Shear-stress fluctuations in self-assembled transient elastic networks

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Focusing on shear-stress fluctuations we investigate numerically a simple generic model for self-assembled transient networks formed by repulsive beads reversibly bridged by ideal springs. With Δt being the sampling time and t⋆(f) ~ 1/f the Maxwell relaxation time (set by the spring recombination frequency f) the dimensionless parameter Δx = Δt/Δg is dimensionless parameter Δx = ∆t/t⋆(f) is systematically scanned from the liquid limit (∆x ≫ 1) to the solid limit (∆x ≪ 1) where the network topology is quenched and an ensemble average over m independent configurations is required. Generalizing previous work on permanent networks it is shown that the shear-stress relaxation modulus G(t) may be efficiently determined for all ∆x using the simple-average expression G(t) = µA − h(t) with µA = G(0) characterizing the canonical-affine shear transformation of the system at t = 0 and h(t) the (rescaled) mean-square displacement of the instantaneous shear stress as a function of time t. This relation is compared to the standard expression G(t) = c̃(t) using the (rescaled) shear-stress autocorrelation function c̃(t). Lower bounds for the m configurations required by both relations are given.

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I. INTRODUCTION

A. Background: Permanent networks

A central rheological property characterizing the linear rheological property characterizing the linear shear-stress response in isotropic amorphous solids and glasses [1–3] and visco-elastic fluids [4–7] is the shear relaxation modulus G(t) sketched in panel (a) of Fig. 1. Experimentally, G(t) = δτ(t)/δγ may be obtained from the average stress increment δτ(t) as a function of time t after a small step strain δγ has been imposed at t = 0. As indicated by the solid horizontal line in panel (a), G(t) yields the equilibrium shear modulus Geq of the system in the long-time limit for t ≫ t⋆, with t⋆ being the terminal stress relaxation time [1–7]. Focusing on permanent elastic networks above the percolation threshold [1–3] with a finite shear modulus Geq as sketched in panel (b) of Fig. 1, it has been shown [10] that G(t) may be determined conveniently in computer simulations using the “simple average” expression

G(t) = µA − h(t)  (1)

with µA = G(0) being the “affine shear elasticity” characterizing the canonical-affine shear transformation (Appendix A) of the system at t = 0 [10–14] and h(t) = βV/2 ⟨(τ(t) − τ(0))2⟩ the (rescaled) mean-square displacement (MSD) of the instantaneous shear stress ̃τ(t). Here β = 1/T stands for the inverse temperature and V for the volume of the simulation box. See Appendix B for the related definitions of the instantaneous shear stress ̃τ and the instantaneous affine shear elasticity µA. Interestingly, the expectation value of Eq. (1) does not depend on the sampling time Δt even if much smaller times than the terminal time t⋆ are probed [10]. For sufficiently large systems Eq. (1) can be demonstrated using the simple-average transformation behavior [15–16] of µA and h(t) between the NVγT-ensemble at constant particle number N, volume V, shear strain γ and temperature T and the conjugated NVτT-ensemble at an imposed average shear stress τ [10].

Albeit the equilibrium shear modulus Geq may in principal be determined from the long-time limit of Eq. (1),

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most numerical studies [10–14, 17, 21] use instead the stress-fluctuation formula \( G_{\text{eq}} = G_F \) with

\[
G_F \equiv \mu \Delta - \mu_F = (\mu_A - \mu_F) + \mu_* \quad (2)
\]

and \( \mu_F \equiv \beta V \langle \dot{\gamma}^2 \rangle = \bar{\mu}_F - \mu_* \quad (3) \)

standing for the rescaled shear-stress fluctuations. We have introduced here for later convenience the two terms \( \bar{\mu}_F \equiv \beta V \langle \dot{\gamma}^2 \rangle \) and \( \mu_* \equiv \beta V \langle \dot{\gamma} \rangle^2 \). As sketched in panel (a) of Fig. 1, \( \mu_F \) corresponds to the (free) energy relaxed by non-affine displacements after an initial canonical-affine shear strain \( \delta \gamma \) is imposed. Note that \( G_F \) is a special case of the general stress-fluctuation relations for elastic moduli [17, 22–24]. As stressed elsewhere [10–12], being “fluctuations” (not “simple averages”) the expectation values of \( G_F, \mu_F \) and \( \mu_* \) may depend strongly on the sampling time \( \Delta t \) (as often marked below by indicating \( \Delta t \) as additional argument) and converge very slowly to their asymptotic static limit for \( \Delta t \gg t_* \). This behavior is not due to aging or equilibration problems but simply caused by the finite time needed for the stress fluctuations to explore the phase space [11]. Interestingly, using Eq. (1) and assuming time translational invariance it can be shown that \( G_F(\Delta t) \) and \( G(t) \) are related by

\[
G_F(\Delta t) = \frac{2}{\Delta t^2} \int_0^{\Delta t} (\Delta t - t) G(t) \, dt, \quad (4)
\]

i.e. \( G_F(\Delta t) \) is a (weighted) average of \( G(t) \) [25, 26]. It converges thus more slowly to \( G_{\text{eq}} \) but this with a better statistics. See Ref. [12] and Appendix F for details.

### B. New focus: Transient self-assembled networks

We generalize here our previous work on solid bodies [10–12] to visco-elastic liquids [4, 6, 7]. The first goal of the present work is to introduce and to characterize numerically a simple model for transient self-assembled networks [27–33]. As sketched in panel (c) of Fig. 1 repulsive “harmonic spheres” [34, 35] are reversibly bridged by ideal springs. It is assumed that the springs break and recombine locally with a Monte Carlo (MC) hopping frequency \( f \) in a similar manner as in earlier work on equilibrium polymer systems [36, 37]. As sketched by the bold dashed line in panel (a) of Fig. 1, these transient networks are shown to be simple Maxwell fluids [7], i.e. the shear-stress relaxation modulus decays exponentially

\[
G(t) \approx G_* \exp(-x) \quad \text{with} \quad x \equiv t/t_*(f) \quad \text{for} \quad t/t_* \gg 1 \quad (5)
\]

with \( t_* \) being a local time scale characterizing the decay of the initial affine displacements, \( t_*(f) \approx 1/f \) the Maxwell time and \( G_* \) the intermediate plateau modulus set by the equilibrium shear modulus \( G_{\text{eq}} \) for permanent springs (\( f = 0 \)). From the rheological point of view our model is very similar to patchy colloids [31, 32] or “vitrimers” [39], i.e. covalent polymer networks that can rearrange their topology via a bond shuffling mechanism.

