Supplementary Material

Stress versus Strain Controlled Shear: Yielding and Relaxation of Concentrated Colloidal Suspensions

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Information on the response of the rheometers and tools (as well as samples) upon changes in the commanded applied shear is provided in this supplementary material. The different rheometers and tools as well as the different tests are considered.

The start-up as well as the cessation of shear ideally involve sudden changes of the applied stress or shear rate. However, the actual change depends on the specific rheometer, including the tool, as well as the sample. Especially the interplay between instrument inertia, sample elasticity and shear wave propagation determine the response of the whole system.[1–9] It is hence crucial to take into account the actual responses of the rheometers under the specific conditions of the actual measurements. In particular the shear rate cannot be changed abruptly. We hence measure the actually applied shear rate after commanding the rheometer to apply a constant shear rate and, for the cessation experiments, upon setting the shear rate to zero. Similarly, the actually applied stress was determined. These measurements yield an estimate of the time required for a rheometer to apply a desired shear rate or stress value. These measurements do not provide separate information on the individual contributions leading to the response and we do not attempt to model the observed response.[1–9] Nevertheless, the obtained data quantify the cumulated effect and yield an estimate of the time t^* required for each rheometer and tool to apply the desired shear rate or stress value. Importantly, the determination of these times t^* allows us to restrict the data presented and discussed in the manuscript to the data that were reliably measured for the specific conditions.

When a rheometer is commanded to apply a constant shear rate, after some dead time $t_{d,s}$ it starts to apply a shear rate which, after an additional time $t_{0,s}$, reaches a value close to the desired shear rate (Fig. S1). Similarly, in a cessation experiment the response of the rheometer is also not instantaneous. Upon setting the rheometer to apply a shear rate of zero, after some dead time required by the rheometer control system, $t_{d,c}$, the shear rate is being recorded and has a value close to the previously applied shear rate. The shear rate then drops within $t_{0,c}$ to a value close to zero. Hence, in both cases, after the time $t^* = t_d + t_0$ reliable data can be obtained. For the discussion of the response of the rheometers the time t^* is relevant.

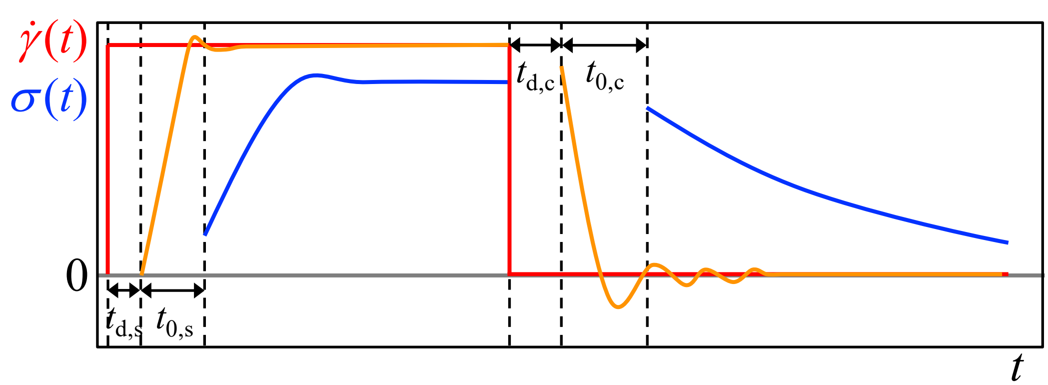

FIG. S1: Schematic representation of the time evolution of the commanded (red) and actually applied (orange) shear rate $\dot{\gamma}(t)$ as well as the reliably measured stress $\sigma(t)$ (blue) in a step-rate experiment followed by a shear cessation experiment. For both, the start-up (s) and cessation (c), after some dead time t_d the shear rate is being significantly changed and, after a further time t_0, reaches approximately the commanded value.

