Interpenetration of fractal clusters drives elasticity in colloidal gels formed upon flow cessation

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Colloidal gels are out of equilibrium soft solids composed of attractive Brownian particles that form a space-spanning network at low volume fractions. The elastic properties of these systems result from the network microstructure, which is very sensitive to shear history. Here, we take advantage of such sensitivity to tune the viscoelastic properties of a colloidal gel made of carbon black nanoparticles. Starting from a fluidized state under an applied shear rate \( \dot{\gamma}_0 \), we use an abrupt flow cessation to trigger a liquid-to-solid transition. We observe that the resulting gel is all the more elastic when the shear rate \( \dot{\gamma}_0 \) is low and that the viscoelastic spectra can be mapped on a master curve. Moreover, coupling rheometry to small angle X-ray scattering allows us to show that the gel microstructure is composed of a percolated network of fractal clusters that interpenetrate each other. Experiments on gels prepared with various shear histories reveal that cluster interpenetration increases with decreasing values of the shear rate \( \dot{\gamma}_0 \) applied before flow cessation. These observations strongly suggest that cluster interpenetration drives the gel elasticity, which we confirm using a structural model. Our results, which are in stark contrast with previous literature, where gel elasticity was either linked to cluster connectivity or to bending modes, highlight a novel local parameter controlling the macroscopic viscoelastic properties of colloidal gels.

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I. INTRODUCTION

Colloidal gels are out of equilibrium amorphous soft solids composed of attractive Brownian particles that aggregate to form a space-spanning network at low concentrations [1]. These viscoelastic materials are ubiquitous both in nature and in industrial applications as diverse as flow batteries, food products and cementitious materials [2–5]. The scenario underlying their formation, namely the sol-gel transition, governs the vast majority of their structural and mechanical properties. In practice, Brownian motion is the driving force that allows colloids to encounter each other, whereas the colloid concentration \( \phi \) and the interaction potential \( U \) set up the aggregation path and the final gel properties [6,7]. In the limit of low concentrations and high interparticle attraction strength, diffusion-limited or reaction-limited cluster aggregation take place and lead to the formation of fractal gels [8,9], whereas at intermediate volume fractions and for moderate attraction strength, the sol-gel transition corresponds to an arrested phase separation [10–12].

Because colloidal gels are out-of-equilibrium, additional parameters play a key role in controlling their properties. External fields that act on the colloids dynamics and compete with Brownian motion may disrupt the direct correspondence between the gel properties and its coordinates (\( \phi, U \)) in the state diagram, leading to gels with a broad variety of structural and mechanical properties from a single colloidal dispersion. Indeed, the energy landscape of suspensions of attractive colloids is complex and strewn with multiple local minima (Fig. 1). Some of those minima are only accessible with an additional input of energy, larger than the thermal energy \( k_B T \). This is precisely the role of external stimuli: leading gelation into local minima inaccessible via Brownian motion. Therefore, the properties of the multiple metastable colloidal gels are a function of the external stimuli intensity. At the fundamental level, an external stimulus is ideal for exploring the interplay between microstructure and mechanics: as the gel originates from the same dispersion, the colloid volume fraction and interactions remain unchanged, while variations in the gel mechanical properties only result from microstructural changes. In practice, different external control parameters such as temperature and external shear have been used as external stimuli. For instance, the microstructure of globular protein gels can be tuned by varying the quench rate during the sol-gel transition: the faster the temperature quench, the smaller the characteristic length of the gel network [18]. In colloidal gels build from depletion interaction, flow cessation from a shear rate of intensity \( \dot{\gamma}_0 \) to \( 0 \) s\(^{-1}\) leads to gels, whose structure and rheology are governed by the intensity of the preshear \( \dot{\gamma}_0 \): a high preshear \( \dot{\gamma}_0 \) leads to homogeneous and strong gels whereas a low preshear \( \dot{\gamma}_0 \) leads to heterogeneous and weak gels [19].

In dispersions of fractal-like particles with attractive interparticle interactions, stress-controlled flow cessation
at various cessation rates yields gels whose strength and connectivity increase for increasing cessation rate \[\dot{\gamma}_0\]. Despite multiple evidence that the mechanical properties of colloidal gels can be tuned by an external stimulus, a quantitative correspondence between the gel microstructure and its mechanical properties is still lacking. We have chosen to take up this challenge in the case of mechanical shear applied to particulate colloidal gels with non-covalent interactions for three reasons. First, such colloidal gels can be rejuvenated by shear, i.e., their microstructure can be reconfigured by an external shear of large enough magnitude for a long enough duration, before the gel reforms upon flow cessation [21, 22]. Shear rejuvenation allows us to conveniently explore different gelation scenarios on the same sample. Second, it is already well established that shear may interfere with the gelation pathway of particulate colloidal gels, thus giving the opportunity to tune gels in term of microstructure [19], connectivity [20] or yield stress [23]. Third, on the application level, such an interplay between shear and gelation is involved in numerous industrial processes, and especially in additive manufacturing where external fields such as an additional shear coupled with 3D printing allows tuning the microstructure and the properties of the printed materials [24].

In practice, we choose to work with gels of carbon black nanoparticles whose properties can be tuned using shear history [20, 23, 24]. Here we influence the gelation pathway of these gels as follows: starting from a fluidized state under an applied shear rate \(\dot{\gamma}_0\), an abrupt flow cessation triggers a liquid-to-solid transition. Varying the shear rate intensity \(\dot{\gamma}_0\) allows us to generate gels whose viscoelastic properties span over a decade in stress units. Specifically, lower shear intensities yield more elastic gels upon flow cessation, while the viscoelastic spectrum for different \(\dot{\gamma}_0\) shows a robust frequency dependence that can be rescaled onto a master curve. Using rheometry coupled to small angle X-ray scattering (SAXS), we further show that the gel microstructure is composed of clusters of size \(\xi_c\) and fractal dimension \(d_f\) separated by a cluster center to center distance \(\xi_s\). Those structural parameters depend on \(\dot{\gamma}_0\). More importantly, we show that \(\xi_s < \xi_c\) meaning that adjacent clusters interpenetrate each others. The degree of interpenetration defined by the ratio \(\xi_c/\xi_s\) decreases for increasing values of \(\dot{\gamma}_0\). The degree of interpenetration is crucial, for it controls the gel elasticity and captures the impact of \(\dot{\gamma}_0\) on the gel viscoelastic properties, as confirmed by a fractal scaling model.