Rheologically similar self-assembled transient networks may also be formed by hyperbranched polymer chains with sticky end-groups [33] or microemulsions bridged by telechelic polymers [27–29]. While mainly keeping the sampling time \( \Delta t \) constant, we systematically scan the dimensionless attempt frequency \( \Delta x \equiv \Delta t/t_* (f) \sim f \) from the liquid state (\( \Delta x \gg 1 \)), where the network topology is annealed, down to the solid limit (\( \Delta x \ll 1 \)), where the recombination events become irrelevant and the particle permutation symmetry is lifted [6]. Due to detailed balance this is done while keeping unchanged all static properties related to pair correlations. The \( \Delta x \)-dependence reported below for \( G(t) \) or \( G_F \) thus cannot be traced back to pair correlations as often assumed for glass-forming systems [26]. By integration of the general relation Eq. (1) for a Maxwell fluid, Eq. (5), one expects in fact the shear-stress fluctuations to be given by

\[
G_F(\Delta x) \equiv \mu_A - \mu_F(\Delta x) = G_* f_{\text{Debye}}(\Delta x) \quad (6)
\]

with \( f_{\text{Debye}}(x) = 2(\exp(-x) -1 + x)/x^2 \) being the Debye function well-known in polymer physics [5, 7]. We shall see that this important relation allows to interpolate our numerical data between the solid limit, where \( G_F(\Delta x) \rightarrow G_* \) and \( \mu_F(\Delta x) \rightarrow \mu_A - G_* \) for \( \Delta x < 1 \), and the liquid limit, where \( G_F(\Delta x) \rightarrow 0 \) and \( \mu_F(\Delta x) \rightarrow \mu_A \) for \( \Delta x \gg 1 \).

Using our simple model the second goal of this study is to show that Eq. (1) does not only hold for elastic solids (\( \Delta x < 1 \)) but more generally for visco-elastic bodies, i.e. for all values of \( \Delta x \). We shall compare this relation to the widely assumed expression [2, 15, 20, 31, 38, 39]

\[
G(t) = \bar{c}(t) \quad \text{with} \quad \bar{c}(t) \equiv \beta V \langle \dot{\gamma}(t) \dot{\gamma}(0) \rangle \quad (7)
\]

being the (rescaled) shear-stress autocorrelation function (ACF). Albeit Eq. (7) is incorrect for general elastic bodies [10, 12, 14], it may be justified under the condition

\[
\mu_A \frac{1}{\bar{c}(t=0)} \equiv \bar{\mu}_F. \quad (8)
\]

While this condition indeed holds on average for self-assembled networks, it requires on the numerical side that either \( \Delta x \gg 1 \), or, equivalently, an ensemble-average over a large number \( m \) of independent configurations. Being thus both in principle acceptable means to determine \( G(t) \) for any \( \Delta x \), this does, of course, not imply that Eq. (1) and Eq. (7) have the same statistics. We shall thus attempt to characterize the standard deviations of both relations and estimate lower bounds for the number of configurations required.

### C. Outline

Our numerical model is formulated in Sec. III where we also address several technical questions. Our central numerical findings are then discussed in Sec. IIIA. Carefully stating the subsequent time and ensemble averages performed, we present in Sec. IIIB the pertinent static
II. ALGORITHM AND TECHNICAL DETAILS

As sketched in Fig. 1 we use a generic model for self-assembled elastic networks in $d = 2$ dimensions where beads are reversibly bridged by ideal springs. These springs recombine locally with a Monte Carlo (MC) attempt frequency $f$. Lennard-Jones (LJ) units are used throughout this work [15] and the particle mass $m$, Boltzmann’s constant $k_B$ and the temperature $T = 1/\beta$ are set to unity. Periodic simulation boxes of constant volume $V = L^d$ and linear box size $L = 100$ are used. A standard Euclidean metric with a shear strain $\gamma = 0$ can be assumed (square box) if not stated otherwise. Moreover, the total number $N_b$ of beads and the number $N_{sp}$ of springs are kept constant in the present work.

As shown by the bold solid line in panel (a) of Fig. 2, the particles are modeled as “harmonic spheres” [34] interacting through the purely repulsive potential

$$U_b(r) = \frac{K_b}{2} (R_b - r)^2$$

for $r \leq R_b$ and $U_b(r) = 0$ elsewhere. The minimum of the shifted harmonic potential is used as cut-off to avoid truncation effects and impulsive corrections for the determination of the affine shear elasticity $\mu_A$ as described in Ref. [21].

The bead diameter is arbitrarily set to unity, $R_b = 1$, and a rather stiff spring constant $K_{sp} = 100$ is used making the beads very repulsive. The simulation box contains $N_b = 10^4$ beads, i.e. the number density $\rho = N_b/V$ of the beads is set to unity. Due to the strong repulsion and the high number density, the bead distribution is always macroscopically homogeneous and the overall density fluctuations are weak. This has been checked using snapshots, as the one shown in Fig. 3 and the standard radial pair correlation function $g(r)$ and its Fourier transform $S(q)$ [15] as presented in Fig. 4.
The bonding of two beads is described by

\[ U_{sp}(r) = \frac{K_{sp}}{2} (r - R_{sp})^2 \]  

(10)

with \( R_{sp} = 2 \) and \( K_{sp} = 10 \) as shown by the thin line in panel (a) of Fig. 2. Note that the minimum \( R_{sp} \) of the bonding potential is much larger than the bead diameter \( R_b \). There is thus no repulsion between two beads at \( r \approx R_{sp} \) and no sudden acceleration is felt (on average) if a bond is broken. As seen in panel (b) of Fig. 2 the probability distribution \( p(r) \) of springs of length \( r \) has a sharp maximum at \( R_{sp} \) and the number of springs with \( r < 1 \) or \( r > 3 \) is negligible. Our box contains a constant number \( N_{sp} = 4N_b \) of springs, i.e. on average a bead is connected by \( n_{sp} = 8 \) springs. This corresponds roughly to the maximum of the distribution \( p(n_{sp}) \) of the number \( n_{sp} \) of springs connected to a given bead presented in panel (c) of Fig. 2. Since there is no direct interaction (repulsion) between the springs, the maximum number of springs connected to a bead is limited to \( n_{sp} = 12 \) [40].

