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# Simple-average expressions for shear-stress relaxation modulus

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Focusing on isotropic elastic networks we propose a novel simple-average expression  $G(t) = \mu_A - h(t)$  for the computational determination of the shear-stress relaxation modulus  $G(t)$  of a classical elastic solid or fluid and its equilibrium modulus  $G_{\text{eq}} = \lim_{t \rightarrow \infty} G(t)$ . Here,  $\mu_A = G(0)$  characterizes the shear transformation of the system at  $t = 0$  and  $h(t)$  the (rescaled) mean-square displacement of the instantaneous shear stress  $\hat{\tau}(t)$  as a function of time  $t$ . While investigating sampling time effects we also discuss the related expressions in terms of shear-stress autocorrelation functions. We argue finally that our key relation may be readily adapted for more general linear response functions.

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## I. INTRODUCTION

*Background.* A central rheological property characterizing the linear response of (visco)elastic bodies is the shear relaxation modulus  $G(t)$  [1–3]. Assuming for simplicity an isotropic body,  $G(t) = \delta\tau(t)/\delta\gamma$  may be obtained from the stress increment  $\delta\tau(t)$  after a small step strain  $\delta\gamma$  has been imposed at time  $t = 0$  as sketched in panel (a) of Fig. 1. The instantaneous shear stress  $\hat{\tau}(t)$  may be determined in a numerical study, as shown in panel (b) for a sheared periodic simulation box, from the model Hamiltonian and the particle positions and momenta [4]. The long-time response yields the equilibrium shear modulus  $G_{\text{eq}} = \lim_{t \rightarrow \infty} G(t)$  as shown in panel (c). More readily, one may obtain  $G_{\text{eq}}$  by means of equilibrium simulations performed at constant volume  $V$  and shear strain  $\gamma$  using the stress-fluctuation relation [5–12]

$$G_{\text{eq}} = g \equiv \mu_A - \sigma \quad (1)$$

with  $\mu_A$  being the “affine shear-elasticity” [10–12], a simple average characterizing the second order energy change under a canonical-affine shear strain [12]. The second contribution  $\sigma \equiv \beta V \langle \delta\hat{\tau}^2 \rangle = \bar{\sigma} - \sigma_*$  stands for the rescaled shear stress fluctuation with  $\beta$  being the inverse temperature and where we have introduced for later convenience the two terms  $\bar{\sigma} \equiv \beta V \langle \hat{\tau}^2 \rangle$  and  $\sigma_* \equiv \beta V \langle \hat{\tau} \rangle^2$ . As shown in Refs. [10–12] Eq. (1) can be derived using the general transformation relation for fluctuations between conjugated ensembles [13]. Using these transforms for the shear-stress autocorrelation function (ACF)  $c(t) \equiv \beta V \langle \delta\hat{\tau}(t)\delta\hat{\tau}(0) \rangle \equiv \tilde{c}(t) - \sigma_*$ , Eq. (1) can be extended into the time domain [11, 12]. This allows the determination of the shear relaxation modulus using

$$G(t) = G_{\text{eq}} + c(t) \quad (2)$$

as illustrated by the thin dash-dotted line in panel (c). Note that Eq. (2) is more general than the relation

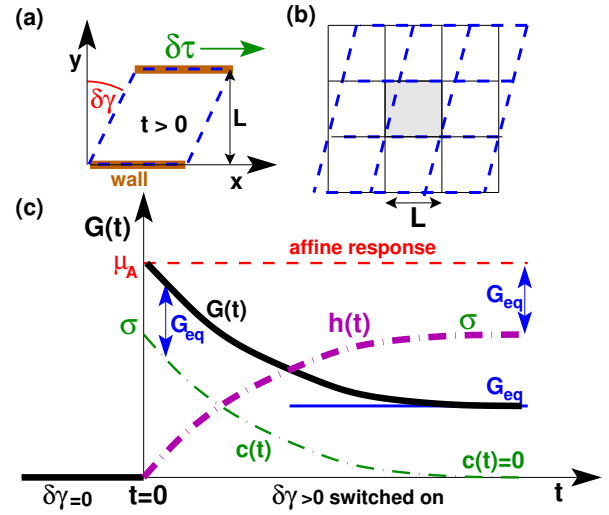


FIG. 1: Notations and addressed problem: (a) experimental setup with  $\delta\gamma$  being the shear strain,  $\delta\tau$  the shear stress increment and  $L$  the system size, (b) affine plain shear with periodic boundary conditions, (c) sketch of Eq. (2) and Eq. (3) with  $G(t)$  being the response modulus (bold solid line),  $G_{\text{eq}}$  the equilibrium shear modulus (thin solid horizontal line),  $\mu_A$  the affine shear-elasticity (thin dashed horizontal line),  $\sigma$  the shear-stress fluctuations,  $c(t)$  the ACF (thin dash-dotted line) and  $h(t) = \sigma - c(t)$  the MSD (bold dash-dotted line).

