Supporting Information:

Divergence of third harmonic stress response to oscillatory strain approaching the glass transition

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The supplemental material contains experimental and theoretical details.

I. EXPERIMENTAL DETAILS

A. Specifications of experimental procedure

For the rheological experiments we use a polydisperse suspension of thermo-responsive core-shell particles 1 in 0.05 M potassium chloride solution with a solid content of 8.85%. The core of the particles consists of polystyrene and has a diameter of 70 nm, whereas the shell is a slightly crosslinked network of poly(N-isopropylacrylamide) with a degree of crosslinking of 2.5%. N,N’-methylenebisacrylamide was used as crosslinker. For the specific sample used here the hydrodynamic radius shows a linear dependence on the temperature according to $R_H = -0.6909 \, \text{nm}/^\circ\text{C} \times T + 94.11 \, \text{nm}$, which has been determined by dynamic light scattering experiments.

The rheological experiments were conducted on an ARES-G2 (TA Instruments) strain controlled rheometer using a Couette geometry (bob diameter 18.6 mm, cup diameter 20 mm) with a Peltier temperature control system. Each experiment was preceded by a pre-shear step at a shear rate of 50 s$^{-1}$ for 200 s in order to erase the previous shear history. A solvent trap was used to minimize water evaporation and allowed experiment durations of up to 3 days. Flow curves were recorded at shear rates in the range of $1 \times 10^{-4}$ to $10^0$ s$^{-1}$, linear viscoelastic moduli were measured at a strain amplitude of $\gamma = 0.01$ in the angular frequency range of $2.1 \times 10^{-5}$ to $250$ rad/s. Additional high frequency measurements of the linear viscoelastic moduli in the range $60 \, \text{rad/s} < \omega < 12500 \, \text{rad/s}$ were made using a piezo-axial vibrator 3 using a 50 mm spacer ring. For the medium amplitude oscillatory shear experiments, strain amplitude sweeps (0.001 $< \gamma < 0.3$) in the angular frequency range $2.1 \times 10^{-5}$ to $83$ rad/s were conducted to observe the strain amplitude dependent relative intensity of the third harmonic $|G_3''|/|G_1'|$, from which the intrinsic nonlinearity $Q_0(\omega)$ defined in Eq. (5) was deduced.

B. Determination of intrinsic parameters $[G_3']$ and $[G_3'']$

The intrinsic parameters $[G_3'(\omega)]$ and $[G_3''(\omega)]$ in Fig. 5 have been determined by fitting the strain amplitude dependent real and imaginary third harmonic intensities, $G_3'(\omega, \gamma_0)$ and $G_3''(\omega, \gamma_0)$, with a quadratic function, $G_3' = [G_3'']^2 \gamma_0$ and $G_3'' = [G_3'']^2 \gamma_0$, as depicted in Fig. S1. Data at large $\gamma_0$, where fifth order contributions become significant, were excluded from the fit. Exemplary results for the volume fractions $\phi = 0.614$, $\phi = 0.62$ and $\phi = 0.637$ show the general behavior of $G_3'$ and $G_3''$ as well as the fit of the quadratic term. Figure S1 (a) shows a typical result where $[G_3'] > 0$ and $[G_3''] > 0$. In Fig. S1 (b), $[G_3'] > 0$ and $[G_3''] < 0$. Figure S1 (c) displays a case where $[G_3'] > 0$ and $[G_3''] < 0$. At small $\gamma_0$, the intensities scatter around 0, this range of the measurements corresponds to the linear viscoelastic regime, where these intensities are vanishingly small. With increasing $\gamma_0$, $G_3'(\gamma_0)$ and $G_3''(\gamma_0)$ exhibit finite values with different trends depending on the volume fraction and the angular frequency. For $G_3'(\gamma_0)$, two cases were observed. Either an initially negative intensity which decreases to a minimum (Fig. S1(a)) at small frequencies or, at high frequencies, an initially positive intensity, followed by a maximum and a decrease that leads to a sign change with increasing $\gamma_0$ (Fig. S1(c)). For $G_3''(\gamma_0)$, two different behaviors were observed as well, but the trends are reversed in comparison to $G_3'(\gamma_0)$: Either an initially positive intensity, followed by a maximum and a decrease that leads to a sign change with increasing $\gamma_0$ for small frequencies (Fig. S1(a) and (b)) or initially negative intensity, followed by a minimum and an increase that leads to a sign change with increasing $\gamma_0$ for high frequencies (Fig. S1(c)). The intrinsic moduli give only the quadratic dependence for small $\gamma_0$. The change of sign of $|G_3'(\omega)|$ and $|G_3''(\omega)|$ moved to smaller frequencies for increasing volume fractions. At the lowest volume fraction of 0.614, a sign change in $|G_3'(\omega)|$ in a frequency window $10^{-3} < \omega R_H^2/\mu < 10^{-1}$ was expected from the prediction (Fig. 5). The experimental results in this range, however, were ambiguous with only one or two points of negative intensities (Fig. S1(d)) around $\gamma_0 \approx 0.03$ before strongly positive intensities took over. Due to the limited data and the resulting uncertainty of the fit, the last three data points in the $|G_3'(\omega)|$ curve of Fig. 5 could not be determined.