As sketched in panel (c) of Fig. 1 the network is reorganized by attempting with a frequency \( f \) local hopping moves for each spring. This is done by choosing first randomly a spring \( s \) connecting two beads \( i \) and \( j \). If the spring length \( r \) is smaller than a cut-off radius \( r_c = 5 \), the connection to one bead is broken, say bead \( j \), and we attempt to reconnect the spring to a randomly chosen monomer \( k \) (different from \( i \) or \( j \)) taken randomly from a neighbor list of beads with distance \( r < r_c \) from the pivot monomer \( i \) and having less than \( n_{sp} = 12 \) springs attached [41]. Using the energy change due to the different lengths of the suggested and the original spring state, the move is accepted subjected to a standard Metropolis acceptance criterion [15] [42]. The parameter \( r_c \) is chosen sufficiently small to reduce the neighbor list and to yield a reasonable, not too small acceptance rate \( A \approx 0.1 \) (found to be identical for all \( f \)). The computational load required by the reorganization of the network topology becomes negligible below an attempt frequency \( f = 0.01 \).

In addition to the MC moves changing the connectivity matrix of the network standard velocity-Verlet molecular dynamics (MD) [15] is used to move the beads through the phase space. The temperature \( T = 1 \) is imposed using a Langevin thermostat of friction constant \( \zeta = 1 \). This allows to suppress long-range hydrodynamic modes otherwise relevant for two-dimensional systems. A velocity-Verlet time step \( \delta t_{MD} = 10^{-2} \) is used. Every time step \( \delta t_{MD} \) a certain number of springs corresponding to the frequency \( f \) is considered for an MC hopping move. We start by equilibrating \( m = 100 \) independent configurations at \( f = 1 \). The frequency is then decreased with steps \( f = 1, 0.3, 0.1, 0.03, 0.01, \ldots, 10^{-7} \) and finally \( f = 0 \). At each step the configurations are tempered over a time interval \( t_{temp} = 10^4 \) and then sampled over \( t_{traj} = 10^5 \). Due to detailed balance changing \( f \) does not change the standard static properties, such as described by the pair correlation functions \( g(r) \) and \( S(q) \) (Fig. 4) or the energy per bead \( e \) or the normal pressure \( P \) shown in Table I. As we have checked, one could have also considered a much more rapid quench without changing these static properties. As seen from Fig. 3 we obtain homogeneous and isotropic elastic networks well above the percolation threshold [44] [8]. This is consistent with the large values \( G_F \approx 18 \) for small \( f \) in Table I.

### III. COMPUTATIONAL RESULTS

#### A. Static and quasi-static properties

We begin the description of our transient networks by discussing the static and quasi-static properties pre-
P, the shear stress τ, the affine shear elasticity μ_A and the contribution \( \bar{\mu}_F \) to the shear-stress fluctuation \( \mu_F \) do not depend on \( \Delta x \), i.e. the same values \( P \approx 1.7, \tau \approx 0 \) and \( \mu_A \approx \bar{\mu}_F \approx 33.2 \) have been obtained for all \( f \). The expectation values of these truly “static” properties cannot depend on \( \Delta t \) or on \( f \) since time and ensemble averages do “commute” [10], i.e. can be exchanged as

\[
\langle \bar{u} \rangle = \langle \bar{a} \rangle \quad \text{with} \quad \bar{a} = \bar{P}, \tau, \bar{\mu}_A \text{ or } \beta V \tau^2,
\]

and since the thermodynamic ensemble average \( \langle \ldots \rangle \) does not depend on \( \Delta t \) or \( f \). Although \( P, \tau, \mu_A \) and \( \bar{\mu}_F \) are all \( \Delta x \)-independent, this does not imply that they have the same statistics. The “simple averages” \( P, \tau \) and \( \mu_A \) have been obtained with a high precision while the “fluctuation” \( \bar{\mu}_F \) is rather noisy [10, 15].

A qualitatively different behavior is observed for the observables \( \mu_A(\Delta x), \mu_F(\Delta x) \) and \( G_F(\Delta x) \) also represented in Fig. 5. Please note that Eq. (18) does not hold for these properties as may be seen for \( \mu_A(\Delta x) = (\bar{\tau}^2) \geq 0 \) with \( s = \sqrt{\beta V} \tau \). Obviously, this differs from \( \langle \bar{\tau}^2 \rangle \sim \tau^2 \) which vanishes due to symmetry for all \( \Delta x \) for a sufficiently large ensemble. Ergodicity implies \( \bar{s} \equiv \langle s \rangle \) for large \( \Delta x \) and all \( \Delta x \)-effects become thus irrelevant. As seen from Fig. 5, this implies \( \mu_A(\Delta x) \rightarrow \beta V \bar{\tau}^2 = 0 \) for \( \Delta x \gg 1 \). Similarly, one observes \( G_F(\Delta x) = \mu_A - \mu_F(\Delta x) \rightarrow 0 \) and thus \( \mu_F(\Delta x) \rightarrow \mu_A \) as expected for liquids [11, 12]. The quasi-static properties become also constant for \( \Delta x \ll 1 \), where \( G_F(\Delta x) \rightarrow G_{\alpha}(f = 0) \approx 18 \) and \( \mu_F(\Delta x) \rightarrow \mu_f(f = 0) \approx 15 \). Interestingly, the transition between both limits around \( \Delta x \approx 1 \) is rather broad corresponding to several orders of magnitude. Our data are nicely fitted over the full range of \( \Delta x \) by the expected behavior Eq. (19) for a Maxwell fluid as indicated by the thin solid line for \( G_F(\Delta x) \approx \mu_A(\Delta x) \) and by the dashed-dotted line for \( \mu_F(\Delta x) = \mu_A - G_F(\Delta x) \). We remind that \( f_{\text{Debye}}(x) \rightarrow 1 \) for \( x \rightarrow 0 \) and \( f_{\text{Debye}}(x) \rightarrow 2/\pi x \) for \( x \gg 1 \). This implies that \( G_F(\Delta x) \) decays as \( 2G_*/\Delta x \) in the liquid limit as shown by the dotted line.

Let us finally consider the scaling of the two contributions \( \bar{\mu}_F\mu_F(\Delta x) \) to the shear-stress fluctuation \( \mu_F(\Delta x) \). As seen from Fig. 5, we have \( \bar{\mu}_F \approx \mu_A \) in agreement with Eq. (8) and in addition

\[
\mu_A(\Delta x) \approx G_F(\Delta x)
\]

for all \( \Delta x \). As already stressed, the expectation value of \( \bar{\mu}_F(\Delta x) \) does not depend on \( \Delta x \). This must especially hold for large \( \Delta x \) where the average shear stress \( \bar{\tau} \equiv \sqrt{\beta V} \bar{\tau} \) must vanish for each configuration and, hence, \( \mu_A(\Delta x) = (\bar{\tau}^2) \approx 0 \). Since the stress-fluctuation estimate \( G_F \) for the shear modulus, Eq. (2), must also vanish in the liquid limit, this implies \( 0 \approx \mu_A - \bar{\mu}_F \) for \( \Delta x \gg 1 \). Since \( \bar{\mu}_F \) does not depend on \( \Delta x \), this demonstrates Eq. (6) and using Eq. (2) this implies in turn Eq. (19). Please note that Eq. (8) and Eq. (19) do not hold for an arbitrary elastic body as shown, e.g., in Ref. [10]. In fact they do not necessarily hold even for one configuration of our ensemble if \( \Delta x \ll 1 \). As we shall see in Sec. III D they
been computed using number for vant. The two indicated solid lines form a lower en-

te the reorganization of the spring network is still irrele-

tenv.