$G(t) = \tilde{c}(t)$  commonly used for liquids [3, 9, 14, 15]. One important consequence of Eq. (2) is that a *finite* shear modulus  $G_{\text{eq}}$  is only probed by  $G(t)$  on time scales where  $c(t)$  actually vanishes. While  $G_{\text{eq}}$  can be obtained from Eq. (1), this is not possible using *only*  $c(t)$  or  $\tilde{c}(t)$  [11].

*Key points made.* Note that both Eq. (1) and Eq. (2) assume that the sampling time  $\Delta t$  is much larger than the longest, terminal relaxation time  $t_*$  of the system and that, hence, time and ensemble averages are equivalent. Since both relations are formulated in terms of fluctuating properties, not in terms of “simple averages” [4], this suggests that they might converge slowly with increasing

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$\Delta t$  to their respective thermodynamic limits. The aim of the present study is to rewrite and generalize (where necessary) both relations in terms of simple averages allowing an accurate determination even for  $\Delta t \ll t_*$ . As we shall demonstrate this can be achieved by rewriting Eq. (2) simply as

$$G(t) = \mu_A - \tilde{\sigma} + \tilde{c}(t) = G(0) - h(t) \quad (3)$$

with  $G(0) = \mu_A$  and  $h(t) = \beta V/2 \langle (\hat{\tau}(t) - \hat{\tau}(0))^2 \rangle$  being the shear-stress mean-square displacement (MSD). We have used in the second step of Eq. (3) the exact identity

$$h(t) = \tilde{c}(0) - \tilde{c}(t) = c(0) - c(t) \quad (4)$$

with  $\tilde{c}(0) = \tilde{\sigma}$  and  $c(0) = \sigma$ . Both expressions given in Eq. (3) are numerically equivalent  $\Delta t$ -independent simple averages.

*Outline.* We begin by presenting in Sec. II the numerical model and remind some properties of the specific elastic network investigated already described elsewhere [11, 12]. Our numerical results are then discussed in Sec. III. Carefully stating the subsequent time and ensemble averages performed we present in Sec. III A the pertinent static properties as a function of the sampling time  $\Delta t$ . We emphasize in Sec. III B that the MSD  $h(t)$  is a simple average not explicitly depending on the sampling time and on the thermodynamic ensemble. It will be demonstrated that our key relation Eq. (3) is a direct consequence of this simple-average behavior. We shall then turn in Sec. III C to the scaling of the ACF  $c(t)$ . We come back to the  $\Delta t$ -dependence of some static properties in Sec. III D where we compare several methods for the computation of  $G_{\text{eq}}$ . Our work is summarized in Sec. IV where we discuss some consequences for the liquid limit and outline finally how Eq. (3) may be adapted for more general response functions.

## II. SOME ALGORITHMIC DETAILS

*Model Hamiltonian.* As in previous work [10–12] we illustrate the suggested general relations by molecular dynamics (MD) simulations [4] of a periodic two-dimensional network of ideal harmonic springs of interaction energy  $\hat{H}_{\text{ex}} = \frac{1}{2} \sum_l K_l (r_l - R_l)^2$  with  $K_l$  being the spring constant,  $R_l$  the reference length and  $r_l = |r_i - r_j|$  the length of spring  $l$ . (The sum runs over all springs  $l$  between topologically connected vertices  $i$  and  $j$  of the network at positions  $r_i$  and  $r_j$ .) The mass  $m$  of the (monodisperse) particles and Boltzmann’s constant  $k_B$  are set to unity and Lennard-Jones (LJ) units are assumed throughout this paper.

*Specific network.* As explained elsewhere [10, 12] our network has been constructed using the dynamical matrix of a strongly polydisperse LJ bead glass quenched down to  $T = 0$  using a constant quenching rate and imposing a relatively large average normal pressure  $P = 2$ . This yields systems of number density  $\rho \approx 0.96$ , i.e.

linear length  $L \approx 102.3$  for the periodic square box. Since the network topology is by construction *permanently fixed*, the shear response  $G(t)$  must approach a finite shear modulus  $G_{\text{eq}}$  for  $t \rightarrow \infty$  for all temperatures at variance to systems with plastic rearrangements. If not stated otherwise below, we use an NV $\gamma$ T-ensemble with constant particle number  $N = 10^4$ , volume  $V = L^2$ , shear strain  $\gamma = 0.00071$  [16] and temperature  $T = 1/\beta = 0.001$ . Due to the low temperature the ideal contributions to the average shear stress  $\tau$  or the affine shear-elasticity  $\mu_A$  are negligible compared to the excess contributions. The static (ensemble averaged) thermodynamic properties of our finite-temperature network relevant for the present study are  $P \approx 2$ ,  $\tau \approx \sigma_* \approx 0$ ,  $\sigma \approx \tilde{\sigma} \approx 18$ ,  $\mu_A \approx 34$  and  $G_{\text{eq}} = \mu_A - \sigma \approx 16$  as already shown elsewhere [10, 12].