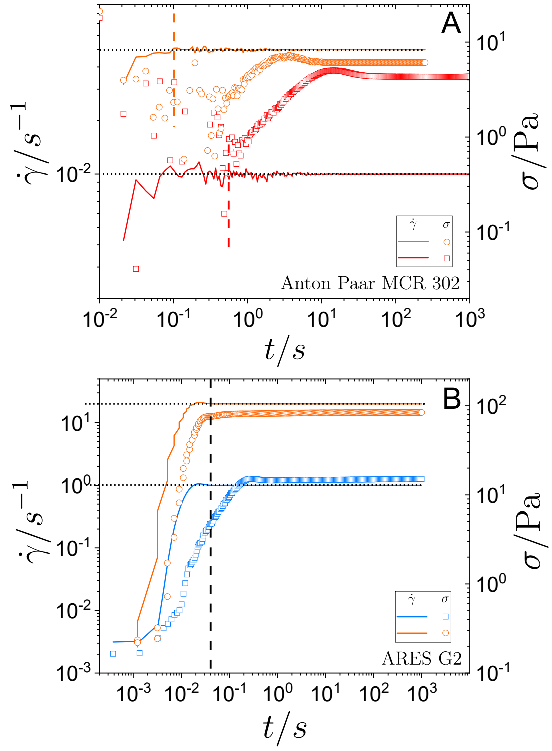

FIG. S2: Response of the rheometer, $\dot{\gamma}(t)$ (solid lines), and sample, $\sigma(t)$ (symbols), after **(A)** the stress-controlled MRC-302 WESP rheometer has been commanded to apply constant shear rates $\dot{\gamma} = 0.01\,\mathrm{s}^{-1}$ and $0.1\,\mathrm{s}^{-1}$ (solid horizontal lines) and **(B)** the strain-controlled ARES G2 rheometer to apply constant shear rates $\dot{\gamma} = 1.0\,\mathrm{s}^{-1}$ and $20\,\mathrm{s}^{-1}$ (solid horizontal lines). Vertical dashed lines indicate when the constant shear rate is considered to be reached; data obtained before the desired shear rate was applied are not considered and not shown in Fig. 2B. Volume fraction $\phi = 0.602$.

By the time t^*, the sample was exposed to the desired shear rate for only approximately t_0. Thus, the time t_0 rather than the time t^* is relevant for the sample and only data after this time t_0 are considered and shown in the corresponding figures (Figs. 2, 4, 7, 8 and 10). To determine the time t_0 from the time t^*, the dead time t_d is required. The dead time depends not only on the specific rheometer but also on the specific change in the conditions. If the strain-controlled ARES G2 rheometer is commanded to set the shear rate to zero, $\dot{\gamma} = 0\,\mathrm{s}^{-1}$, the dead time $t_\mathrm{d} \approx 30$ ms. Similarly, if the stress-controlled AR2000EX rheometer is commanded to set the stress to zero, $\sigma = 0$, then $t_\mathrm{d} \lesssim 10$ ms. In the case of the MCR-302 WESP rheometer, a more complicated control loop is involved and hence the dead time is considerably longer and depends on the previous conditions. To set $\dot{\gamma} = 0\,\mathrm{s}^{-1}$ involves a dead time in the range $200\,\mathrm{ms} \lesssim t_\mathrm{d} \lesssim 900\,\mathrm{ms}$ depending on whether a low or high shear rate was applied before. Moreover, to set $\sigma = 0$ Pa, the dead time $t_\mathrm{d} \approx 400$ ms.

I. STRAIN-CONTROLLED EXPERIMENTS: STEP-RATE AND RELAXATION

Step-rate measurements were conducted (Fig. 2A-C) which require a fast change of the strain rate.[1,2] They were performed with the stress-controlled MCR-302 WESP rheometer for applied shear rates $\dot{\gamma} < 0.5\,\mathrm{s}^{-1}$ and the faster, strain-controlled ARES G2 rheometer for applied shear rates $\dot{\gamma} \geq 0.5\,\mathrm{s}^{-1}$. The response of the MCR-302 WESP and ARES G2 rheometers were recorded after they have been commanded to apply constant shear rates as done in step-rate experiments. Depending on the shear rate, it took $70\,\mathrm{ms} \lesssim t^* \lesssim 500\,\mathrm{ms}$ for the tool of the MCR-302 WESP rheometer to reach the desired value as shown by the solid lines in Fig. S2A. For the ARES G2 rheometer the response time was much shorter. It lasted $t^* \approx 40$ ms for the tool to reach the commanded shear rate as shown by the solid lines in Fig. S2B.