B. Shear-stress mean-square displacement

The shear-stress MSD $h(t)$ is presented in Fig. 6 for a broad range of attempt frequencies $f$. The data have been computed using

$$h(t) = \frac{\beta V}{2} \left\langle \left( \hat{\tau}(t + t_0) - \hat{\tau}(t_0) \right)^2 \right\rangle$$

(20)

where the horizontal bar stands for the gliding average over $t_0 \equiv 12$ for each configuration using a fixed time window $\Delta t = 10^5$ and $\langle \ldots \rangle$ for the ensemble average over $m = 100$ configurations. Time and ensemble averages commute, Eq. (18), i.e. the expectation value of the MSD does not depend explicitly on the sampling time as emphasized in Ref. 10. Let us focus first on the main panel of Fig. 6 where the unscaled $h(t)$ is presented using double-logarithmic coordinates. Three dynamical regimes can be distinguished corresponding to the time windows (i) $t \ll t_A$, (ii) $t_A \ll t \ll t_s(f)$ and (iii) $t_s(f) \ll t$. The MSD does not depend on the attempt frequency $f$ in the first two regimes, i.e. the reorganization of the spring network is still irrelevant. The two indicated solid lines form a lower envelope for $h(t)$ for $f \to 0$. The MSD increases as $h(t) \sim t^2$ in the first regime $f = 0$ and shows an intermediate plateau with $h(t) \approx \mu_F(f = 0)$ in the second. Following Refs. 1014 the value of the crossover time $t_A \approx 0.12$ is fixed by matching the asymptotics as indicated by the vertical dash-dotted line. The second regime is consistent with the equilibrium modulus of the quenched network $G_{eq}(f = 0) = G_{eq}(f = 0) \approx \mu_A - h(t) \approx 18$ for $t_A \ll t \ll t_s(f)$. The spring recombinations become relevant for times of order $t_s(f)$. Depending on $f$ the MSD $h(t)$ increases now further approaching from below the long time limit $h(t) \to \mu_F(f > 0) = \mu_A$ and the $f$-dependence thus drops out again.

We have yet to verify the scaling of the network relaxation time $t_s(f)$ which characterizes the crossover from the second to the third regime. This is done in the inset of Fig. 6 where $h(t)$ is replotted using a half-logarithmic representation. The axes are made dimensionless by plotting $y(x) = (\mu_A - h(t))/G_s$ as a function of the reduced time $x \equiv t/t_s(f)$ where we set $G_s \equiv G_{eq}(f = 0)$ for the intermediate plateau modulus and $t_s(f) = 16/f$ for the network relaxation time. This rescaling leads to a perfect collapse of the data for $x \gg x_A(f) = t_A/t_s(f)$, especially for the $f$-dependent regime seen in the main panel. Moreover, the reduced MSD is seen to decay exponentially as $y(x) = \exp(-x)$ for $x \gg x_A(f)$ (dash-dotted line). The prefactor 16 for $t_s(f)$ has been introduced for convenience. For not too small attempt frequencies $f \geq 10^{-4}$, the exponential decay and the scaling of the relaxation time $t_s(f)$ may also be checked by plotting the unscaled $\mu_A - h(t)$ vs. $t$ using a linear-logarithmic representation (not shown).

Due to the uncorrelated recombinations of the springs a Maxwell fluid relaxation is expected for our simple model. The observed exponential decay, Eq. (6), thus confirms Eq. (1). This is also demonstrated by the comparison with the directly computed relaxation moduli for the two attempt frequencies $f = 0.01$ and $f = 10^{-6}$ corresponding, respectively, to the liquid limit ($\Delta x = 0.5 \gg 1$) and the solid limit ($\Delta x = 0.00025 \ll 1$). As in our recent studies on permanent elastic networks 101214 the relaxation modulus has been computed from the shear-stress increment $\langle \delta \hat{\tau}(t) \rangle$ with $\delta \hat{\tau}(t) \equiv \hat{\tau}(t) - \hat{\tau}(0)$ measured after a step-strain $\delta \gamma = 0.01$ has been applied at $t = 0$. This was done by applying a canonical-affine shear transformation (Appendix A) and by averaging over $m = 100$ independent configurations. The perfect data collapse for all times confirms Eq. (1).

C. Shear-stress auto-correlation function

Instead of using the MSD $h(t)$ the response modulus is generally estimated in computational studies using the shear-stress ACF $\dot{c}(t) \equiv \beta V \langle \dot{\tau}(t + t_0)\dot{\tau}(t_0) \rangle$ presented in Fig. 7. Time and ensemble averages do again commute and the expectation value does thus not depend on $f$ or $\Delta t$. As suggested in Ref. 10, one can instead of using the MSD $h(t)$ and Eq. (1) equivalently determine the relaxation modulus using

$$G(t) = \mu_A - \dot{\mu}_F + \dot{c}(t).$$

(21)
This is justified under the condition that the measured values for $\mu_A$ and $\tilde{\mu}_F$ for each $f$ are taken. Due to the exact identity $[5]$

$$h(t) = \tilde{c}(0) - \tilde{c}(t) = \tilde{\mu}_F - \tilde{c}(t)$$

(22)

this yields precisely the same results (not shown) as already presented in the inset of Fig. 8. Please note that for a general solid body, $\mu_A - \tilde{\mu}_F$ may be very different from zero and cannot be neglected in general [10].

Albeit the expectation value of this difference (obtained for asymptotically large $m$ or $\Delta x$) does vanish for any liquid (Fig. 5), the difference found for $m = 100$ configurations is apparently not small enough. This explains the bad scaling for small $f$ shown in Fig. 7 where $\tilde{c}(t)/G_*$ is traced as a function of $x = t/t_*$ as in the inset of Fig. 6. The approximation Eq. (7) thus does not have the same status as the fundamental relation Eq. (1).