*Technicalities.* As in Ref. [12] the data have been obtained using a Langevin thermostat of friction constant  $\zeta = 1$  and a tiny velocity-Verlet time step  $\delta t_{\text{MD}} = 10^{-4}$ . The instantaneous shear stress  $\hat{\tau}$  and several other useful properties such as the instantaneous affine shear-elasticity  $\hat{\mu}_A$  [12] are written down every  $10\delta t_{\text{MD}}$  over several trajectories of length  $t_{\text{traj}} = 10^5$ . This is much larger than the longest stress relaxation time  $t_* \approx 10$  of the network properly defined in Sec. III A. Packages of various sampling times  $\Delta t \leq t_{\text{traj}}$ , as shown in Fig. 2, are then analyzed in turn using first time (gliding) averages within each package [4]. Finally, we ensemble-average over different  $\Delta t$ -packages.

## III. COMPUTATIONAL RESULTS

### A. Sampling-time dependence of static properties

*Notations.* A time average of a property  $a$  within a  $\Delta t$ -package is denoted below by a horizontal bar,  $\bar{a}$ , and an ensemble average by  $\langle a \rangle$ . While “simple averages” of form  $\langle \bar{a} \rangle$  generally do not depend on the sampling time, this may be different for averages of type  $\langle \bar{a}^2 \rangle$  and similar non-linear “fluctuations”. To mark this sampling time dependence we often note  $\Delta t$  as an (additional) argument for the relevant property. Obviously, ergodicity implies  $\bar{a} \rightarrow \langle a \rangle$  for large sampling times  $\Delta t \gg t_*$  for all properties considered. Hence,  $\langle \bar{a}^2 \rangle \rightarrow \langle \langle a \rangle^2 \rangle = \langle a \rangle^2$ , i.e. all  $\Delta t$ -effects must ultimately become irrelevant and the argument  $\Delta t$  is dropped again to emphasize the thermodynamic limit.

*Simple averages.* We begin by verifying the (slightly trivial)  $\Delta t$ -dependence of the simple averages

$$\mu_A(\Delta t) \equiv \langle \bar{\hat{\mu}}_A \rangle \quad (5)$$

$$\tilde{\sigma}(\Delta t) \equiv \beta V \langle \bar{\hat{\tau}}^2 \rangle \quad (6)$$

$$\tilde{g}(\Delta t) \equiv \mu_A(\Delta t) - \tilde{\sigma}(\Delta t) \quad (7)$$

as shown in Fig. 2 (filled symbols). As expected, all three simple averages do indeed not depend on the sampling time and we shall drop below the argument  $\Delta t$ . We

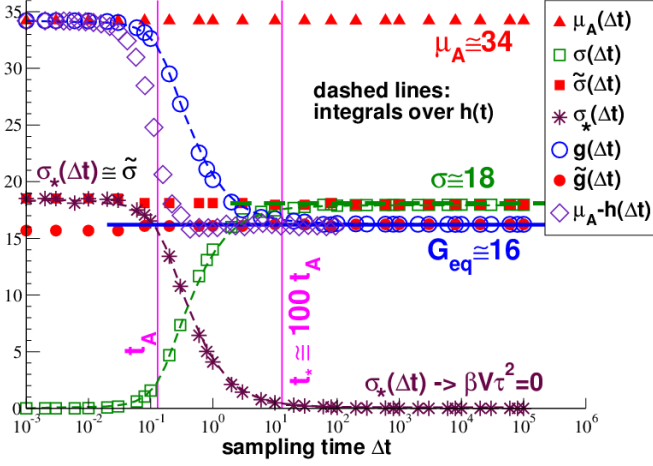


FIG. 2: Sampling time dependence of various static properties. The “simple averages”  $\mu_A$ ,  $\tilde{\sigma}$  and  $\tilde{g} = \mu_A - \tilde{\sigma}$  do not depend on  $\Delta t$  (filled symbols), while  $\sigma_*(\Delta t)$ ,  $\sigma(\Delta t)$  and  $g(\Delta t)$  do for  $\Delta t \ll t_* \approx 10 \approx 100t_A$ . Only for  $\Delta t \gg t_*$  these “fluctuations” converge to their thermodynamic limits  $\sigma_* = 0$ ,  $\sigma \approx 18$  and  $g = G_{\text{eq}} \approx 16$ . The dashed lines indicate for  $\sigma_*(\Delta t)$ ,  $\sigma(\Delta t)$  and  $g(\Delta t)$  the respective integrals over the MSD  $h(t)$  according to Eq. (19). The diamonds represent  $\mu_A - h(t = \Delta t)$  ensemble-averaged over  $10^4$   $\Delta t$ -packages.

remind that according to the stress-fluctuation formula Eq. (1)  $\mu_A$  gives an upper bound for the shear-modulus  $G_{\text{eq}}$  [10], while the rescaled second shear stress moment  $\tilde{\sigma}$  gives the leading term to the shear-stress fluctuation  $\sigma(\Delta t)$ . Consistently with other work [7, 10]  $\mu_A$  is about twice as large as  $\tilde{\sigma}$  and  $\tilde{g}$  is thus finite. As can be seen,  $\tilde{g}$  is essentially identical (for reasons given below) to the shear modulus  $G_{\text{eq}} \approx 16$  indicated by the bold solid line.