II. THEORETICAL DETAILS

The properties of $Q_0$ discussed in the main text are derived using an expansion of the equations of motion of the density correlation function for small shear strain amplitudes. Here we present the explicit calculations.

Taylor expansion of the schematic model, Eq (6)-(9) yields for the two leading functions $f_0$ (at the fundamental fre-
FIG. S1. Experimentally determined $G'_3(\omega, \gamma_0)$ and $G''_3(\omega, \gamma_0)$ (rescaled by particle radius $R_H$ and thermal energy $k_B T$), depending on the strain amplitude $\gamma_0$. Lines show fits of $G'_3 = [G'_3(\gamma_0)^2$ (solid line) and $G''_3 = [G''_3(\gamma_0)^2$ (dashed lines) that were used to determine the intrinsic quantities $[G'_3(\omega)]$ and $[G''_3(\omega)]$.

FIG. S2. Perturbation of the correlator, $f_R$, for different frequencies and separations ($\varepsilon < 0$) to the glass transition. Left: Amplitude of $f_R$ as function of time for various frequencies as labeled and fixed separation $\varepsilon = -10^{-4}$. The quasi-static limit is included as dotted lines; it is valid for short times before the oscillations, as well as for small $\omega < 1/\tau T \approx 10^{-9}$. Right: Amplitude of $f_R$ for various fixed products $\omega \nu$ as labeled and two values of $\varepsilon$ (solid lines $\varepsilon = -10^{-6}$, dashed lines $\varepsilon = -10^{-7}$). The region of validity of the power-laws extends on $\varepsilon \to 0-$ and their vertical shift is given by $x(\nu \omega)$ or $\tilde{x}(\omega \nu)$. 
quency) and \( f_1 = f_R + i f_i \) (at the shifted frequency) defined in Eq. (12) linear integro-differential equations with the known equilibrium correlator taken from MCT \([4]\) as input. They depend on the time-difference which will be nondimensionalized in the following \( v = (t - t') \Gamma \); analogously \( \bar{\omega} = \omega / \Gamma \).

The equation for \( f_0(v) \in \mathbb{R} \) with the initial condition \( f_0(0) = 0 \) is:

\[
\begin{align*}
0 &= f'_0(v) + (1 + \mathcal{F}[\Phi_{eq}](0)) f_0(v) \\
&+ \int_0^v ds \ f_0(v - s) \Phi'_eq(s) \ [\mathcal{F}[\Phi_{eq}](v-s) + \mathcal{F}[\Phi_{eq}](s)] \\
&+ (2 - \cos \bar{\omega}v) (\Phi'_eq(v) + \Phi_{eq}(v)) \\
&+ \int_0^v ds \ \Phi'_eq(s) \cdot \mathcal{F}[\Phi_{eq}](v-s) \cos \bar{\omega}(v-s),
\end{align*}
\] (S.1)

with \( \mathcal{F}[\Phi](t) = \delta \mathcal{F}(t)/\delta \Phi \). The equation for \( f_1(v) = f_R(v) + i f_i(v) \) with initial condition \( f_1(0) = 0 \) takes the form:

\[
\begin{align*}
0 &= f'_1(v) + (1 + \mathcal{F}[\Phi_{eq}](0) + i \bar{\omega}) f_1(v) \\
&+ \int_0^v ds \ f_1(v - s) \Phi'_eq(s) \\
&\cdot \left[ e^{i \bar{\omega}s} \mathcal{F}[\Phi_{eq}](v-s) + e^{-i \bar{\omega}s} \mathcal{F}[\Phi_{eq}](s) \right] \\
&+ \frac{1}{2} \left( 1 - \cos \bar{\omega}v \right) (\Phi'_eq(v) + \Phi_{eq}(v)) \\
&- \frac{1}{2} \int_0^v ds \ e^{i \bar{\omega}s} \Phi'_eq(s) \cdot \mathcal{F}[\Phi_{eq}](v-s) \left[ 1 - \cos \bar{\omega}(v-s) \right].
\end{align*}
\] (S.2)

### A. Numerical solution

Close to the glass transition, the decay time of the correlator diverges. To calculate the functions \( f_j \) numerically, we therefore straightforwardly adapted the strategy developed for numerically obtaining \( \Phi_{eq}(t) \) \([5]\). After a fixed number of time-steps, the step-size is doubled. To ensure stability over long times, the discretization of the derivatives and integrals has to preserve the long-time behavior. We checked that step-sizes large with respect to the oscillation time yield correct results by comparing with an alternative implementation where a maximal step-size was chosen. We also verified the numerical solutions with long-time behavior expected in the glass, and with the numerical solution of the full problem \([6]\).

