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Attractive carbon black dispersions: structural and mechanical responses to shear

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The rheological behavior of colloidal dispersions is of paramount importance in a wide range of applications, including construction materials, energy storage systems and food industry products. These dispersions consistently exhibit non-Newtonian behaviors, a consequence of intricate interplays involving colloids morphology, volume fraction, and inter-particle forces. Understanding how colloids structure under flow remains a challenge, particularly in the presence of attractive forces leading to clusters formation. In this study, we adopt a synergistic approach, combining rheology with ultra small-angle X-ray scattering (USAXS), to probe the flow-induced structural transformations of attractive carbon black (CB) dispersions and their effects on the viscosity. Our key findings can be summarized as follow. First, testing different CB volume fractions, in the high shear rate hydrodynamic regime, CB particles aggregate to form fractal clusters. Their size conforms to a power law of the shear rate, $\xi_c \propto \dot{\gamma}^{-m}$, with $m \simeq 0.5$. Second, drawing insights from the fractal cluster structure, we compute an effective volume fraction ϕ_{eff} and find that the microstructural Krieger-Dougherty model adeptly accounts for the hydrodynamic stress contributions. We identify a critical shear rate $\dot{\gamma}^*$ and a critical volume fraction ϕ_{eff}^* , at which the clusters percolate to form a dynamical networks. Third, we show that the apparent yield stress measured at low shear rates inherits its properties from the percolation point. Finally, through data scaling and the integration of the Einstein's viscosity equation, we revisit and discuss the Caggoni-Trappe-Spicer model, revealing a significant connection between its empirical parameters and the structural properties of CB dispersions under flow.

I. INTRODUCTION

Colloidal dispersions are encountered in numerous application fields, for instance as cement paste in construction industry¹, as drilling mud during extraction operations², as flowable electrodes used for energy storage³, or as oil in water emulsions in food industry^{4,5}. In the aforementioned examples, predicting and controlling the viscosity of the dispersions is of key importance to optimize their use. The rheological behavior of colloidal dispersions is usually non-Newtonian, and will depend on the shape, volume fraction and interaction potential between the particles⁶. In scenario with low volume fractions ϕ_{r_0} and strong attractive forces, colloidal dispersions become unstable, and particles of radius r_0 aggregate into "flocs" or "clusters" of radius ξ_c . These clusters exhibit a fractal structure, where the number of particles N_c in a cluster of size ξ_c scales as⁷:

$$N_c = \left(\frac{\xi_c}{r_0} \right)^{d_f} \quad (1)$$

with d_f the fractal dimension of clusters. The shear-dependent structure of clusters is a crucial factor for understanding the dispersion properties, whether the dispersion is at rest or subjected to shear.

Under quiescent conditions, aggregation is driven by the thermal energy. The aggregation rate is either limited by particles diffusion⁸ or by the reaction probability upon collision⁹,

leading to loosely structured clusters⁷ with $1.7 < d_f < 2.1$. When the volume fraction is sufficiently high, further aggregation of clusters leads to the formation of a space-spanning network called a "gel" that displays an elastic modulus and a yield stress¹⁰.

When attractive dispersions experience flow, clusters tend to condense, resulting in $d_f > 2.4$ ¹¹⁻¹³. The equilibrium cluster size ξ_c is determined by the balance between the viscous drag force acting on a particle F_{visc} and the attractive forces holding particles together F_{attr} . This balance is quantified by the Mason number, expressed as¹⁴:

$$\text{Mn} = \frac{F_{\text{visc}}}{F_{\text{attr}}} = \frac{6\pi\eta r_0^2 \dot{\gamma}}{U/\delta} \quad (2)$$

