincides with the experimental points at 202 K.

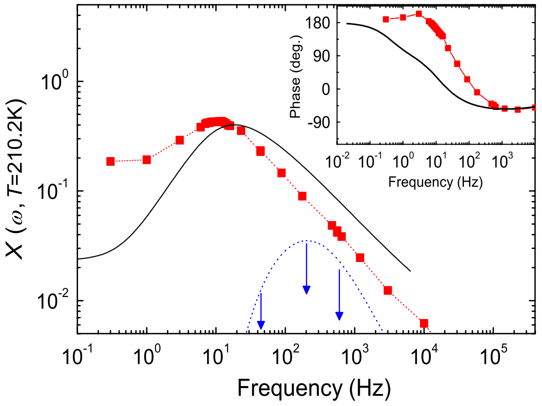

FIG. 4 (color online). The measured quantity $X(\omega, T)$ at 210.2 K (filled squares with dashed line) is compared to the same quantity calculated by using Eq. (2) with $\kappa \approx 7.6 \times 10^{-17}$ K(m/V)^2. Dotted line: Calculated heating contribution (upper limit, the arrows indicate the possible reduction [14]). Inset: The phase of $\chi_3(\omega, T)$ at 210.2 K (same symbols as for the main figure, dotted line not shown).

forward a phenomenological model [21,24,25] which accounts for their nonlinear susceptibility data at 1ω. In this model, the supercooled liquid is thought of as a collection of "Debye-like" dynamical heterogeneities (DHs), each of them having its own relaxation time $\tau_{\rm dh}$. The model posits that the electrical power absorbed by each DH raises its temperature above that of the phonon bath. A nontrivial and crucial assumption is that heat exchange between the slow degrees of freedom and the phonon bath is set by the local relaxation time $\tau_{\rm dh}$, and not by a microscopic vibration time. As a result, each DH has its own fictive temperature with a dc and an ac component. Again, the ac component $\delta T_{{\rm dh},2\omega}(t)$ leads to a 3ω "heating" contribution to the polarization $P(t)$. Such a contribution to χ_3 should however not be considered to be in competition with the critical dynamical correlations related to the glassy dynamics [12,13]. As this model assumes *a priori* the existence of dynamical heterogeneities, it should be seen as a phenomenological description of the influence of dynamical correlations on the nonlinear susceptibility. We calculated the prediction of this model for the 3ω nonlinear response and found that $\chi_3(\omega)$ is indeed peaked at a frequency of the order of $1/\tau(T)$. However, some assumptions are needed to generalize the model to the 3ω response. These assumptions influence the magnitude and position of the peak and deserve further scrutiny. A detailed comparison of this model to our data will be presented in a subsequent paper. In any case, we believe that for a proper prediction of $\chi_3(\omega, T)$ close to T_g, a theory of supercooled liquids able to account for dynamical correlations is required.

To conclude, we have provided the first direct experimental evidence that a supercooled liquid responds in an increasingly nonlinear way approaching the glass transition. By measuring the frequency dependent third harmonics response $\chi_3(\omega, T)$ to a periodic electric field, which is tightly related to the dynamical correlation length, we showed that the number of correlated molecules increases as T decreases towards T_g, confirmed the validity of previous estimates, and found that χ_3 scales as a function of $\omega\tau$. This opens a new path for probing the spatial correlations in both fragile and strong supercooled liquids and in the aging regime of glasses and spin glasses, by systematic studies of nonlinear responses. Future investigations along these lines might help to unveil the possible critical nature of the glass transition.

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