Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information: Anisotropic and heterogeneous dynamics in an aging colloidal gel

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Calculation of the temporal fluctuations in $C(q,t_1,t_2)$, $\chi_t(q,\tau,t_{max})$

The figure below presents a visual aid to equation 6 in the main text.

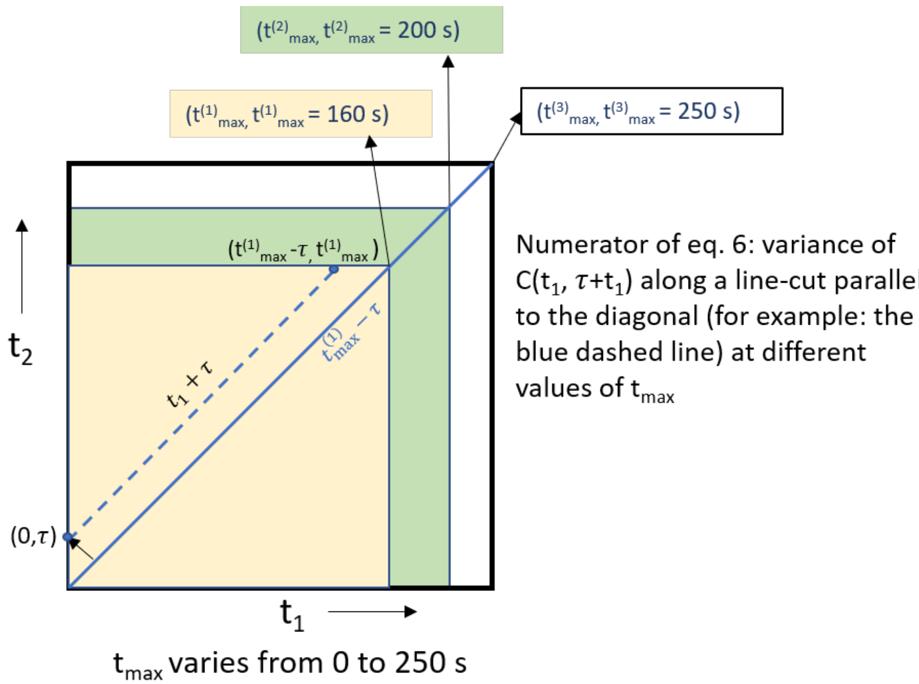

Fig. S1. 1 Calculation of the dynamical heterogeneity, χ_t for different values of t_{max} from the two-times correlation function, $C(t_1,t_2)$ at a given value of q.

Contribution of aging on χ_t

We calculate the influence of aging dynamics on the normalized variance of fluctuations in $C(q,t_1,t_2)$, χ_t using the procedure described in[1]. χ_t can be written as follows,

$$\chi_t(q,\tau,t_{max}) = \sigma^2_{g_2}/b^2(q), \tag{S1.1}$$

where $\sigma^2_{g_2}$ is the variance of the fluctuations of the intensity autocorrelation function, g_2, and $b^2(q)$ is a normalization factor representing the square of the short-time plateau value (or optical contrast) of the corresponding intensity autocorrelation functions. To calculate the effect of aging (i.e., increase of the characteristic relaxation time, τ_c during the experiment duration), we recall that the variance of a quantity y that depends on p variables is expressed as follows,

$$\sigma^2_y = \sum_{i=1}^{p}\left[\frac{\partial y}{\partial x_i}\right]^2 \sigma^2_{x_i} + \sum_{i\neq j}\left[\frac{\partial y}{\partial x_i}\frac{\partial y}{\partial x_j}\right]\sigma_{x_i,x_j}. \tag{S1.2}$$

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Here, $\sigma_{x_i}^2 = \langle x_i^2 \rangle - \langle x_i \rangle^2$ is the variance of x_i and $\sigma_{x_i,x_j} = \langle x_i x_j \rangle - \langle x_i \rangle \langle x_j \rangle$ is the covariance between x_i and x_j. The second sum vanishes if the distinct variables x_i's are uncorrelated. Using equation S1.2 to calculate the contribution of the variable τ_c and assuming that the quantity τ_c is uncorrelated with any other variable, we can write,

$$\sigma_{g_2,\tau_c}^2 = \left[\frac{\partial g_2}{\partial \tau_c}\right]^2 \sigma_{\tau_c}^2. \tag{S1.3}$$