The outline of the paper is as follows. We first introduce carbon black gels as well as our experimental toolbox in Section II. Second, in Section III, we present our experimental results. We show how shear history allows tuning the gel viscoelastic properties, which can be rescaled onto a master curve. We then establish that the gel structures in fractal clusters that interpenetrate each other. Third, in Section IV, after dismissing a superposition principle to account for the scaling of the viscoelastic properties of the gel, we derive a fractal scaling model establishing a direct link between the gel microstructure and the gel network elasticity as a function of the shear rate intensity \(\dot{\gamma}_0\) applied before flow cessation.

II. MATERIALS AND METHODS

A. Carbon black dispersions

Carbon black (CB) particles are fractal carbonated colloids that result from the partial combustion of hydrocarbon oils [26–28]. These particles are widely used in the industry for mechanical reinforcement or to enhance the electrical conductivity of plastic and rubber materials [29]. Among the large variety of carbon black particles [25, 50, 53], we choose to work with Vulcan PF particles (Cabot, density \(d_{cb} = 2.26 \pm 0.03\)). The density of Vulcan PF particles is \(d_{cb} = 2.26 \pm 0.03\) and we estimate their radius of gyration to \(r_g = 35 \text{ nm}\) with a 20% polydispersity, and their fractal dimension to \(d_f = 2.9\) (see Appendix A for details).

When dispersed in mineral oil (RTM17 Mineral Oil Rotational Viscometer Standard, Paragon Scientific, viscosity \(\eta = 354 \text{ mPa.s at } T = 20^\circ\text{C}, \text{ density } d_{ck} = 0.871\)), CB particles are weakly attractive. The depth \(U\) of the interparticle potential depends on the type of CB particles, the solvent, and the presence of dispersant, and falls typically in the range \(U \sim 10 − 30k_BT\) [34, 35]. At a working weight concentration in CB particles of \(c_w = 4\%\), the particles aggregate to form a gel, i.e., a space-spanning network, which behaves as a viscoelastic soft solid. Indeed, at rest, the elastic modulus \(G'\) dominates the viscous modulus \(G''\) in the limit of low frequencies, whereas the sample displays a solid-to-liquid transition beyond a critical strain \(\gamma_y \sim 10\%\). Moreover, under steady shear, the flow curve that links the shear stress \(\sigma\) to the shear rate \(\dot{\gamma}\) is well fitted by the Herschel-Bulkley model, \(\sigma = \sigma_y + K\dot{\gamma}^n\) [36], with a dynamical yield stress \(\sigma_y = 4.5 \text{ Pa}\), a consistency index \(K = 1.0 \text{ Pa.s}^{1/0.83}\), and a fluidity index \(n = 0.83\) (see Fig. S in appendix B).
B. Rheology

In the present work, we use a rheometer both to measure the mechanical properties of CB gels and to shape up their microstructure. We carry out our experiments with two stress-controlled rheometers: (i) a MCR301 (Anton Paar) equipped with a rough cone (radius 40 mm, angle 1°) and a smooth bottom plate both made of steel, and (ii) a Haake RS6000 (Thermo Scientific) equipped with a Couette geometry composed of concentric polycarbonate cylinders (inner diameter 20 mm, outer diameter 22 mm, and height 40 mm) for rheo-SAXS experiments. Both apparatuses give identical results provided that the shear intensity by imposing a quench from 1000 s$^{-1}$ to $\gamma_0$ yielding a stress response $\sigma(t)$ pictured in (a), followed by a complete flow cessation which results in (b) the relaxation of $|\gamma|(t)$ when imposing $\sigma = 0$ Pa. In (a) and (b) colors encode the value of $\gamma_0$ ranging from 1500 (black) to 0.1 s$^{-1}$ (yellow), see legend in (b).

C. Small angle X-ray scattering

The microstructural properties of the carbon black dispersion are investigated using rheo-SAXS measurements carried out on the ID02 beamline at the European Synchrotron Radiation Facility (ESRF, Grenoble, France) [35]. The incident X-ray beam of wavelength 0.1 nm is collimated to a vertical size of 50 $\mu$m and a horizontal size of 100 $\mu$m. The 2D scattering patterns were measured using an Eiger2 4M pixel array detector and the subsequent data reduction procedure is described elsewhere [36]. The scattering intensity $I(q)$ is obtained by subtracting the two-dimensional scattering patterns of the carbon black gel and the mineral oil. The resulting scattering intensity presented in this article always remained isotropic (see Fig. 12 in Appendix [E]). Therefore, we radially averaged the normalized intensity pattern to obtain one dimensional $I(q)$. Note that measurements were performed in both radial and tangential configurations, and they turn out to be equivalent due to the isotropy of the gel microstructure.

D. Rheological protocol

We apply the protocol sketched in Fig. 2, which is divided in two sequences: a flow cessation sequence to shape up the gel properties followed by a sequence of characterization of the gel mechanical properties inherited from the flow cessation protocol.

In practice, the flow cessation protocol is divided into three steps. First, we carry out a rejuvenation step during which the sample is sheared at $\dot{\gamma} = 1000$ s$^{-1}$ for $\Delta t = 60$ s to erase any shear history that would influence the gel mechanical properties later on. Second, we modify the shear intensity by imposing a quench from $\dot{\gamma} = 1000$ s$^{-1}$ to a constant shear rate $\dot{\gamma}_0 \in [0.1, 1500]$ s$^{-1}$ for a duration $\Delta t_0 \in [20,200]$ s. Figure 3(a) shows the stress response $\sigma(t)$ of the CB gel resulting from quenches to various values of $\dot{\gamma}_0$. For high shear rates $\dot{\gamma}_0$, a duration of $\Delta t_0 = 20$ s is sufficient to reach a steady state. However, for $\dot{\gamma}_0 < 10$ s$^{-1}$, we must impose $\dot{\gamma}_0$ for longer durations, as $\sigma$ increases significantly, before reaching a maximum and then slowly decreases. The increase of $\sigma$ at short time scales corresponds to a transient regime neces-
sary for the system to adapt to the new shear rate \( \dot{\gamma}_0 \) applied before flow cessation. (b) Normalized viscoelastic spectrum: \( G'/G_c \) and \( G''/G_c \) vs. the normalized frequency \( f/f_c \), where \( G_c \) and \( f_c \) denote respectively the modulus and the frequency at which \( G' = G'' \) in (a). The blue curves correspond to a Kelvin-Voigt model (see Appendix C). The grey curves correspond to the master curves obtained for normalized frequency \( f/f_c \). The red dotted line is the best linear fit of the data: \( G_c = 14.5f_c \). (c) Evolution of \( G_c \) (top) and \( f_c \) (bottom) vs. \( \dot{\gamma}_0 \). The red line is the best fit of the data using Eq. (1) and the structural information reported in Fig. 6. The best fit is obtained with a single adjustable parameter, namely the prefactor \( G_i = 15 \) mPa.