*Fluctuations.* While the simple averages are  $\Delta t$ -independent, this is qualitatively different for the three “fluctuations”

$$\sigma_*(\Delta t) \equiv \beta V \langle \tilde{\tau}^2 \rangle \quad (8)$$

$$\sigma(\Delta t) \equiv \tilde{\sigma} - \sigma_*(\Delta t) \quad (9)$$

$$g(\Delta t) \equiv \mu_A - \sigma(\Delta t) = \tilde{g} + \sigma_*(\Delta t) \quad (10)$$

presented in Fig. 2 which reveal three distinct sampling time regimes. For very small  $\Delta t \ll t_A \approx 0.13$  (with  $t_A$  being properly defined below in Sec. III B) the shear-stress fluctuations  $\sigma(\Delta t)$  do naturally vanish since the instantaneous shear-stress  $\hat{\tau}$  has no time to evolve and to explore the phase space. (There is no fluctuation for just one data entry.) Since  $\sigma(\Delta t) \approx 0$ , this implies that  $\sigma_*(\Delta t) \approx \tilde{\sigma}$  must have a constant shoulder and the same applies to the generalized stress-fluctuation formula  $g(\Delta t)$ , Eq. (10). The second time regime of about two orders of magnitude between  $t_A$  (left vertical line) and  $t_* \approx 10 \approx 100t_A$  (right vertical line) is due to the monotonous decay of  $\sigma_*(\Delta t)$ , i.e. the ensemble averaged *squared* time-averaged shear stress indicated by stars. As a consequence,  $\sigma(\Delta t)$  increases monotonously in this interval while  $g(\Delta t)$  decreases. The time scale  $t_*$  is the

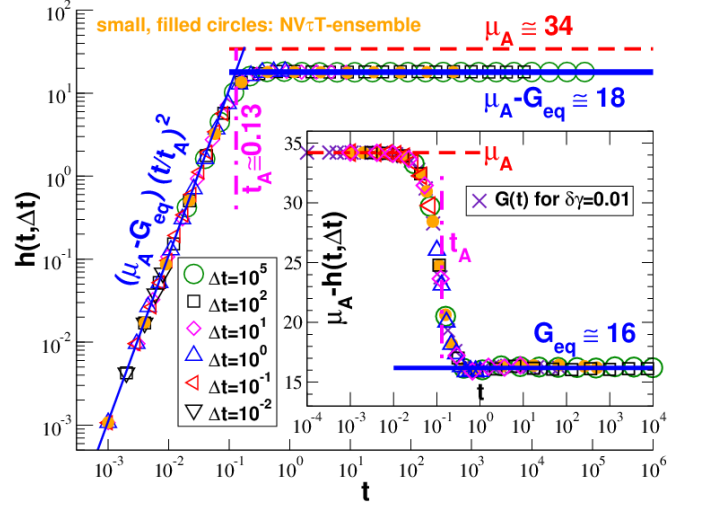


FIG. 3: Shear-stress MSD  $h(t, \Delta t)$  as a function of time  $t$ . The filled circles refer to  $\text{NV}\tau\text{T}$ -ensemble simulations for a sampling time  $\Delta t = 10^3$ , all open symbols to the corresponding  $\text{NV}\gamma\text{T}$ -ensemble for a broad range of  $\Delta t$ . All data collapse. Main panel: The MSD increases as  $h(t) \sim t^2$  for small times  $t \ll t_A$  (thin solid line) and becomes constant for  $t \gg t_A$  (bold solid line). The crossover time  $t_A \approx 0.13$  is obtained by matching both regimes. Inset: Comparison of  $\mu_A - h(t)$  with the shear-stress response function  $G(t)$  obtained from the shear-stress increment  $\langle \delta\hat{\tau}(t) \rangle$  after applying a step-strain increment  $\delta\gamma = 0.01$  at  $t = 0$  (crosses).

longest (terminal) time scale in this problem. Due to ergodicity time and ensemble averages become identical in the third sampling time regime for  $\Delta t \gg t_*$  where  $\tilde{\tau} \rightarrow \langle \hat{\tau} \rangle = \tau$ ,  $\sigma_*(\Delta t) \rightarrow \beta V \tau^2$ ,  $\sigma(\Delta t) \rightarrow \tilde{\sigma} - \beta V \tau^2$  and  $g(\Delta t) \rightarrow g = G_{\text{eq}}$  in agreement with the stress-fluctuation formula, Eq. (1).