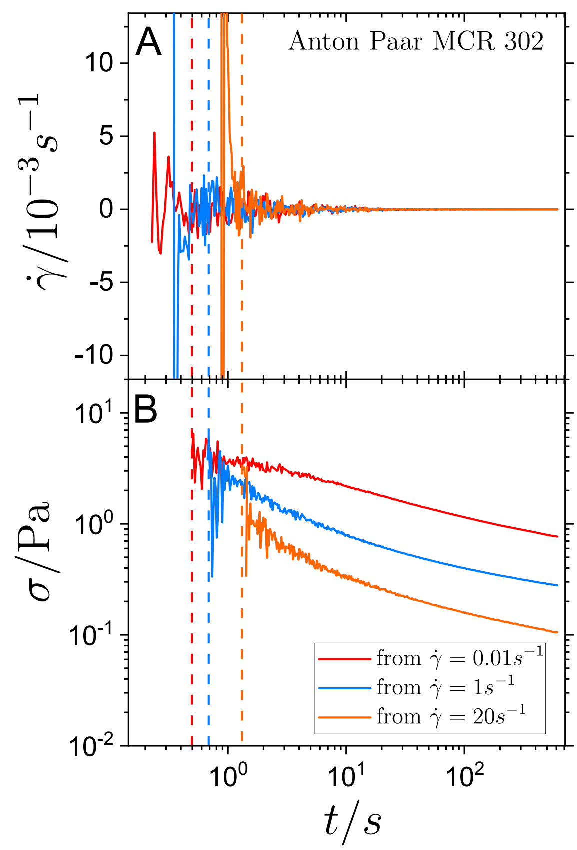

FIG. S3: Response of **(A)** the stress-controlled MCR-302 WESP rheometer, $\dot{\gamma}(t)$, and **(B)** sample, $\sigma(t)$, after the shear rate was set to $\dot{\gamma} = 0\,\mathrm{s}^{-1}$. Before the cessation of shear a constant shear rate $\dot{\gamma}$ has been applied (as indicated). Vertical dashed lines indicate when the tool is considered to apply a negligible shear rate; data obtained earlier are not considered and not shown in Fig. 2E. Volume fraction $\phi = 0.602$.

Step-rate experiments were followed by stress relaxation measurements with $\dot{\gamma} = 0\,\mathrm{s}^{-1}$ (Fig. 2D-F). All these experiments were performed with the MCR-302 WESP rheometer. Once the rheometer is set to $\dot{\gamma} = 0\,\mathrm{s}^{-1}$, depending on the previously applied shear rate it took $500 \lesssim t^* \lesssim 1500$ ms for the tool to move with a negligible angular velocity (Fig. S3A).

In addition, step-stress (creep) experiments and subsequent stress relaxation measurements under strain control (Fig. 4G-I) were performed with the AR2000EX rheometer. Having applied a constant stress during the creep experiment, a stress in the opposite direction was applied for a very short time (a few tens of ms) and then the rheometer was set to $\gamma = 0$. A constant strain and hence a negligible shear rate were reached after $t^* \approx 100$ ms (Fig. S4A).

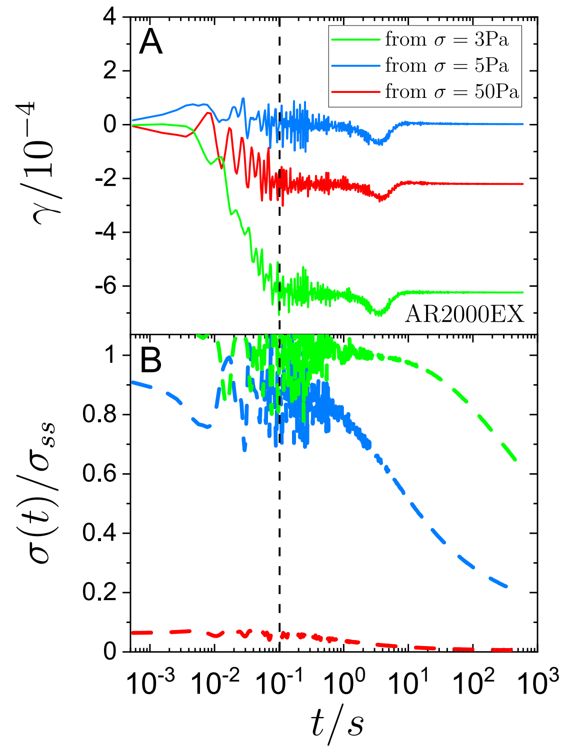

FIG. S4: Response of **(A)** the stress-controlled AR2000EX rheometer, $\gamma(t)$, and **(B)** sample, $\sigma(t)/\sigma_{\mathrm{ss}}$, after the shear rate was set to $\gamma = 0$. Before the cessation of shear a constant stress σ has been applied (as indicated). A vertical dashed line indicates when the tool is considered to have stopped; data obtained earlier are not considered and not shown in Fig. 4H. Volume fraction $\phi = 0.602$.

II. STRESS-CONTROLLED EXPERIMENTS: STEP-STRESS AND RECOVERY

The step-stress experiments (Fig. 4A-C) were performed with the AR2000EX rheometer. The software indicates an instantaneous response. Although this is not possible, it suggests that the desired stress was reached within a very short, negligible time.[9] Nevertheless, in future experiments the raw signal will be used to study the response of the rheometer in detail.

Following the step-stress experiments, recovery experiments were performed (Fig. 4D-F) using the AR2000EX rheometer. In this case, a stress of approximately zero was applied within $t^* \approx 100$ ms.

In addition, step-rate experiments were followed by recovery experiments (Fig. 2G-I) using the AR2000EX rheometer. After applying a constant shear rate, the shear rate was briefly (20 ms) set to zero. Subsequently the stress was set to zero, which resulted in the rheometer applying zero stress essentially immediately.

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