**III. RESULTS**

**A. Impact of the shear rate \( \dot{\gamma}_0 \) on the gel linear viscoelastic spectrum**

We first focus on the impact of \( \dot{\gamma}_0 \) on the linear viscoelastic properties of the gel formed upon flow cessation (see “Frequency sweep” in the characterization sequence sketched in Fig. 2). The gel frequency spectrum is reported in Fig. 4(a) for various values of the shear rate intensity \( \dot{\gamma}_0 \) spanning over four decades. Overall, we observe that low \( \dot{\gamma}_0 \) produce more elastic gels. More precisely, whatever the shear rate intensity \( \dot{\gamma}_0 \), the elastic and viscous moduli are increasing functions of the frequency and cross at a frequency \( f_c \) that shifts towards larger values for decreasing \( \dot{\gamma}_0 \). Moreover, in the limit of low frequencies, all spectra show a plateau in elasticity with \( G' > G'' \), which confirms the solid-like behavior of the sample, regardless of the shear rate intensity applied prior to flow cessation. The shape of the viscoelastic spectrum is robust, and appears merely shifted, which prompts us to construct a master curve from the data in Fig. 4(a). By normalizing each spectra by the coordinate \((f_c, G_c)\) defined by the crossover of \( G' \) and \( G'' \), we obtain the master curve reported in Fig. 4(b). The asymptotic behavior of the master curve corresponds to a Kelvin-Voigt model (see Appendix C) displayed as blue lines in Fig. 4(b). At low frequencies, i.e., \( f \ll f_c \), the elastic modulus \( G' \) tends towards a plateau value much larger than \( G'' \), which is the hallmark of a solid-like behavior at

Finally, the characterization sequence following flow cessation consists in three steps. First, we let the system rest for 360 s, while measuring the elastic \( G' \) and viscous \( G'' \) modulus using oscillations of small amplitude \( \gamma = 0.1 \% \) at a frequency \( f = 1 \) Hz. Second, we perform a frequency sweep at \( \gamma = 0.3 \% \) with 10 points per decade for frequencies \( f \) ranging from 0.02 to 20 Hz. To gain some insights on the gel microstructure during these two sequences, the entire protocol was carried out in the rheo-SAXS setup for four distinct shear intensity \( \dot{\gamma}_0 \). The scattered intensity \( I(q) \) of the gel obtained after flow cessation is discussed in the next section.
rest. At high frequencies, i.e., \( f \gg f_c \), the viscous modulus \( G'' \) dominates and increases linearly with the frequency and the solvent viscosity \( \eta \), such that \( G'' = 2\pi f \eta \).

In this range of frequencies, the variations of \( G'' \) correspond to the viscous dissipation due to the thermal fluctuations of the gel network in the background solvent. We note that the master curve can be fully fitted by a fractional Kelvin-Voigt model (see Appendix C). Such a master curve is strongly reminiscent of that obtained on fractal gels by varying the particle volume fraction, and master curve is strongly reminiscent of that obtained on depletion gels, whose microstructure shares some similarity with that generated by varying the colloid volume fraction.

Moreover, for a fixed shear intensity \( \dot{\gamma}_0 \), the modulus \( G_c \) increases as a power law of \( c_w \), \( G_c = (c_w/C_1)^\alpha \) with an exponent \( \alpha \) that depends on \( \dot{\gamma}_0 \) [Fig. 5(b)]. While a power-law increase of the gel elasticity for increasing particle weight concentration or volume fraction is classically reported in colloidal gels with an exponent \( \alpha \) ranging between 2 and 4.5 depending on the range of the interparticle potential and the nature of the particles [11, 15, 19], the sensitivity of \( \alpha \) to shear history is a key result of the present study. Here, in Fig. 5(b), we show that \( \alpha \) increases for increasing shear rate intensity applied before flow cessation, varying between \( \alpha \approx 3 \) for \( \dot{\gamma}_0 = 0.1 \, \text{s}^{-1} \) to surprisingly high values, i.e. \( \alpha \approx 7 \) for \( \dot{\gamma}_0 = 1500 \, \text{s}^{-1} \). Finally, in Fig. 5(c), we show that \( G_c \) follows a master curve driven by a dimensionless concentration and shear rate intensity. Although this dependence remains empirical, this master curve highlights the fact that there are many ways to obtain gels with identical \( G_c \). For instance to get \( G_c \approx 3 \, \text{Pa} \) one can either prepare a gel at \( (c_w = 4 \, \text{\%}, \dot{\gamma}_0 = 1500 \, \text{s}^{-1}) \), \( (c_w = 3 \, \text{\%}, \dot{\gamma}_0 = 100 \, \text{s}^{-1}) \) or \( (c_w = 2 \, \text{\%}, \dot{\gamma}_0 = 2 \, \text{s}^{-1}) \).

To connect these results to the gel microstructure, one can be tempted to combine the power-law exponent \( \alpha \)

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**FIG. 5.** (a) Evolution of \( G_c \) as a function of the weight concentration in carbon black particles \( c_w \) for various shear rates applied prior to flow cessation: \( \dot{\gamma}_0 = 0.1 \, \text{s}^{-1} \) (circle), \( 2 \, \text{s}^{-1} \) (diamond), \( 100 \, \text{s}^{-1} \) (triangle) and \( 1500 \, \text{s}^{-1} \) (square). Red lines are the best power-law fit of the data \( G_c = (c_w/C_1)^\alpha \). Both \( \alpha \) and \( C_1 \) depend on \( \dot{\gamma}_0 \). (b) \( \alpha \) and \( C_1 \) vs. the shear rate \( \dot{\gamma}_0 \). Red lines are the best logarithmic fit of the data: \( \alpha = \log_{10}(\dot{\gamma}_0/C_1) \) with \( C_1 = 2.3 \log_{10}(\dot{\gamma}_0/\dot{\gamma}_1) \) with \( C_2 = 0.7 \, \text{\%} \) and \( \dot{\gamma}_1 = 0.015 \, \text{s}^{-1} \). Dotted lines are the best power law fits. (c) Evolution of \( G_c \) as function of the weight concentration in carbon black particles \( c_w \). As shown in Fig. 4(c), both \( G_c \) and \( \dot{\gamma}_0 \) from 0.1 s\(^{-1}\) to 1500 s\(^{-1}\) decrease by almost two orders of magnitude.