*Imposed zero average shear stress.* Since for convenience we have chosen  $\tau = 0$  for our network, this implies that  $\sigma_*(\Delta t)$  must vanish and in turn that  $\sigma(\Delta t) \rightarrow \tilde{\sigma}$  and  $g \rightarrow \tilde{g}$  as observed. It is thus strictly speaking due to the choice  $\tau = 0$ , that the simple mean  $\tilde{g}$  actually corresponds to the shear modulus  $g = G_{\text{eq}}$ . For a more general imposed mean shear stress  $\tau$  one might, however, readily use the shifted simple average

$$\tilde{g} \Rightarrow \tilde{g} + \beta V \tau^2 = g = G_{\text{eq}} \quad (11)$$

using the known/imposed (not the sampled)  $\tau$  as a fast and reliable estimate of the shear modulus  $G_{\text{eq}}$  converging several orders of magnitude more rapidly than the classical (albeit slightly generalized) stress-fluctuation formula  $g(\Delta t)$ . We shall come back to the  $\Delta t$ -dependence of  $\sigma_*(\Delta t)$  and  $g(\Delta t)$  in Sec. III D.

## B. Shear-stress mean-square displacement

*$\Delta t$ -independence.* The MSD  $h(t, \Delta t)$  is presented in Fig. 3 as a function of time  $t$  for a broad range of sampling

times  $\Delta t$ . The data have been computed using

$$h(t, \Delta t) \equiv \frac{\beta V}{2} \left\langle \overline{(\hat{\tau}(t+t_0) - \hat{\tau}(t_0))^2} \right\rangle \text{ for } t \leq \Delta t \quad (12)$$

where the horizontal bar stands for the gliding average over  $t_0$  within a  $\Delta t$ -package [4] and  $\langle \dots \rangle$  for the final ensemble average over the packages. The first remarkable point in Fig. 3 is the perfect data collapse for all sampling times  $\Delta t$ , i.e. the MSD does not depend explicitly on  $\Delta t$ . This scaling is not surprising since  $h(t, \Delta t)$  is a simple average measuring the *difference* of the shear stresses  $\hat{\tau}(t+t_0)$  and  $\hat{\tau}(t_0)$  along the trajectory and increasing  $\Delta t/\delta t_{\text{MD}}$  only improves the statistics but does not change the expectation value. The second argument  $\Delta t$  is dropped from now on.

*Ensemble-independence of MSD.* The small filled circles in Fig. 3 have been obtained for  $\Delta t = 10^3$  in the NV $\tau$ T-ensemble at an imposed average shear stress  $\tau = 0$ . An ensemble of 1000 configurations with quenched shear strains  $\hat{\gamma}$  distributed according to the NV $\tau$ T-ensemble has been used [12, 17]. All other data presented have been obtained in the corresponding NV $\gamma$ T-ensemble [16]. As already emphasized elsewhere [12], it is inessential in which ensemble we sample the MSD, i.e.

$$h(t)|_{\tau} = h(t)|_{\gamma} \text{ for } t \leq \Delta t. \quad (13)$$

The MSD  $h(t)$  thus does not transform as a fluctuation, but as a simple average [4]. Interestingly, assuming this fundamental scaling property one may (alternatively) demonstrate Eq. (3). To see this let us write down the exact identity Eq. (4) in the NV $\tau$ T-ensemble

$$h(t)|_{\tau} = c(0)|_{\tau} - c(t)|_{\tau} = G(0) - G(t) \quad (14)$$

using in the last step that  $G(t) = c(t)|_{\tau}$  [18] as shown by integration by parts in Eq. (15) of Ref. [11]. Due to Eq. (13) and  $G(0) = \mu_A = \sigma|_{\tau}$  [11], this directly demonstrates  $G(t) = \mu_A - h(t)|_{\tau}$  in agreement with Eq. (3). (For convenience  $|_{\gamma}$  is dropped elsewhere.)

*Time-dependence of MSD.* As seen from the main panel of Fig. 3, the MSD  $h(t)$  of our extremely simple elastic network shows only two dynamical regimes. For small times  $t \ll t_A \approx 0.13$  the MSD increases quadratically as indicated by the thin solid line. This is to be expected if the MSD and/or the ACF are analytic around  $t = 0$  [12, 14]. (Strictly speaking, this argument requires time-reversal symmetry, i.e. begs for an asymptotically small Langevin thermostat friction constant.) For larger times  $h(t)$  becomes a constant given by  $h(t) = \mu_A - G_{\text{eq}} = \sigma$  (bold solid line) in agreement with Eq. (3) and  $G(t) \rightarrow G_{\text{eq}}$  for  $t \rightarrow \infty$ . As seen in the main panel, the crossover time  $t_A$  is determined from the matching of both regimes. It marks the time where all forces created by an affine shear transformation have been relaxed by non-affine displacements [12].