D. Minimal number of configurations required

Using the $m$ independent configurations for each $f$ we have computed the standard deviations $\delta o \equiv \langle (\hat{o} - \langle \hat{o} \rangle)^2 \rangle^{1/2}$ and error bars $\delta o/\sqrt{m}$ associated with the average properties $\langle \hat{o} \rangle$ discussed above. Let us first summarize the standard deviations $\delta \mu_A$, $\delta \tilde{\mu}_F$ and $\delta G_F$ associated to $\mu_A$, $\tilde{\mu}_F$ and $G_F = \mu_A - \tilde{\mu}_F$. The corresponding error bars are traced in Fig. 8. As one expects assuming an increasing number $\propto \Delta x$ of independent networks probed by each configuration, all properties decay as $1/\sqrt{\Delta x}$ (dashed lines) in the liquid limit ($\Delta x \gg 1$).

Note that $\delta \mu_A$ and $\delta \tilde{\mu}_F$ become constant for $\Delta x \ll 1$ where each configuration only probes one network topology. As indicated by the bold horizontal line [44],

$$\delta \mu_F \approx \sqrt{2} \delta G_0(f = 0) \quad \text{for} \quad \Delta x \ll 1.$$  

Interestingly, $\delta G_F$ reveals a qualitatively different non-monotonic behavior with a clear maximum at the transition at $\Delta x \approx 1$ between the liquid and the solid limit. While $\delta G_F \approx \delta \tilde{\mu}_F$ for $\Delta x \gg 1$, $\delta G_F$ becomes several orders of magnitude smaller than $\delta \tilde{\mu}_F$ for $\Delta x \ll 1$ and even becomes similar to $\delta \mu_A$ for very small $\Delta x$. More details on the fluctuations of static properties (especially on their scaling with system size) will be given elsewhere.

Figure 9 presents the standard deviations $\delta (\mu_A - h(t))$ (filled symbols) and $\delta \tilde{c}(t)$ (open symbols) for several attempt frequencies $f$ as indicated. While $\delta \tilde{c}(t)$ becomes similar to this bound for $\Delta x \ll 1$, $\delta (\mu_A - h(t))$ is orders of magnitude smaller in the same limit. The thin horizontal lines indicate $\delta G_F(f = 0)$ for $f = 0$ (bottom), $f = 10^{-3}$, $f = 0.01$ and $10^{-3}$ (top). $\delta (\mu_A - h(t))$ is seen to approach this limit for $t \rightarrow \Delta t$.

FIG. 7: (Color online) Rescaled shear-stress ACF $\tilde{c}(t)/G_*$ vs. dimensionless time $x = t/t_*(f)$ for a broad range of $f$. Also indicated are the similarly rescaled relaxation moduli $G(t)$ obtained for $f = 0.01$ and $f = 10^{-6}$ by applying a step strain $\delta \gamma = 0.01$. The scaling clearly fails for small $f$ (small $\Delta x$).

FIG. 8: (Color online) Error bars $\delta o/\sqrt{m}$ for $o = \mu_A$, $\tilde{\mu}_F$ and $G_F = \mu_A - \tilde{\mu}_F$ as a function of $\Delta x = \Delta t/t_*(f)$. The error bars for $\mu_A$ are several orders of magnitude smaller than those for $\tilde{\mu}_F$. The deviations from $\mu_A - \tilde{\mu}_F = 0$ observed in Fig. 7 for small $f$ are thus due to the fluctuations of $\tilde{\mu}_F$.
and $\delta \tilde{c}(t)$ associated with Eq. (1) and Eq. (7). $\delta \tilde{c}(t)$ is apparently time-independent. One verifies that

$$\delta \tilde{c}(t) \approx \delta (\mu_A - \tilde{\mu}_F) \approx \delta \tilde{\mu}_F,$$

(24)
i.e. the noise is set by the fluctuations of the neglected term $\mu_A - \tilde{\mu}_F$. (As known from Fig. 8 $\delta \mu_A$ is negligible.) The limit Eq. (23) for $\delta \tilde{\mu}_F$ is thus also an upper bound for $\delta \tilde{c}(t)$ (bold horizontal line). The time-dependence of $\delta (\mu_A - h(t))$ is more intricate (filled symbols). One (slightly trivial) reason for this is that gliding dependence of $\delta$ and $\tilde{\mu}_F$ increases monotonously with time. It becomes similar to $\delta G (f)$ for $t \rightarrow \Delta t$ as indicated by thin horizontal lines. We emphasize that $\delta (\mu_A - h(t))$ is several orders of magnitude smaller than $\delta \tilde{c}(t)$ for most times $t$ and attempt frequencies $f$. Both fluctuations become similar only for large times $t \approx \Delta t$ in the liquid limit above $\Delta x \approx 1$.

The goal is now to characterize roughly the lower bound $m_{\text{min}}$ of configurations required for a given $\Delta x$ for both methods Eq. (1) and Eq. (7). Let us suppose that the relaxation modulus $G(t)$ is needed with a fixed precision $\delta G$, say $\delta G = 1$. As explained above, the problem with Eq. (7) is that $\tilde{\mu}_F$ is a strongly fluctuating quantity. Using Eq. (24) this leads to the criterion

$$m \gg m_{\text{min}} = (\delta \tilde{\mu}_F/\delta G)^2$$

for Eq. (7).

According to the upper limit Eq. (23) this corresponds to a minimal number of $m_{\text{min}} = 2(G_{\text{eq}}/\delta G)^2 \approx 650$ configurations in the solid limit which exceeds by nearly an order of magnitude the number of configurations we have been able to simulate. This is consistent with the bad scaling found in this limit in Fig. 7. As shown in Fig. 1 $\delta (\mu_A - h(t))$ is monotonously increasing with time approaching $\delta G (f)$ from below. Replacing the detailed time dependence by this upper limit yields the simple, albeit rather conservative criterion

$$m \gg m_{\text{min}} = (\delta G / \delta G)^2$$

for Eq. (1).

Both criteria are identical in the liquid limit where $\delta \tilde{\mu}_F \approx \delta G$. However, Eq. (26) corresponds to a pronounced maximum at $\Delta x \approx 1$ and decreases then by several orders of magnitude if we enter further into the solid limit. Note that the bound $m_{\text{min}}$ implied by Eq. (26) remains everywhere below $m = 100$. This is consistent with the excellent statistics observed in Fig. 6 for all $f$.