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**B. Influence of the carbon black weight concentration**

The rescaling and the master curve introduced in Section III A are robust to changes in the CB weight concentration, from \( c_w = 2 \) to 8 \%. For instance, the viscoelastic spectrum of a \( c_w = 2\% \) carbon black dispersion obtained with various shear rate \( \dot{\gamma}_0 \) applied before flow cessation can be rescaled on the same master curve as that displayed in Fig. 5(b) (see Fig. 10 in appendix D). Moreover, for a fixed shear intensity \( \dot{\gamma}_0 \), the modulus \( G_c \) increases as a power law of \( c_w \), \( G_c = (c_w/C_1)^\alpha \) with a concentration \( C_1 \) and an exponent \( \alpha \) that depends on \( \dot{\gamma}_0 \) [Fig. 5(b)]. While a power-law increase of the gel elasticity for increasing particle weight concentration or volume fraction is classically reported in colloidal gels with an exponent \( \alpha \) ranging between 2 and 4.5 depending on the range of the interparticle potential and the nature of the particles [11, 15, 19], the sensitivity of \( \alpha \) to shear history is a key result of the present study. Here, in Fig. 5(b), we show that \( \alpha \) increases for increasing shear rate intensity applied before flow cessation, varying between \( \alpha \approx 3 \) for \( \dot{\gamma}_0 = 0.1 \, \text{s}^{-1} \) to surprisingly high values, i.e. \( \alpha \approx 7 \) for \( \dot{\gamma}_0 = 1500 \, \text{s}^{-1} \). Finally, in Fig. 5(c), we show that \( G_c \) follows a master curve driven by a dimensionless concentration and shear rate intensity. Although this dependence remains empirical, this master curve highlights the fact that there are many ways to obtain gels with identical \( G_c \). For instance to get \( G_c \approx 3 \, \text{Pa} \) one can either prepare a gel at \( (c_w = 4 \, \text{\%}, \dot{\gamma}_0 = 1500 \, \text{s}^{-1}) \), \( (c_w = 3 \, \text{\%}, \dot{\gamma}_0 = 100 \, \text{s}^{-1}) \) or \( (c_w = 2 \, \text{\%}, \dot{\gamma}_0 = 2 \, \text{s}^{-1}) \).

To connect these results to the gel microstructure, one can be tempted to combine the power-law exponent \( \alpha \)}
with the scaling theories developed for fractal gels \[13\], in order to estimate the cluster fractal dimension \(d_f\). The theory developed in the context of Brownian aggregation distinguishes between two types of network, depending on the relative value of the elastic constant of the inter-cluster links to that of the cluster. In the case of weak links \(\alpha = 1/(3-d_f)\), which yields \(2.6 < d_f < 2.9\), whereas in the case of strong links, \(\alpha = (3 + x)/(3 - d_f)\) with \(x < d_f\) the fractal dimension of the gel backbone, and \(1.5 < d_f < 2.5\) (see Fig. 11 in appendix B). These values motivate an experimental characterization of the gel microstructure, and especially of the cluster fractal dimension to test the relevance of such scaling theories.

C. Microstructure of the gel as function of the shear \(\dot{\gamma}_0\) applied before flow cessation

To better understand the interplay between shear history and the gel microstructural properties, we perform rheo-SAXS experiments using the protocol sketched in Fig. 2. The scattering intensity \(I(q)\) measured 360 s after flow cessation protocol for four different shear rate intensities \(\dot{\gamma}_0\) prior to flow cessation is reported in Fig. 3(a), as a function of the wave number \(q\). In all four cases, the scattered intensity \(I(q)\) presents similar features. First, \(I(q)\) is isotropic, i.e., tangential and radial measurements are equivalent (see Fig. 12 in Appendix E). Therefore, the gel displays an isotropic structure, which is why we only report the azimuthally averaged \(I(q)\). Second, \(I(q)\) presents three characteristic bumps around 0.04, 0.01 and 0.002 nm\(^{-1}\). We attribute the high-\(q\) bump to the CB particles of size \(r_0\), the low-\(q\) bump to clusters of size \(\xi_c\) and fractal dimension \(d_f\), and the bump at intermediate \(q\) to the structural distance \(\xi_s\) between the centers of two adjacent clusters. Those bumps appear more clearly in the Kratky-like representation \(I(q \sigma^{d_f−1})\) reported in Fig. 6(a). In the Kratky-like representation we used the \(d_f\) displayed in Fig. 3(b). This structure is atypical for colloidal gels. Indeed, \(I(q)\) classically displays only two characteristic length scales: the particle size \(r_0\) and the cluster size \(\xi_c\) separated by a power-law regime, and the exponent of which is related to the cluster fractal dimension \[20\].

A description of the gel microstructure based on three characteristic length scales is implemented in a modified two-level Beaucage model. In short, the two-level Beaucage model \[51, 52\] accounts for the scattering of clusters of size \(\xi_c\) and fractal dimension \(d_f\) composed of particles of size \(r_0\). To account for the increase of scattering at \(\xi_s\), we have multiplied the cluster scattering intensity term in the Beaucage model by an ad-hoc inter-cluster structure factor (see appendix E for more details). This modified Beaucage model provides an excellent fit to the experimental data obtained for different shear histories [Fig. 3(a)]. Moreover, since the gel weight concentration is identical in the four measurements, the fit parameters \(r_0\), \(\xi_c\), \(d_f\) and \(\xi_s\) should obey mass conservation. In practice, such a constraint can be expressed at the scale of the unit cell of the gel network, i.e., the minimum structural repeating unit necessary to construct the gel structure defined by the correlation length \(\xi_c\). The number of particles \(N = (\xi_c/r_0)^{d_f}\) in a unit cell corresponds to the number of particles in the cluster of size \(\xi_c\) and fractal dimension \(d_f\). Based on the values of the fit parameters obtained from adjusting the modified two-level Beaucage model to the SAXS data, we check that, indeed, \(\rho = (\xi_c/r_0)^{d_f}/\xi_c^3\) remains constant across the four measurements with \(\rho = 7250 \pm 230\) particles/\(\mu\text{m}^3\). This value is also in agreement with the carbon black weight concentration \(c_w = 4\%\) (see Fig. 14 in appendix E), which confirms that our analysis of the scattering data is self-consistent.