*Comparison with response function.* The key relation Eq. (3) is put to the test for all times  $t$  in the inset of

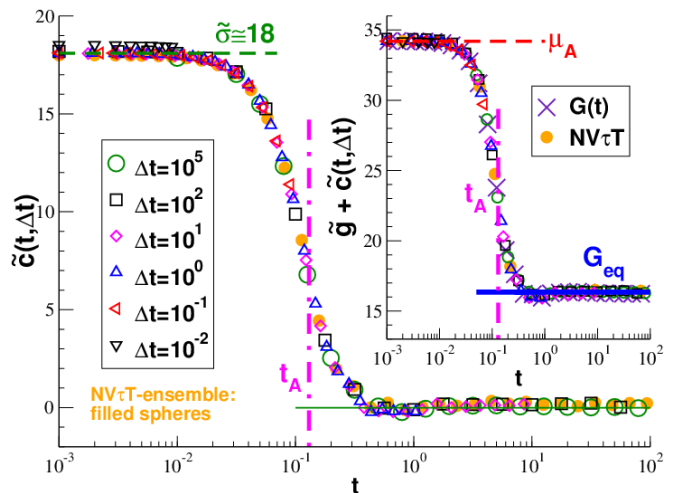


FIG. 4: Shear-stress ACF  $\tilde{c}(t, \Delta t) = \tilde{\sigma} - h(t, \Delta t)$  as a function of time  $t$  for different sampling times  $\Delta t$  as indicated. The filled spheres indicate results obtained in the NV $\tau$ T-ensemble. As the MSD  $h(t)$  the ACF  $\tilde{c}(t)$  is a simple average neither depending on  $\Delta t$  or the ensemble. Main panel:  $\tilde{c}(t) \rightarrow \tilde{\sigma}$  for  $t \rightarrow 0$  and  $\tilde{c}(t) \rightarrow \sigma_* = 0$  for  $t \gg t_A$ . Inset: Confirming Eq. (17) the shifted ACF  $\tilde{g} + \tilde{c}(t)$  collapses perfectly on the directly measured response function  $G(t)$ .

Fig. 3. We compare here  $\mu_A - h(t)$  obtained for different  $\Delta t$  with the shear-stress response  $G(t)$ . The latter quantity 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 is done using a metric-change of the periodic simulation box as illustrated in panel (b) of Fig. 1. As in Ref. [11]  $\langle \delta \hat{\tau}(t) \rangle$  has been averaged over 1000 configurations. The perfect collapse of all data presented confirms the key relation and this for all sampling times  $\Delta t$ . This is the main computational result of the present work.

### C. Shear-stress autocorrelation function

We present in Fig. 4 the shear-stress ACF

$$\tilde{c}(t, \Delta t) \equiv \beta V \left\langle \overline{\hat{\tau}(t+t_0)\hat{\tau}(t_0)} \right\rangle \text{ for } t \leq \Delta t \quad (15)$$

as a function of  $t$  comparing different  $\Delta t$  for the NV $\gamma$ T-ensemble (open symbols) and one example with  $\Delta t = 10^3$  for the NV $\tau$ T-ensemble (filled spheres). Since  $\tilde{c}(t) = \tilde{\sigma} - h(t)$ , this is essentially just a replot of the data already seen in Fig. 3 using, however, a more common representation. As one expects the ACF does depend neither on the sampling time nor on the ensemble, i.e.  $\tilde{c}(t)$  is a simple average just as  $h(t)$ . Interestingly, by writing the identity Eq. (4) for the NV $\gamma$ T-ensemble

$$h(t)|_{\gamma} = \tilde{c}(0)|_{\gamma} - \tilde{c}(t)|_{\gamma} = \tilde{\sigma}|_{\gamma} - \tilde{c}(t)|_{\gamma} \quad (16)$$

and using again Eq. (13) and Eq. (14) one verifies directly that within the NV $\gamma$ T-ensemble

$$G(t) = \tilde{g} + \tilde{c}(t) \quad (17)$$

$$= g(\Delta t) + c(t, \Delta t) \quad (18)$$

holds where for convenience  $|\gamma$  has been dropped and the same notations  $g(\Delta t) = \tilde{g} + \sigma_*(\Delta t)$  are used as in Sec. III A. Since  $g(\Delta t) \rightarrow g = G_{\text{eq}}$  for  $\Delta t \gg t_*$ , Eq. (18) thus confirms Eq. (2) but generalizes it to finite sampling times  $\Delta t$ . As seen in the inset the response function  $G(t)$  can be obtained by shifting  $\tilde{c}(t) \rightarrow \tilde{g} + \tilde{c}(t)$  confirming thus Eq. (18). We emphasize that while  $\tilde{c}(t)$  is a sampling-time independent simple average, the associated ACF  $c(t, \Delta t) = \tilde{c}(t) - \sigma_*(\Delta t)$  appearing in Eq. (16) and Eq. (18) is a *fluctuation*. It depends on the ensemble [11, 12] and on the sampling time due to the subtracted reference  $\sigma_*(\Delta t)$ . It is simply for this reason that for  $\Delta t \ll t_*$ ,  $c(t, \Delta t)$  is numerically less convenient than  $\tilde{c}(t)$ . However, for  $\Delta t \gg t_*$  both ACF become identical (not shown) since  $\tilde{c}(t) \rightarrow \sigma_* = \beta V \tau^2 = 0$  due to the zero average shear stress  $\tau = 0$  chosen.