In Fig. [S2] we show numerical results for the amplitude of \( f_R(v) \), for different values of the shearing frequency \( \bar{\omega} \) and different distances from the glass transition \( \varepsilon \). The numerical \( f_1 \) show oscillations with a slowly varying amplitude around a value close to zero. On large time-scales, the enveloping function decays to zero during the \( \alpha \)-process of the liquid close to the glass transition \( \varepsilon \rightarrow 0 \). Shear moduli shown in the main text are calculated with numerical solutions of \( f_1 \) for (low) frequencies where stable numerical solutions could be achieved.

### B. Scaling behavior of the Taylor expansion

To lowest order in the shear amplitude, only the function \( f_1 \) influences \( Q_0 \). Here we analyze its scaling behavior, which then gives results for the scaling of \( Q_0 \).

Upon approaching the glass transition, the time-scales of different processes in the liquid diverge for the unsheared system. As the time scales of the \( \alpha \)- and \( \beta \)-processes depend on separation \( \varepsilon \) differently, each process can be analyzed separately. Close to the glass transition, the equilibrium correlator behaves in the \( \beta \)-process window as \([4]\)

\[
\Phi_{eq}(v) = f_c + \sqrt{|\varepsilon|} g_\beta \left( \frac{v}{t_c} \right) + O(\varepsilon).
\] (S.3)

This can be used to expand the equilibrium memory kernel \( \mathcal{F} \) as well,

\[
\begin{align*}
F(v) &= m_c + m'_c \sqrt{|\varepsilon|} g_\beta \left( \frac{v}{t_c} \right) + O(\varepsilon) \quad (S.4) \\
F'(v) &= m'_c + m''_c \sqrt{|\varepsilon|} g_\beta \left( \frac{v}{t_c} \right) + O(\varepsilon), \quad (S.5)
\end{align*}
\]

with \( m_c = f_c/(1 - f_c) \), \( m'_c = (1 - f_c)^{-2} \) and \( m''_c = 2 \lambda \rho m'_c/f_c \) for the present model. Further, we renormalize time and frequency, \( v' = v/t_c \) and \( \bar{\omega}' = \bar{\omega} t_c \). With this, the linearized equation \( [S.2] \) can be solved on fixed time \( v' = \) const. for small separations \( \varepsilon \) from the glass transition.

\[
\begin{align*}
&-\lambda g_\beta(v') f_1(v') \quad (S.6) \\
&+ \frac{1}{2} e^{i \bar{\omega}v'} \frac{d}{dv'} \int_0^{v'} dr' g_\beta(v' - r') e^{-i \bar{\omega}r'} f_1(r') \quad (S.7) \\
&+ \frac{1}{2} e^{-i \bar{\omega}v'} \frac{d}{dv'} \int_0^{v'} dr' g_\beta(v' - r') e^{i \bar{\omega}r'} f_1(r') \quad (S.8)
\end{align*}
\]

\[
= - \frac{f_c}{\sqrt{|\varepsilon|} m'_c} (1 - \cos(\bar{\omega}v')) + O(\varepsilon^0). \quad (S.9)
\]

We can then analyze the limit \( v' \rightarrow 0 \) with \( \bar{\omega}' \rightarrow \infty \), so that \( v' \bar{\omega}' = \bar{\omega}v \) remains fixed, with \( g_\beta(v') \rightarrow A v'^{-a} \). Similarly, we can analyze the opposite limit \( v' \rightarrow \infty \) with \( \bar{\omega}' \rightarrow 0 \), so that \( v' \bar{\omega}' = \bar{\omega}v \) again remains fixed, with \( g_\beta(v') \rightarrow -B v'^b \).

We find

\[
\begin{align*}
v'^{-a} f_R(v' \rightarrow 0) &\rightarrow \frac{x(\bar{\omega}v)}{\sqrt{|\varepsilon|}} \quad (S.10) \\
v'^b f_R(v' \rightarrow \infty) &\rightarrow \frac{\tilde{x}(\bar{\omega}v)}{\sqrt{|\varepsilon|}}, \quad (S.11)
\end{align*}
\]

where \( x(y) \) and \( \tilde{x}(y) \) can be obtained numerically. The two power-law scalings are shown in Fig. [S2]b for different fixed \( \bar{\omega} v \) and two different separations \( \varepsilon \). This proves the divergence of the shear-induced perturbation increasing as \( 1/\sqrt{|\varepsilon|} \) and the numerically observed power laws. It leads to the observed scalings of \( Q_0 \).