Figure 2(b) shows the dependence of the fit parameters \(\xi_c\), \(\xi_s\), and \(d_f\) with the shear rate intensity \(\dot{\gamma}_0\) applied before flow cessation. A gel prepared with a lower shear intensity shows a larger and looser microstructure since \(\xi_c\) increases and \(d_f\) decreases for decreasing \(\dot{\gamma}_0\). Considering the evolution of only those two parameters suggests a decrease of the gel elasticity for decreasing values of \(\dot{\gamma}_0\), in stark contrast with our observations. However, \(\xi_c\) and \(d_f\) are not the only parameters, and the correlation length \(\xi_s\), which corresponds to the cluster to cluster center distance, plays an important role. In particular, \(\xi_s\) is smaller than the cluster size \(\xi_c\), indicating that the clusters interpenetrate each other. Such cluster interpenetration has recently been suggested in carbon black gels to interpret step down shear rate rheology experiments \[53\]. In our case, for lower shear rate intensity \(\dot{\gamma}_0\) prior to flow cessation, the ratio \(\xi_c/\xi_s\) increases, i.e., the clusters become more interpenetrated, accounting for the reinforcement of the gel elasticity. We therefore hypothesize that the gel elasticity is related to the cluster interpenetration, increasing the elasticity of the gel network as compared to the case where clusters would be packed in a random close-pack configuration [Fig. 6(c)].

IV. DISCUSSION

We have used mechanical shear to explore various configurations of carbon black gels. Starting from a fluidized state under an applied shear rate \(\dot{\gamma}_0\), we use an abrupt flow cessation to trigger a liquid-to-solid transition. Varying \(\dot{\gamma}_0\) allows us to tune the gel viscoelastic properties, whose spectrum can be mapped on a single master curve asymptotically defined at low frequencies by the elasticity of the gel network \(G_\infty\) and at high frequencies by the viscosity \(\eta\) of the background solvent. Coupling rheometry and SAXS, we have shown that the gel microstructure is composed of fractal clusters that interpenetrate each other, and the degree of interpenetration appears to be a key parameter contributing to the gel elasticity.
A. Is the scaling behavior of the viscoelastic spectrum a consequence of an underlying superposition principle?

In light of the scaling behavior of the viscoelastic spectrum, it is tempting to interpret the master curve obtained by varying $\gamma_0$ as the result of some shear-frequency superposition principle. Superposition principles in soft matter mechanics rely on the idea that dynamical processes in soft materials can be accessed equivalently using time or frequency and another well-chosen variable. For example, time-temperature superposition in polymer melts relies on the acceleration of all activated processes at high temperatures, enabling probing of longer effective time scales at high temperatures. In other words, the average relaxation time of the material changes with temperature without affecting the shape of its viscoelastic spectrum.

This is not what we observe here, for the rescaling of the viscoelastic spectrum requires a shift along the frequency axis and a shift along the viscoelastic moduli. Such behavior has, however, been observed in different systems and still attributed to a superposition principle such as in colloidal low-methoxyl pectin in the context of diffusion-limited cluster aggregation (DLCA) and reaction-limited cluster aggregation (RLCA) in the context of diffusion-limited cluster aggregation (DLCA) and reaction-limited cluster aggregation (RLCA). However, these models do not take into consideration the case where shear history interferes with the gelation pathway activated by thermal energy. Therefore, unsurprisingly, such models cannot capture our observations (see Fig. 11 in Appendix E). These models notably predict that the cluster size $\xi_c$ is set by its fractal dimension $d_f$ and the particle volume fraction $\phi$ and the particle size $r_0$ in stark contrast.

B. A structure based model to account for the gel elasticity

There are numerous models accounting for the elastic properties of fractal gels derived from microscopic considerations, especially in the context of diffusion-limited cluster aggregation (DLCA) and reaction-limited cluster aggregation (RLCA) in the context of diffusion-limited cluster aggregation (DLCA) and reaction-limited cluster aggregation (RLCA). However, these models do not take into consideration the case where shear history interferes with the gelation pathway activated by thermal energy. Therefore, unsurprisingly, such models cannot capture our observations (see Fig. 11 in Appendix E). These models notably predict that the cluster size $\xi_c$ is set by its fractal dimension $d_f$, the particle volume fraction $\phi$ and the particle size $r_0$ in stark contrast.
trast with our observations where the shear applied prior to flow cessation appears as an additional key control parameter. Moreover, in these models, the elastic properties of colloidal gels are either connected to the local bending cost of the particle network, or to the cluster connectivity. However, to the best of our knowledge, none of these approaches accounts for an overlap, or equivalently for an interpenetration, of two neighboring clusters.

Here, we introduce a model that takes into account cluster interpenetration. In practice, we assume that the gel is composed of particles of size $r_0$ that form clusters of size $\xi$ and fractal dimension $d_f$ separated by a center-to-center distance $\xi_s$. If $\xi_s > \xi_c$, the clusters are independent and the dispersion is a fluid. However, if $\xi_s < \xi_c$, clusters interpenetrate each other and form a gel. The gel elastic modulus $G'_\infty$ at low frequencies is attributed to the number of contact between interpenetrating clusters and its derivation (see Appendix F) yields the following expression:

$$G'_\infty = G'_i \left( \frac{\xi}{r_0} \right)^{d_f} \left( 1 + \frac{\xi_s}{2\xi_c} \right)^{d_f/3} \left( 1 - \frac{\xi_s}{\xi_c} \right)^{2d_f/3}$$

(1)

where $G'_i$ is used as a fitting parameter that depends on the particle volume fraction, the particle size, the nature of the particle interactions, and the geometry of the system. To test the relevance of our model, we report in Fig. 4(c) the best fit of $G_c$ as a function of the $\dot{\gamma}_0$ using Eq. (1) with the values of the structural parameters inferred from Fig. 3(b), the fact that $G_\infty = 0.3G_c$ (see Appendix F), and the sole adjustable parameter $G'_i = 15 \text{ mPa}$. The model correctly captures the decrease of the elasticity of the gel network as $\dot{\gamma}_0$ increases. This empirical structural model thus shows that cluster interpenetration accounts for the mechanical properties of the gels and allows to rationalize the counter-intuitive observation that lower shear rate intensities before flow cessation yield stronger gels. Such results raise open questions, which are listed below.