#### D. Sampling-time effects revisited

We return now to the sampling-time behavior of the fluctuations  $\sigma_*(\Delta t)$ ,  $\sigma(\Delta t)$  and  $g(\Delta t)$  shown in Fig. 2. As seen, e.g., from Eq. (20) of Ref. [11], the  $\Delta t$ -effects can be understood by noticing that  $\sigma(\Delta t)$  may be written as a weighted integral over the MSD  $h(t)$  [19]

$$\sigma(\Delta t) = \frac{2}{\Delta t^2} \int_0^{\Delta t} dt (\Delta t - t)h(t). \quad (19)$$

Time translational invariance is assumed here and we have used that the MSD does not explicitly depend  $\Delta t$ . The sampling-time dependence of  $\sigma(\Delta t)$  is thus reduced to the time dependence of  $h(t)$ . Equation (19) and the corresponding relations for  $g(\Delta t) = \mu_A - \sigma(\Delta t)$  and  $\sigma_*(\Delta t) = \tilde{\sigma} - \sigma(\Delta t)$  are indicated by thin dashed lines in Fig. 2. Also given is the simple-average expression  $\mu_A - h(t = \Delta t)$  for  $\Delta t \leq 10^2$  (diamonds) using only the end-points of  $\Delta t$ -packages which are then in addition ensemble-averaged over  $10^4$  independent packages. Since this corresponds to the response modulus  $G(t)$  taken at  $t = \Delta t$ , it converges to  $G_{\text{eq}}$  already for sampling times  $\Delta t \gg t_A$ , i.e. two orders of magnitude earlier than the stress-fluctuation formula  $g(\Delta t)$  which only converges for  $\Delta t \gg t_* \approx 100t_A$ . The reason for this stems simply from the inequality

$$h(t = \Delta t) \geq \frac{2}{\Delta t^2} \int_0^{\Delta t} dt (\Delta t - t)h(t) \quad (20)$$

for a monotonously increasing function  $h(t)$ . Unfortunately, assuming the same number of  $\Delta t$ -packages,  $\mu_A - h(\Delta t)$  fluctuates much more strongly than  $g(\Delta t)$ ,

just as the end-to-end distance of a polymer chain fluctuates much more strongly as its radius of gyration. Equation (3) is thus only of interest for the determination of  $G_{\text{eq}}$  if a large ensemble of short trajectories with  $t_A \ll \Delta t \ll t_*$  has been computed. As already pointed out in Sec. III A, the most efficient property for the computation of the modulus is the simple average  $\tilde{g} + \beta V \tau^2$ . We note finally that since  $h(t)$  is characterized by only one characteristic time, the crossover time  $t_A$ , Eq. (19) implies that the terminal time  $t_*$  must be a unique function of  $t_A$  [20]. Our simple network is thus only characterized by *one* characteristic time.

## IV. CONCLUSION

*Summary.* Rewriting the central relation Eq. (2) of Ref. [11] it is shown that the shear-relaxation modulus  $G(t)$  of an isotropic elastic body may be computed as  $G(t) = \mu_A - h(t)$  in terms of the difference of the two simple averages  $\mu_A$  and  $h(t)$  characterizing, respectively, the canonical-affine strain response  $G(0)$  at  $t = 0$  and the subsequent stress relaxation process for  $t > 0$ . Interestingly, Eq. (2) and Eq. (3) may be directly demonstrated from the fundamental scaling  $h(t)|_\gamma = h(t)|_\tau$  (Sec. III B). Note that  $G(t) = \mu_A - h(t)$  and  $G(t) = \tilde{g} + \tilde{c}(t)$  are equivalent simple-average expressions as shown, respectively in Fig. 3 and Fig. 4. From the practical point of view it is important that  $h(t)$  or  $\tilde{c}(t)$  do not depend explicitly on the sampling time  $\Delta t$  and the response function  $G(t)$  may thus be computed even if  $\Delta t$  is much smaller than the terminal relaxation time  $t_*$  of the system. (For our simple networks  $t_* \approx 100t_A$  with  $t_A$  being the crossover time of the MSD.) As shown in Sec. III C, the relaxation modulus may be also obtained from the ACF  $c(t, \Delta t) = \tilde{c}(t) - \sigma_*(\Delta t)$  using  $G(t) = g(\Delta t) + c(t, \Delta t)$  with  $g(\Delta t) = \tilde{g} + \sigma_*(\Delta t)$  being the generalized, sampling-time dependent stress-fluctuation estimate for the shear modulus  $G_{\text{eq}}$ . For  $\Delta t \gg t_*$  these relations reduce to Eq. (2). Finally, comparing  $\mu_A - h(t \approx \Delta t)$  with the stress-fluctuation formula  $g(\Delta t)$  it has been shown (Sec. III D) that the former expression converges about two orders of magnitude more rapid, albeit with lesser accuracy depending on the number of independent  $\Delta t$ -packages used. The fastest convergence has been obtained, however, using the simple average  $\tilde{g} + \beta V \tau^2$  (Fig. 2).