IV. CONCLUSION

A. Summary

The present study had two main goals. One was to introduce a simple generic model for self-assembled elastic networks (Sec. III) and to characterize it numerically (Sec. III). In this model repulsive beads are reversibly bridged by ideal springs which recombine locally with an MC attempt frequency $f$ (Fig. 1). By construction our transient networks are Maxwell fluids with a longest relaxation time $t_s (f) \sim 1/f$ and an intermediate plateau modulus $G_s$ given by the equilibrium shear modulus $G_{eq}$ for quenched network topologies ($f = 0$). By varying the dimensionless attempt frequency $\Delta x = \Delta t / t_s$ one may thus scan continuously between the liquid limit ($\Delta x \gg 1$) and the solid limit ($\Delta x \ll 1$). This was done by varying the attempt frequency $f$ (Figs. 15 and 16) and, more briefly, by changing the sampling time $\Delta t$ (Figs. 10 and 11). Due to detailed balance all static properties related to particle pair correlations (Fig. 4) are kept constant. This is different for the quasi-static properties $\mu_s (\Delta x)$, $\mu_F (\Delta x)$ and $G_F (\Delta x)$ due to the finite time needed for stress fluctuations to explore the phase space (Fig. 5). The $\Delta x$-dependence of these properties are perfectly described by the prediction Eq. (4) made for Maxwell fluids.

The second goal of this work was to use this deliberately simple model to verify (Fig. 6) the simple-average relation Eq. (1) recently proposed for the computational determination of the shear-stress relaxation modulus $G (t)$.[10] An alternative derivation of Eq. (1) was given (Appendix D) which does not rely on the steepest-descend assumption implicit to the Lebowitz-Percus-Verlet transformation between conjugated ensembles[15][16] used in our previous work [10][12][14]. The formula Eq. (1) has been compared (Fig. 16) with the generally assumed Eq. (7) using only the shear-stress autocorrelation function $c(t)$. While from the theoretical point of view the latter relation is applicable for liquids since Eq. (9) holds on average (Fig. 5), it imposes severe restrictions on computational studies due to the large fluctuations of $\tilde{\mu}_F$ (Fig. 5). This implies that at least $m_{\text{min}} \approx 2(G_{eq}/\delta G)^2$ independent configurations are needed for $\Delta x \ll 1$. At contrast to this Eq. (1) provides an approximation-free alternative with a much better statistics in the solid limit (Fig. 9).

B. Outlook

The present study has focused on the variation of the attempt frequency $f$ while keeping fixed other parameters such as the volume $V$, the bead density $\rho$, the spring density $\rho_p$ or the temperature $T$. It should be particularly rewarding to systematically investigate system size effects. While most properties discussed here, such as $\mu_A$, $\tilde{\mu}_F$, $h(t)$ or $c(t)$, are defined such that their expectation values, i.e. their first moments over the ensemble of independent configurations, should not depend explicitly on $V$, this is less obvious for their respective standard deviations. As stated by the criterion Eq. (25), we expect a strong lack of self-averaging[15][42] for $\delta \tilde{\mu}_F$, i.e. the approximation Eq. (7) should not improve with increasing system size, while strong self-averaging is expected for Eq. (1) in the low-$\Delta x$ limit. As already stated.


in the Introduction, our transient networks are rheologically similar to the Maxwell fluids formed by patchy colloids [31, 32] or by so-called “vitrimers” [30]. Interestingly, these physical gels can be reworked (just as silica glasses) to any shape by tuning gradually the system temperature $T$ which is the central experimental control parameter. Since our model potentials are rather stiff (Fig. 2), changing slightly $T$ will not alter much the local static structure, i.e., $\mu_a$ and $G_{eq}$ should remain essentially constant. However, by assuming the MC attempt frequency $f$ of our transient networks to be thermally activated, i.e. $f(T) \sim \exp(-B/T)$ as for patchy colloids [31], this should imply a strong Arrhenius behavior for the Maxwell relaxation time $t_*(f)$ and the shear viscosity

$$\eta \approx G_\star t_*(f) \sim 1/f \sim \exp(B/T).$$

(27)

Our networks should thus behave as “strong glasses” [2].

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Appendix A: Canonical-affine shear transformation

Let us apply an infinitesimal shear strain increment $\gamma \rightarrow \gamma + \delta \gamma$ to a periodic simulation box at constant box volume $V$ at a reference shear strain $\gamma$. (For simplicity all particles are in the principal box [15].) The positions $\mathbf{x}_i$ and the velocities $\mathbf{v}_i$ [15] of all particles $i$ are assumed to follow the “macroscopic” constraint in a both affine [18, 19] and canonical [46] manner according to

$$r_{i,x} \rightarrow r_{i,x} + \delta \gamma r_{i,y}, \quad v_{i,x} \rightarrow v_{i,x} - \delta \gamma v_{i,y} \quad (A1)$$

with $|\delta \gamma| \ll 1$. All other coordinates and velocities remain unchanged by the transformation as well as the network of springs connecting the particles. The negative sign for the velocities assures that the transform is “canonical” [45] and that, hence, Liouville’s theorem is obeyed [14, 46]. The transformation Eq. (A1) is used in Sec. [11, 13] to test our key relation Eq. (1).

Appendix B: Shear stress and affine shear elasticity

Let $\hat{\mathcal{H}}(\sigma, \gamma)$ denote the system Hamiltonian of a given state $\sigma$ at an imposed shear strain $\gamma$ of the simulation box. The state $\sigma$ of the system specifies the positions and velocities of the particles and the connectivity matrix of the ideal springs connecting them. The two configurations shown in panel (c) of Fig. 1 thus correspond to two different states. The instantaneous affine shear stress $\hat{\tau}$ and the instantaneous affine shear elasticity $\mu_a$ are defined by functional derivatives of the Hamiltonian with respect to the transform Eq. (A1)

$$\hat{\tau}(\sigma, \gamma) \equiv \left. \frac{\delta \hat{\mathcal{H}}(\sigma, \gamma)}{\delta \gamma} \right|_{\gamma=0} \quad (B1)$$

$$\mu_a(\sigma, \gamma) \equiv \left. \frac{\delta^2 \hat{\mathcal{H}}(\sigma, \gamma)}{\delta \gamma^2} \right|_{\gamma=0} \quad (B2)$$