C. Physical origin of the gel structure

The multiple metastable gels formed following various shear preparations belong to the category of fractal gels. This is probably why our results do not match the trends observed in Ref. 19 which belong to gels formed through arrested phase separation. We find clusters of fractal dimension $d_f \in [2.3, 2.5]$ larger than the prediction from diffusion-limited cluster aggregation DLCA where $d_f \sim 1.8$ 3 or reaction-limited cluster aggregation RLCA where $d_f \sim 2.1$ 9 but smaller than the value obtained for sheared fractal aggregates where $d_f \sim 2.6$ 60.

In our system, the Brownian time $\tau_B = R^36\pi\eta/k_BT \in [0.07; 1600] \text{ s}$ is set by the diffusion of particles of size $R$ ranging from the CB dimension $r_0 = 35 \text{ nm}$ to the cluster size $\xi_c \sim 1 \text{ nm}$. $\tau_B$ compares to the time necessary for flow cessation to take place $\tau_{fc} < 4 \text{ s}$ (Fig. 5) supporting again the fact that aggregation and flow cessation are coupled.

The interplay between flow and structure in gels has been tackled mainly in the flow regime 33-69 but has not been formalized to model multiple metastable gel states induced by a shear protocol. This is an important challenge in the pursuit of memory materials 70 which aim to encode, access, and erase signatures of past history in the state of a system.

The flow cessation protocol inducing the sol-gel transition could be addressed qualitatively through the use the Mason number Mn 71, 72, which is here in the range $[3.5 \times 10^{-4}, 5.2]$, and agrees rather well with the values in 72-73, or the adhesion number Ad 74-76, which is here in the range $[3.6, 5.5 \times 10^4]$ weighting the relative importance of adhesion forces compared to shear forces and quantitatively using coagulation-fragmentation equation 77-79 which embrace the competition between different aggregation mechanism and fragmentation through shear or collisions.

Finally, we suggest another way to apprehend the multiple metastable gels formed through flow cessation. Indeed, carbon black gels as many other systems display delayed yielding 80-82, i.e., when pushed at a constant shear stress $\sigma$, the gel initially at rest will start flowing on time scales that decrease exponentially with increasing value of $\sigma$. Our results prompt us to revisit delayed yielding phenomena and answer the following questions: How does gel prepared through flow cessation impact the delayed yielding mechanism? Is delayed yielding still characterized by an Arrhenius law? If so, is the energy barrier necessary to flow in the delayed yielding experiment related to the energy barrier to form the gel state induced by flow cessation?

V. CONCLUSION

In conclusion, we have quantified the impact of shear history on the viscoelastic properties of carbon black gels. We observe that, for a fixed content in nanoparticles, low shear intensities yield strong gels upon flow cessation, whereas larger shear intensities yield weaker gels. Such a variation in the gel strength was linked to the degree of interpenetration of the clusters that compose the gel microstructure. In that framework, we have introduced a simple model that captures the impact of shear history on the gel elasticity, yielding a prediction for the scaling exponent that links the gel elasticity to the weight concentration in carbon black particles. These results highlight the power of shear history as an experimental tool to tune the viscoelastic properties of colloidal gels without changing the content in nanoparticles or their interactions. In addition, our work raises several fundamental questions, such as predicting for any type of colloids, the respective contributions of cluster interpenetration, cluster connectivity, and bending to a colloidal gel elasticity. Finally, future work should focus on determining the role of clus-
interpenetration into the gel non-linear mechanical response, which might be a versatile parameter to tune the failure scenario of soft viscoelastic gels.

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Appendix A: Carbon black particles

Fig. 7 shows the scattering intensity vs. wave vector $q$ for a dilute dispersion of CB particles (Vulcan PF, Cabot). Individual CB particle are fractal-like particles composed of fused nanoparticles of carbon [28, 31], which motivates the use of a mass fractal model [83] to fit $I(q)$. The fit yields a radius of gyration $r_g = 35$ nm with 20% polydispersity and a fractal dimension $d_f = 2.9$. Density measurements of CB powder were performed by helium pycnometer (AccuPyc II 1340, Micromeritics). Before the measurements, the powder was dried in an oven at 80°C during 72 hours (2% in weight was lost). Two sets of measurements were done with 5 measures in a row for the first sample ($m = 0.8619$ g) and 10 measurements in a row for the second sample ($m = 0.779$ g). The samples were poured in a 10 cm$^3$ aluminum vessel. We obtained a density of the carbon black particles $d_{cb} = 2.26 \pm 0.03$ g/cm$^3$.

Appendix B: Flow properties of Carbon black gels

Figure 8 reports the flow curve $\sigma(\dot{\gamma})$ of a $c_w = 4\%w$ CB dispersion obtained by a decreasing ramp of shear rate. The flow curve is fitted with a Herschel-Bulkley model, $\sigma = \sigma_y + K\dot{\gamma}^\alpha$, and yields a dynamical yield stress $\sigma_y = 4.5$ Pa, a fluidity index $n = 0.83$, and a consistency index $K = 1.0$ Pa.s$^{1/0.83}$. In Fig. 8 we also show flow curve extracted from the preshear at $\dot{\gamma}_0$. We observe that those flow curve are not stationary. This is mostly due to the fact that the dispersion needs time to adapt from the jump in shear from 1000 s$^{-1}$ to $\dot{\gamma}_0$.