Using the KWW function to describe g_2 (equation 3 in the main text), we find

$$\left[\frac{\partial g_2}{\partial \tau_c}\right]^2 = 4(g_2(q,\tau)-1)^2\left(\frac{\tau}{\tau_c}\right)^{2\gamma}\left(\frac{\gamma}{\tau_c}\right)^2. \tag{S1.4}$$

Meanwhile, the aging dynamics in the gels has been described (equation 5 in the main text), where

$$\tau_c(q,t_w) = \frac{\alpha(t_w+\tau_0)}{q}. \tag{S1.5}$$

The variance of τ_c within a certain window of measurement, t_{max}, is simply, $\sigma_{\tau_c}^2 = \frac{1}{12}\left(\frac{\alpha t_{\mathrm{max}}}{q}\right)^2$. Upon combining the above expressions, equation S1.3 becomes

$$\sigma_{g_2,\tau_c}^2(q,\tau,t_{\mathrm{max}}) = \frac{1}{3}(g_2-1)^2\left(\frac{\tau}{\tau_c}\right)^{2\gamma}\left(\frac{\gamma\alpha t_{\mathrm{max}}}{\tau_c q}\right)^2. \tag{S1.6}$$

Using equatonS1.6, for a given value of q and t_{max}, one can evaluate the aging contribution $\sigma_{g_2,\tau_c}^2(\tau)$. Firstly, one evaluates the autocorrelation function, $g_2(\tau)$. Using the KWW-equation, one then determines the fit parameters of the characteristic relaxation time (τ_c) and stretching exponent (γ). The value of α is used from the analysis of the sample aging behaviour. Note that the value of α may change depending on the sample conditions and t_{max}.

Characteristic time-scale of the heterogeneity vs. q, χ_t at longer waiting times

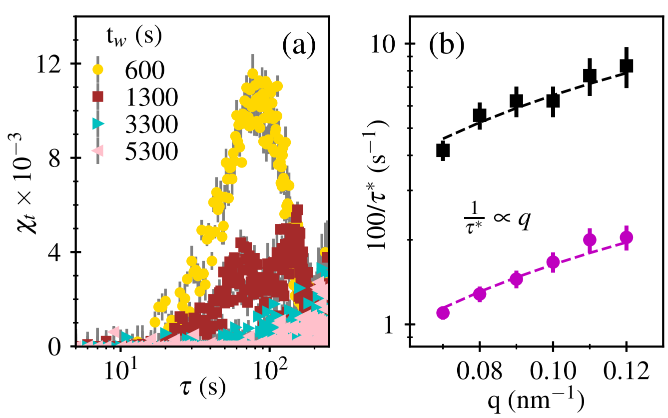

Fig. S1. 2 (a) χ_t curves averaged over all wave vectors are reported for different waiting times, t_w, at $q = 0.07\,\mathrm{nm}^{-1}$, and (b) τ^* vs. q at the earliest waiting time for the gels at temperatures T^* (black squares) and $T^* - 2$ K (magenta circles).

In Fig. 2 (a), χ_t curves averaged over all wave vectors are reported for different waiting times, t_w, at $q = 0.07\,\mathrm{nm}^{-1}$. Here, we observe at $t_w = 1300$ s, the χ_t profile displays a double peak suggesting the presence of multiple underlying dynamical entities. At longer waiting times, the dynamical heterogeneities level off over the range of delay times, implying that at $q = 0.07\,\mathrm{nm}^{-1}$, either the timescale of the heterogeneity is beyond the measured time window or simply, in order to resolve the dynamic susceptibility for these considerably slow dynamics, a higher value of t_{max} (or, duration of the measurement) is required. For example, in Fig.6 of the main text, the first peaked $\chi_\mathrm{t}(q_\parallel)$ curve at $t_w = 600s$ could only be calculated for values of $t_{\mathrm{max}} \geq 190$ s. Furthermore, at longer waiting times, as the system has slowed down significantly, the contribution due to aging will be trivial to the measured χ_t. For consistency, we plot the χ_t curve at $t_w = 600$ s. The relatively high peak

amplitude is a direct outcome of the aging contribution in the vertical direction.
In Fig. 2 (b), we track the q dependency of τ^* (the delay time corresponding to the maximum value of the averaged χ_t curve) at the earliest waiting time, $t_w = 600$ s, for the gel at both temperatures. We find that $1/\tau^* \propto q$ similar to the q-scaling of the characteristic relaxation rate (in both directions). This trend has also been reported for previous experiments[2,3]. We note that the slowing down of the relaxation time due to aging also shows a $\propto q$ behaviour, consequently, the timescale of the peak amplitude in the variance or τ^* is unaffected by the aging phenomenon.

Notes and references

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