For the differences of energy and shear stress caused by the transform this implies

$$\delta \hat{\mathcal{H}}/V \equiv (\hat{\mathcal{H}}(\sigma, \gamma + \delta \gamma) - \hat{\mathcal{H}}(\sigma, \gamma))/V$$

$$\approx \hat{\tau}(\sigma, \gamma) \delta \gamma + \frac{1}{2} \mu_a(\sigma, \gamma) \delta \gamma^2 \quad (B3)$$

$$\delta \hat{\tau} \equiv \hat{\tau}(\sigma, \gamma + \delta \gamma) - \hat{\tau}(\sigma, \gamma)$$

$$\approx \mu_a(\sigma, \gamma) \delta \gamma. \quad (B4)$$

With $\hat{\mathcal{H}}_{id}(\sigma, \gamma)$ and $\hat{\mathcal{H}}_{ex}(\sigma, \gamma)$ being the standard kinetic and the (conservative) excess interaction contributions to the Hamiltonian $\hat{\mathcal{H}}(\sigma, \gamma) = \hat{\mathcal{H}}_{id}(\sigma, \gamma) + \hat{\mathcal{H}}_{ex}(\sigma, \gamma)$, this implies similar relations for the corresponding contributions $\hat{\tau}_{id}$ and $\hat{\tau}_{ex}$ to $\hat{\tau} = \hat{\tau}_{id} + \hat{\tau}_{ex}$ and for the contributions $\mu_{a, id}$ and $\mu_{a, ex}$ to $\mu_a = \mu_{a, id} + \mu_{a, ex}$. For the ideal contributions this yields [13, 14, 45]

$$\hat{\tau}_{id}(\sigma, \gamma) = -\frac{1}{V} \sum_{i=1}^{N} v_{i,x} v_{i,y} \quad (B5)$$

$$\mu_{a, id}(\sigma, \gamma) = \frac{1}{V} \sum_{i=1}^{N} u_{i,y}^2 \quad (B6)$$

where the minus sign for the shear stress is due to the minus sign in Eq. (A1). In this study we focus on pairwise additive excess energies $\hat{\mathcal{H}}_{ex} = \sum_j u(r_{ij})$ with $u(r)$ being a pair potential and where the running index $l$ labels the interaction between two particles $i < j$. Straightforward application of the chain rule [11] shows that

$$\hat{\tau}_{ex}(\sigma, \gamma) = \frac{1}{V} \sum_{l} r_l u'(r_l) n_{l,x} n_{l,y} \quad (B7)$$

$$\mu_{a, ex}(\sigma, \gamma) = \frac{1}{V} \sum_{l} (r_l^2 u''(r_l) - r_l u'(r_l)) n_{l,x}^2 n_{l,y}^2$$

$$+ \frac{1}{V} \sum_{l} r_l u''(r_l) n_{l,y}^2 \quad (B8)$$

with $r_l$ being the distance between the beads and $n_l = \mathbf{r}_l/r_l$ the normalized distance vector. Note that Eq. (B7) is identical to the off-diagonal term of the standard Kirkwood stress tensor [15].

Appendix C: Shear-stress fluctuation formula

The stress-fluctuation formula Eq. (2) may be demonstrated elegantly [11, 14] using the Lebowitz-Percus-Verlet transformations between conjugated ensembles
applied to the \( NV^\gamma T \)- and \( NV\tau T \)-ensembles. However, due to the steepest-descent approximation implicit to this approach, which requires \( \beta VG_{eq} \gg 1 \), this approach cannot be used for transient networks since \( G_{eq}(f > 0) = 0 \). We give here a more general demonstration of Eq. \( 2 \). The average equilibrium shear stress at a strain \( \gamma \) is given by

\[
\tau(\gamma) = \sum_\sigma \hat{\tau}(\sigma, \gamma) p_{eq}(\sigma, \gamma)
\]

(C1)

where the sum runs over all accessible states \( \sigma \). The shear stress \( \hat{\tau}(\sigma, \gamma) \) of the state is given by Eq. \( \ref{eq:e2} \) and the normalized equilibrium distribution \( p_{eq}(\sigma, \gamma) \) by

\[
p_{eq}(\sigma, \gamma) = e^{-\beta \hat{H}(\sigma, \gamma)} / \sum_\sigma e^{-\beta \hat{H}(\sigma, \gamma)}.
\]

(C2)

The task is now to compute the difference \( \tau(\gamma + \delta\gamma) - \tau(\gamma) \) of the equilibrium shear stresses after and before the transform Eq. \( \ref{eq:e1} \). Using that

\[
\exp[-\beta \hat{H}(\sigma, \gamma + \delta\gamma)] \approx \exp[-\beta \hat{H}(\sigma, \gamma)] (1 - \beta \delta\hat{H})
\]

(C3)

with \( \delta\hat{H} \) being given by Eq. \( \ref{eq:e3} \) one shows that to leading order the equilibrium distribution after the shear transformation may be expressed as

\[
\frac{p_{eq}(\sigma, \gamma + \delta\gamma)}{p_{eq}(\sigma, \gamma)} \approx 1 - \beta \delta\hat{H} + \beta \langle \delta\hat{H} \rangle.
\]

(C4)

Using in addition Eq. \( \ref{eq:e4} \) it is then readily seen that

\[
\tau(\gamma + \delta\gamma) - \tau(\gamma) \approx \langle \mu_\Lambda \delta\gamma \rangle - \beta \left( \langle \hat{\tau}(\sigma, \gamma) \delta\hat{H} \rangle - \langle \hat{\tau}(\sigma, \gamma) \rangle \langle \delta\hat{H} \rangle \right)
\]

(C5)

to leading order. Since according to Eq. \( \ref{eq:e3} \) we have \( \delta\hat{H} \approx V \hat{\tau}(\sigma, \gamma) \delta\gamma \), this leads to linear order in \( \delta\gamma \) to

\[
\frac{\tau(\gamma + \delta\gamma) - \tau(\gamma)}{\delta\gamma} \approx \mu_\Lambda - \mu_\Phi + \mu_+.
\]

We have thus confirmed Eq. \( \ref{eq:e2} \) by only taking advantage of \( \delta\gamma \) being arbitrarily small. This shows that Eq. \( \ref{eq:e2} \) may also be used for liquids \( (G_{eq} = 0) \) or for systems where \( \beta VG_{eq} \ll 1 \). In the latter cases \( \mu_\Lambda \) and \( \mu_\Phi \) simply become, respectively, identical or similar.