Appendix C: Model for the normalized viscoelastic spectrum of carbon black gels

The master curve reported in Fig. 3 is fitted using a Kelvin-Voigt model and a fractional Kelvin-Voigt model [84], as illustrated in Fig. 4. The fractional Kelvin-Voigt model consists of two springpots in parallel, defined by their quasi-properties (V, E) and their dimensionless exponents ($\alpha$, $\beta$). Each springpot can be understood as a mechanical element having intermediate properties between that of a spring when its exponent is 0 and a dashpot when its exponent is 1. The resolution of the
fractional Kelvin-Voigt model leads to

\[
\begin{aligned}
G' &= E f^\beta \cos(\beta \pi f/2) + V f^\alpha \cos(\alpha \pi f/2) \\
G'' &= E f^\beta \sin(\beta \pi f/2) + V f^\alpha \sin(\alpha \pi f/2)
\end{aligned}
\]  

(C1)

In the limit where \(\alpha = 1\) and \(\beta = 0\) we recover the classical Kelvin-Voigt model, which is defined by a dashpot of viscosity \(\eta\) in parallel with a spring of elasticity \(G_\infty\).

\[
\begin{aligned}
G' &= E = G_\infty \\
G'' &= V f = 2\pi \eta f
\end{aligned}
\]  

(C2)

As shown in Fig. 9 the fractional model fits relatively well the normalized viscoelastic spectrum of carbon black gels in mineral oil using \((V/G_c = 0.56, \alpha = 0.91)\) and \((E/G_c = 1.09, \beta = 0.11)\). Its classical counterpart can only capture the asymptotic behavior of the viscoelastic spectrum, i.e., the network elasticity \(G_\infty = G'(f \ll f_c)\) and the background viscosity \(\eta = G''(f \gg f_c)/(2\pi f)\). We note that \(G_\infty = 0.3 G_c\).

**Appendix D: Influence of the concentration \(c_w\)**

Following the protocol displays in Fig. 2 we test the influence of the concentration for \(c_w = 2, 3, 6\) and \(8\%\) in addition to \(c_w = 4\%\). Such concentration series are presented in Fig. 10 for \(\gamma_0 = 1500\, \text{s}^{-1}\). We observe that high concentration shift the viscoelastic spectrum to higher elasticities. The cross over point is not always reachable within the frequency window. We scale the viscoelastic spectrum \(G', G''\) on the master curve displayed in Fig. 4b to determine \((f_c, G_c)\) and plot the results in Fig. 5.

**FIG. 10.** Evolution of the viscoelastic spectrum for different gel concentration \(c_w\) at \(\gamma_0 = 1500\, \text{s}^{-1}\). (a) \(G'\) (line) and \(G''\) (dash) as a function of \(f\). The concentration is varied from \(c_w = 2\) (blue) to \(8\%\) (green). (b) Rescaled viscoelastic spectrum. The grey curves are taken from [10] and corresponds to the master curve obtained by scaling a concentration series of carbon black dispersion in oil.

**FIG. 9.** Model of the normalized viscoelastic spectrum. Evolution of the normalized elastic \(G'/G_c\) (grey line) and viscous \(G''/G_c\) (dashed grey line) modulus as a function of the frequency \(f/f_c\), extracted from [10]. \((f_c, G_c)\) are the coordinates of the crossover between \(G'\) and \(G''\). The Kelvin-Voigt model is pictured in blue and the fractional Kelvin-Voigt model in red.

**Appendix E: Analysis of the rheo-SAXS data**

The CB gel scattered intensities \(I_{\text{rad}}(q)\) and \(I_{\text{tan}}(q)\) are respectively measured in the radial and the tangential configuration. In the radial configuration, the X-ray beam probe the microstructure in the flow-vorticity plane, while in the tangential configuration, the X-ray beam probe the sample along velocity gradient-vorticity plane as sketch in Fig. 12. After the rest in the protocol from Fig. 2 the radial and tangential scattered intensity are compared. More precisely the radial scattering \(I_{\text{rad}}\) is decomposed in its perpendicular \(I_{\text{rad} \perp}\) and parallel \(I_{\text{rad} ||}\) components. In Fig. 12 we observe that \(I_{\text{tan}} = I_{\text{rad} \perp} + I_{\text{rad} ||}\). The scattering intensity is isotropic and equal in all configurations. For better...
The intensity scattered by the carbon black is fitted in log scale using a modified Beaucage model [51, 52, 85]. In Eq. (E1), \( I_2(q) \) refers to scattering due to the CB particle of size \( r_0 = r_2 \) and fractal dimension \( d_{f0} = -p_2 \). The scattering due to the clusters of size \( \xi_c = r_1 \) and fractal dimension \( d_f = -p_1 \) is contained in the term \( I_1(q) \). The modification of the two level Beaucage model consists in introducing an inter cluster structure factor \( S_1(q) \) that accounts for the center-to-center distance between adjacent clusters, \( \xi_s = 2\pi/q_s \). \( S_1(q) \) is a function that peaks at \( q_s \) to a maximum value \( S_1(q_s) = 1 + C_0/2 \) and that converge to 1 away from \( q_s \).

This fit is constrained by mass conservation. Indeed, as the multi-stable gels results from the same carbon black dispersion, all the gels have the exact same number of particles at the macroscopic scale and in their unit cell. The unit cell is the minimum structural repeating unit necessary to construct the gel. In our case, the gel network unit cell is defined by the structural length \( \xi_s \). The number of particles \( N = (\xi_c/r_0)^{d_f} \) in a unit cell corresponds to the number of particles in the cluster of size \( \xi_c \) and fractal dimension \( d_f \). This gives a particle density \( \rho = (\xi_c/r_0)^{d_f}/\xi_c = \text{cste} \). This constrain is well verified based on parameters obtained by fitting the SAXS data. As shown in Fig. 14, \( \rho = 7250 \pm 230 \, \text{particles/\micro m}^3 \) is constant within a margin of error of 3%. Moreover, \( \rho \) can be related to the particle concentration \( c_w \) provided a good knowledge of the background oil density \( d_{bck} = 0.871 \) (\( T = 20 \, ^\circ C \)), the individual carbon black particle density \( d_{cb} = 2.26 \pm 0.03 \) (\( T = 20 \, ^\circ C \)) and the volume of a carbon black particle \( v_{cb} \). The carbon black density \( \rho \) in the gel is then
\[ \rho = \frac{\phi}{v_{cb}}, \quad \text{with} \quad \phi = \frac{c_w}{\left(c_w + \frac{d_s}{d_w}(1 - c_w)\right)} \quad (F2) \]

As it is hard to measure \( v_{cb} \), the particle fractal nature, \( v_{cb} \) was evaluated from \( \rho \). Using \( v_{cb} = 4/3\pi r_0^3 \), we obtain \( r_0 = 23.7 \text{ nm} \), a value lower than the radius of gyration of 35 nm extracted from the form factor measured in SAXS Fig. 7. This value is a bit smaller because the CB particles are fractal and polydisperse. Moreover, SAXS measurements tend to overestimate the particle size distribution as SAXS is more sensitive to larger particles. The fact that we find \( \rho = \text{cste} \) and a particle radius of gyration close to the value measured by SAXS tell us that the model is self-consistent.