*Discussion.* While the present paper has focused on solids, it should be emphasized that Eq. (3), being derived using quite general arguments not relying on a well-defined particle displacement field, should apply also to systems with plastic rearrangements and to the liquid limit. Due to its  $\Delta t$ -independence it should be useful especially for complex liquids and glass-forming systems [2] with computationally non-accessible terminal relaxation times  $t_*$ . We emphasize that the commonly used expression  $G(t) = \tilde{c}(t)$  requires  $\tilde{g} = \mu_A - \tilde{\sigma} = 0$  to hold [21]. While this condition is justified for a liquid where  $\tilde{g} = g = G_{\text{eq}} = 0$ , it is *incorrect* in general as shown



by the example presented in this work (Fig. 2). Hence, some care is needed when approximating  $G(t)$  by  $\tilde{c}(t)$  for systems below the glass transition [9, 15]. Since Eq. (3) can be used in any case and since it is not much more difficult to compute, it provides a rigorous alternative without additional assumptions [22, 23].

*Outlook.* Naturally, one expects that Eq. (3) can be generalized for more general linear relaxation moduli  $M(t)$  of classical elastic bodies and fluids. With

$$M_A = V \left\langle \frac{\partial \hat{i}_\beta}{\partial x_\alpha} \Big|_{x_\alpha x_\beta} \right\rangle \quad (21)$$

characterizing the initial canonical-affine response  $M(0)$  of the system to an infinitesimal change  $\delta x_\alpha$  of an extensive variable  $x_\alpha$  and  $\delta i_\beta$  the subsequent change of an intensive system variable  $i_\beta$  and

$$h(t) \equiv \frac{\beta V}{2} \left\langle \left( \hat{i}_\alpha(t) - \hat{i}_\alpha(0) \right) \left( \hat{i}_\beta(t) - \hat{i}_\beta(0) \right) \right\rangle \quad (22)$$

being the generalized MSD associated with the instantaneous intensive variables  $\hat{i}_\alpha(t)$  and  $\hat{i}_\beta(t)$ , one expects  $h(t)$  to be a simple average, i.e.  $h(t)|_{x_\alpha x_\beta} = h(t)|_{i_\alpha i_\beta}$ , and a generalized simple-average expression

$$M(t) = M(0) - h(t) \text{ with } M(0) = M_A \quad (23)$$

should thus hold again. The reformulation of the general stress-fluctuation formalism in terms of such simple averages and the test of its computational efficiency are currently under way.

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- [16] The specific network we use has a small, but non-vanishing shear stress  $\tau \approx 0.012$  at a fixed strain  $\gamma = 0$ . If the strain is allowed to fluctuate freely in the NV $\tau$ T-ensemble at an imposed average shear stress  $\tau = 0$  this yields a tiny, non-vanishing average shear strain  $\gamma_0 = 0.00071$  [12]. Since we wish to compare stress fluctuations in the NV $\tau$ T- and the NV $\gamma$ T-ensemble at the same state point with  $\tau = 0$ , all NV $\gamma$ T-ensemble simulations are performed at  $\gamma_0$  as in Ref. [12]. The differences with respect to simulations at  $\gamma = 0$  are obviously negligible.
- [17] As described in more detail in Ref. [12], a similar result is obtained using a very slow switched-on shear-barostat. If a strong shear-barostat is applied,  $h(t)$  approaches instead rapidly  $\sigma|_\tau = \mu_A$ .
- [18] The limit  $\Delta t \gg t_*$  has been taken for  $c(t, \Delta t)$  in Eq. (14). This is allowed since  $h(t)$  does not depend on  $\Delta t$ . The limit is required by the thermodynamic argument leading to  $G(t) = c(t)|_\tau$ .
- [19] A relation similar to Eq. (19) exists in polymer theory [3] expressing the radius of gyration of a polymer chain as a weighted integral over internal mean-squared segment sizes [3].
- [20] The ratio  $t_*/t_A \approx 100$  may be worked out by analyzing the integral  $\int_0^x ds(x-s)h(s)2/x^2$  with  $x = \Delta t/t_A$  and  $s = t/\Delta t$  and using that  $h(s) = \sigma s^2$  for  $s < 1$  and  $h(s) = \sigma$  for  $s > 1$ .
- [21] According to Eq. (10) this condition implies  $g(\Delta t) = \sigma_*(\Delta t)$  for the generalized stress-fluctuation formula for a sampling-time dependent shear modulus.
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- [23] The linear shear viscosity  $\eta$  may be obtained by integrating over  $G(t) = \mu_A - h(t)$ . Note that this integral has a different form as the Einstein relations for the shear-stress response discussed in the literature [4, 22] and that it does *not* suffer from problems related to the periodic boundary conditions.