### Appendix D: Shear-stress relaxation

Following Ref. [1] we present now an alternative demonstration of Eq. \( \ref{eq:e1} \) which does not require a finite equilibrium shear modulus. The time-dependent average shear stress \( \tau(t) \) for \( t > 0 \) is given by

\[
\tau(t) = \sum_\sigma \hat{\tau}(\sigma, \gamma + \delta\gamma) p(t, \sigma)
\]

(D1)

with \( p(t, \sigma) \) being the time-dependent probability distribution of the state \( \sigma \). We have \( p(t = 0, \sigma) = p_{eq}(\sigma, \gamma) \) directly after the transformation at \( t = 0 \) and \( p(t, \sigma) \rightarrow p_{eq}(\sigma, \gamma + \delta\gamma) \) for large times \( t \gg t_\ast \). Consistently with Eq. \( \ref{eq:e4} \) it is useful here to expand the old equilibrium distribution in terms of the new one

\[
p_{eq}(\sigma, \gamma) \approx p_{eq}(\sigma, \gamma + \delta\gamma) \left[ 1 + \beta \delta\hat{H} - \beta \langle \delta\hat{H} \rangle \right].
\]

(D2)

The time-dependent probability distribution is given by the general time evolution equation [2]

\[
p(t, \sigma) = \sum_{\sigma'} G(\sigma, \sigma'; t - t') p(t', 0, \sigma') \text{ for } t > 0
\]

(D3)

with \( G(\sigma, \sigma'; t - t') \) being an unspecified propagator of the system at \( \gamma + \delta\gamma \). We remind that a correlation function may be written as [3]

\[
\langle A(t) B(t') \rangle = \sum_{\sigma, \sigma'} A(\sigma) G(\sigma, \sigma'; t - t') B(\sigma') p(\sigma', t')
\]

(D4)

Inserting Eq. \( \ref{eq:e4} \) into Eq. \( \ref{eq:e4} \) and using Eq. \( \ref{eq:e4} \) this leads to

\[
\tau(t) \approx \langle \hat{\tau} \rangle + \beta \left( \langle \hat{\tau}(t) \delta\hat{H}(t' = 0) \rangle - \langle \hat{\tau} \rangle \langle \delta\hat{H} \rangle \right)
\]

where all averages are computed using the final equilibrium distribution \( p_{eq}(\sigma, \gamma + \delta\gamma) \). Subtracting the reference shear stress before the transform \( \tau(t = 0^-) = \tau(\gamma) \) on both sides of the equation leads to

\[
\frac{\tau(t) - \tau(t = 0^-)}{\delta\gamma} \approx \frac{\tau(\gamma + \delta\gamma) - \tau(\gamma)}{\delta\gamma} = \mu_\Lambda - \mu_\Phi + \mu_+. \quad (D5)
\]

to leading order. Taking finally \( \delta\gamma \rightarrow 0 \) and defining the ACF \( c(t) = \langle \hat{\tau}(t) \rangle - \mu_\Phi \) this is equivalent to \( G(t) = G_{eq} + c(t) \) in agreement with Ref. [12]. Taking in addition advantage of the exact identity \( h(t) = c(t) - c(0) = c(t) - c(0) \) [5] relating the shear-stress ACF with the shear-stress MSD, this implies in turn Eq. \( \ref{eq:e1} \).

### Appendix E: Scaling with sampling time \( \Delta t \)

The dimensionless variable \( \Delta x = \Delta t / t_\ast \) has been changed in the main text only as a function of the attempt frequency \( f \) while the sampling time \( \Delta t \) was kept constant for clarity. The scaling also holds if \( \Delta t \) is varied at a constant terminal time \( t_\ast \) as was done for permanent networks [10]. As shown in Fig. 10 for the stress-fluctuation formula \( G_\tau \), this assumes that both \( \Delta t \) and \( t_\ast(f) \) are sufficiently large. The time average over a sampling time \( \Delta t = t_{traj} = 10^5 \) is replaced by averages over (independent) subintervals of length \( \Delta t \leq t_{traj} \). Note that the largest values of \( \Delta x \) indicated in Fig. 10 for each \( f \) correspond to the data given in Fig. 5. As expected, all
FIG. 10: \( G_F(\Delta t) \) for subtrajectories of length \( \Delta t \leq t_{\text{traj}} \) as a function of \( \Delta t \equiv \Delta t / t_A(t_f) \approx \Delta t \) for different \( f \). The data scales for \( \Delta t \gg 1 \). The existence of an additional time scale is visible for small \( \Delta t \ll 1 \). The thin solid line indicates Eq. (6).

FIG. 11: Comparison of \( G(t) = \mu_A - h(t) \) and \( G_F(\Delta t) \equiv \mu_A - \mu_F(\Delta t) \) for one example in the liquid limit \( (f = 0.01, \Delta x = 62.5) \). Confirming Eq. (4), \( G_F(\Delta t) \) is equivalent to the weighted integral over \( G(t) \) indicated by the dotted line. Note that \( G_F(\Delta t) \approx \mu_A \) for \( \Delta t \ll t_A \) in agreement with Fig. 10.

Appendix F: Comparison of \( G(t) \) and \( G_F(\Delta t) \)

Assuming \( y(t) \) to be an arbitrary well-behaved function of \( t \) let us consider the linear functional

\[ \mathcal{P}_{\Delta t}[y(t)] = \frac{2}{\Delta t^2} \int_{0}^{\Delta t} dt \ (\Delta t - t) \ y(t) \ (F1) \]

motivated by Eq. (4). Note that contributions at the lower boundary of the integral have a strong weight due to the factor \( (\Delta t - t) \) and that for a constant function \( y(t) \equiv c \) we have \( \mathcal{P}_{\Delta t}[c] = c \), i.e. the \( \Delta t \)-dependence drops out. This does even hold to leading order if \( y(t) \approx c \) only for large \( t \) or for a finite \( t \)-window if this window is sufficiently large. Assuming time translational invariance the shear stress fluctuation \( \mu_F(\Delta t) \) is quite generally given by \( \mu_F(\Delta t) = \mathcal{P}_{\Delta t}[h(t)] \) \cite{12, 25}. Since \( \mu_A \) is constant, Eq. (F2) and Eq. (1) imply

\[ G_F(\Delta t) \equiv \mu_A - \mu_F(\Delta t) = \mathcal{P}_{\Delta t}[G(t)] \]

in agreement with Eq. (4). According to Eq. (F2), \( G_F(\Delta t) \) should become similar to \( G(t) \approx \Delta t \) in the three time windows \( t \ll t_A , t_A \ll t \ll t_A(f) \) and \( t_A(f) \ll t \) where \( h(t) \) and \( G(t) \) become approximatively constant (Fig. 6). This is consistent with the data presented in Fig. 11 for \( f = 0.01 \). Note that specifically \( G_F(\Delta t) \approx \mu_A \) for \( \Delta t \ll t_A \) in agreement with Fig. 10.

data points collapse on a master curve (thin solid line) as long as \( \Delta x \) remains sufficiently large. The data for small \( \Delta x \), where the scaling fails, correspond to \( \Delta t \ll 1 \). This merely shows that the additional time scale \( t_A \) (Fig. 6) becomes relevant. Since \( \mu_F \) vanishes for small \( \Delta t \), this leads to the limit \( G_F \rightarrow \mu_A \) indicated by the dashed line.