**Appendix F: Model of the gel elasticity based on scaling arguments**

We assume that the gel is composed of particles of size \( r_0 \) that form clusters of size \( \xi_c \) and fractal dimension \( d_f \) separated by a center to center distance \( \xi_s \). If \( \xi_s > \xi_c \), the clusters are independent and the dispersion is a fluid. However, if \( \xi_s < \xi_c \), clusters interpenetrate each other and form a gel. To model the elastic constant of the gel network, we define the cluster internal stiffness \( k_c \) and the additional stiffness due to interpenetration of the clusters \( k_i \). We model the network by a series of springs as sketch in Fig. 15. The network stiffness \( K \) is then

\[ \frac{1}{K} = \frac{N_C}{k_c} + \frac{N_I}{k_i} \quad (F1) \]

where \( N_C \) and \( N_I \) are the number of clusters and the number of intersection respectively. Given the topology of network structure, we have \( N_C \approx N_I \).

Let us now quantify \( k_i \). \( k_i \) is proportional to the number of contact \( N_i \) between interpenetrating clusters: \( k_i = N_i k_{i0} \), where \( k_{i0} \) is a reference interpenetration stiffness. Due to the fractal nature of the clusters, there are

\[ N_i = \left(\frac{6V_i}{\pi r_0^3}\right)^{d_f} \quad (F2) \]

Due to the fractal nature of the clusters, there are \( N_i \) particles inside the intersection volume \( V_i \):

\[ N_i = \left(\frac{6V_i}{\pi r_0^3}\right)^{d_f} \quad (F3) \]

We assume that each particle brought by each cluster in \( V_i \) form a contact adding rigidity to the whole system. Therefore, the numbers of contact is roughly \( N_i \). Putting together eq. (F2) and (F3), we get

\[ k_i = k_{i0} \left(\frac{\xi_c}{r_0}\right)^{d_f} \left(1 + \frac{\xi_s}{2\xi_c}\right)^{d_f} \left(1 - \frac{\xi_s}{\xi_c}\right)^{2df} 1_{\{\xi_s > \xi_c\}} \quad (F4) \]

Let us now compare \( k_i \) and \( k_c \). There are different ways to consider that \( k_i \ll k_c \). A first way is to say that, the system is in the regime \( \xi_c/\xi_s \gtrsim 1 \). Thus, one can re-write Eq. (F4) as

\[ k_i \propto \frac{k_{i0}}{\xi_c/\xi_s \gtrsim 1} \quad \frac{1}{2} \left(1 - \frac{\xi_s}{\xi_c}\right)^{2df} \quad (F5) \]

telling us that \( k_i \) depends strongly on the distance of \( \xi_c/\xi_s \) from unity. Therefore, \( k_i \) is negligible when \( \xi_c/\xi_s \gtrsim 1 \) compared to \( k_c \) and Eq. (F1), we get \( K \approx k_i/N_i \).

The other way to consider the system is, following previous approaches in [13, 60, 62, 67, 68], estimating \( k_c \propto \xi_s^{-\mu} \) with \( \mu \in [1, 5] \) function of the fractal dimension \( d_f \), the dimension of the elastic backbone and the regime of strong-link or weak-link because \( \xi_s \) is similar to a cluster size with contact. Recalling that \( (\xi_c/r_0)^{d_f} \propto \xi_s^3 \), one gets in this case
\[ \frac{k_i}{k_c} \propto \xi_s^{3+\mu} \left(1 + \frac{\xi_s}{2\xi_c}\right)^{\frac{d_f}{3}} \left(1 - \frac{\xi_s}{\xi_c}\right)^{\frac{2d_f}{3}}. \] (F6)

Assuming that \( \xi_s \) does not vary much, \( k_i/k_c \) is governed by the values of \( x \mapsto (1 + 1/(2x))^{\frac{d_f}{3}} (1 - 1/x)^{\frac{2d_f}{3}} \) on [1.2, 1.8]. Referring to Fig. 16, \( k_i/k_c \) is between 0.1 and 0.3. Therefore, one can assume that \( k_i \ll k_c \), at least for the first values, and following Eq. (F1), we get \( K \approx k_i/N_I \).

FIG. 16. Evolution of \( x \mapsto (1 + 1/(2x))^{\frac{d_f}{3}} (1 - 1/x)^{2\frac{d_f}{3}} \) for different values of \( d_f \) on [1.2, 1.8]

Generally, the more \( k_i \) is getting closer to \( k_c \), the more difficult it is to consider that only one phenomenon prevails. If someone wants to completely understand the balance between the different contributions, she or he needs to model both phenomena and their coupling. This is not the goal of this model which tries to give some orders of magnitude without exhaustively modeling the system.

We have up to now obtained the stiffness of the gel under elongation-compression. How does such a stiffness \( K \) related to the elastic modulus \( G_\infty \) of the gel at low frequencies? By rotating the referential of the sketch in Fig. [16] by \( \pi/4 \) and neglecting transverse interactions between clusters’ chains, the elongation-compression model becomes a shear stress or shear strain model and \( G_\infty = K/L \) where \( L \) is the macroscopic dimension of the system.

To sum up, based on serious approximations, we claim that the elastic plateau of the carbon black gel should scale as

\[ G_\infty = \frac{k_i}{LN_I} = G'_i \left(\frac{\xi_E}{r_0}\right)^{\frac{d_f}{3}} \left(1 + \frac{\xi_s}{2\xi_c}\right)^{\frac{d_f}{3}} \left(1 - \frac{\xi_s}{\xi_c}\right)^{\frac{2d_f}{3}}. \] (F7)

where \( G'_i \) is an elastic modulus. \( G'_i \) depends only on the particle volume fraction, the particle size, the nature of the particle interactions and the geometry of the system and will be used as a fitting parameter.

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