#### 1. Quasi-static limit

For the quasi-static limit \( \bar{\omega} \rightarrow 0 \), we keep the periodicity of the average time variable \( (t + t')/2 \) that we have because of
oscillatory shear, else we had TTI and the higher harmonics would be zero, but perform a Taylor series for the sines and cosines of the time-differences \( v \). Starting from Eqs. (S.1) and (S.2), this gives

\[
f_0(v), 2f_1(v) = \bar{\omega}^2 f_{qs}(v) + O(\bar{\omega}^3) \tag{S.12}
\]

with

\[
0 = f'_{qs}(v) + (1 + \mathcal{F}[\Phi_{eq}](0)) f_{qs}(v) \\
+ \int_0^v ds f_{qs}(v-s) \Phi'_{eq}(s) \mathcal{F}'[\Phi_{eq}](v-s) + \mathcal{F}'[\Phi_{eq}](s) \\
+ \frac{1}{2} \omega^2 (\Phi'_{eq}(v) + \Phi_{eq}(v)) \\
- \frac{1}{2} \int_0^v ds \Phi_{eq}(s) \cdot (v-s)^2 \mathcal{F}[\Phi_{eq}](v-s).
\tag{S.13}
\]

A Taylor expansion for small times for \( \Phi_{eq}(v) \) leads to \( f_{qs}(v) = v^4 \bar{\omega}_s^4 \bar{\omega}_d^2 + O(v^6) \); it is included in Fig. S3(a) as dashed line. Because of the expansion of \( \cos \bar{\omega} v \), the power-law variations of the \( \beta \)-process in \( f_{qs} \) inherit a factor \( v^2 \):

\[
v'^{\alpha} f_{qs}(v') \rightarrow -\frac{C_{-\alpha} v'^{2\alpha}}{|\epsilon|} \tag{S.14}
\]

\[
v^b f_{qs}(v) \rightarrow \frac{C_b v^b}{|\epsilon|}, \tag{S.15}
\]

where the constants \( C_{-\alpha} \) and \( C_b \) are given by

\[
C_x = \frac{f(1-f)^2}{2X} \left[ \frac{\Gamma(x+3) \cdot \Gamma(1+x)}{\Gamma(2x+3)} + f - 1 \right]^{-1} \tag{S.16}
\]

with \( X = A \) for \( x = -\alpha \) and \( X = B \) for \( x = b \), where \( A, B \) are the coefficients of the scaling of \( g_\beta \) in the respective regimes. In Fig. S3(a), the quasi-static correlator \( f_{qs}(v) \) is shown for different distances to the glass transition \( \epsilon \). The scaling behaviors are indicated with black lines. In Fig. S2(a), a comparison of \( \bar{\omega}^2 f_{qs}(v) \) to the exact correction \( f_1(v) \) is shown for a number of frequencies \( \bar{\omega} \). Before the first maximum and the reversal of the shear, the correlator is described well, yet the oscillations at latter times are missed.

The quasi-static limit predicts a cubic increase of the third harmonic spectrum for small frequencies:

\[
|G_3(\omega)| = \bar{\omega}^2 \bar{\omega}_s i \omega F(\Phi_{eq}(v) \cdot f_{qs}(v))(2\bar{\omega}) + O(\bar{\omega}^4) \tag{S.17}
\]

The results from this quasi-static limit are shown in Figs. 3 and 4 in the main text as dotted lines.

We can use Eq. (S.17) to calculate the third-harmonic spectrum \( |G_3(\omega)| \) and \( Q_0 \) from the quasi-static correlator but going beyond the limit \( \omega \tau \ll 1 \), where it is rigorously valid. This leads to the quasi-static approximation [7]. We find that the whole shape of \( |G_3(\omega)| \) is described surprisingly well by this quasi-static approximation, see Fig. S3(b), even though the strong oscillations in \( f_1 \) are absent in \( f_{qs} \). The quasi-static approximation even recovers the sign changes in the moduli, and gives a basis for their explanation. The sign changes follow from the smooth drift of the exponents of power-law behavior in \( f_{qs} \sim t^x \), from \( x = 4 \) down. It leads to an effective exponent \( x \) drifting with frequency in the complex modulus: \( |G_{3,qs}| \sim (i\omega)^{-x} \sim e^{-ix/2} \omega^{-x} \). This identifies the three frequencies where real or imaginary part vanish as the loci where the drifting exponent crosses an integer.