with r_0 (m) the particle radius, $\dot{\gamma}$ the shear rate and η a viscosity that we will define later. U (N.m) and δ (m) are the depth and width of the attractive interaction potential, respectively. An important question revolves around the nature of the viscous force involved in Eq. 2 and the stress experienced by clusters. From the dependence of the cluster size with the shear rate, it was argued that clusters are sufficiently distant, and that the fluid stress $\sigma_f = \eta_f \dot{\gamma}$ was the primary factor^{11,15} with η_f the viscosity of the background fluid. An alternative proposition suggests that interactions between clusters would lead to a substantial increase in hydrodynamic stress¹⁶ and that the dispersion viscosity η that must be taken into account in Eq. 2 to explain the equilibrium cluster size. This debate underscores the complex interplay of factors involved in cluster formation and behavior in attractive colloidal dispersions submitted to flow. The choice between the fluid stress or the dispersion stress as the key determinant might depends on the

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characteristics of the dispersion system and the experimental conditions. In all cases, the Mason number was effectively reported to control the cluster size at high shear^{15–17}.

Under this framework, the structuring degree of the dispersion is set by the flow, and in return the flow is affected by the structure of the dispersion. These reversible and time-dependent flow-induced structural changes are called "thixotropy"¹⁴. Macroscopically, attractive dispersions usually show two regimes, depending on the Mn value. At high Mn, the shear rate dependence of the cluster size leads to a shear thinning behavior and the clusters size was reported to scale as

$$\xi_c \propto \text{Mn}^{-m}, \quad (3)$$

where m is the breaking exponent. There are yet no consensus on the value of the breaking exponent m . Wessel and Ball¹⁸ first proposed that the maximum cluster size should scale with the hydrodynamic stress with $m = 1/3$. More complex models distinguish highly deformable clusters from rigid clusters, yielding $m = 1/2$ and $m = 1/3$, respectively^{19,20}. Recently, Bouthier et al.¹⁷ proposed that m should vary with the fractal dimension of clusters, with $m = 1/(1 + d_f)$. Besides analytical calculations, experiments^{11,16,21,22} and simulation^{15,23} results have reported values for m ranging from 0.2 to 1. At low values of Mn, the cluster size becomes independent of the shear rate¹⁵ as clusters fill the space, forming a transient network and leading to an apparent yield stress σ_y . Varga and Swan¹⁵ proposed that percolation would occur at a critical value of the Mason number, $\text{Mn}_c \propto \phi_{r_0}^{2/(3-d_f)}$ with ϕ_{r_0} the volume fraction of particles.

In practice, the rheological properties of attractive dispersions are assessed by applying a given shear rate $\dot{\gamma}$ and measuring the resulting stress with $\sigma = \eta \dot{\gamma}$. To assess the dependence of the dispersions viscosity with the shear rate, a flow curve test is commonly conducted. This test consists in applying a stepwise increment in shear rate with a given duration Δt . Due to the thixotropic nature of attractive dispersions, a finite amount of time is necessary to reach the equilibrium viscosity. Consequently, a rapid increase in shear rate will only characterize the transient viscosity. Flow curves, whether represented as σ vs $\dot{\gamma}$ or η vs $\dot{\gamma}$, are usually described using the Herschel-Bulkley model²⁴:

$$\sigma = \sigma_y \left[1 + \left(\frac{\dot{\gamma}}{\dot{\gamma}_{HB}^*} \right)^{n_{HB}} \right], \quad (4)$$

where σ_y is the yield stress (Pa), $\dot{\gamma}_{HB}^*$ a critical shear rate and n_{HB} an empirical exponent. This empirical model effectively captures both the yield stress and the shear-thinning behavior of attractive dispersions with $n_{HB} < 1$. However, it does not provides any microscopic interpretation of its parameters as it dismiss the cluster properties. In more developed models, the rheological parameters of the constitutive equation are set as a function of a structural parameter λ ¹⁴, comprised between 0 and 1 for a totally broken or fully developed cluster structure, respectively. By introducing kinetics equation for λ , the structural kinetics models efficiently capture the time-dependent properties of dispersions, but the parameter λ cannot be related with any physical aspects of the microstructure.

In contrast, microstructural models rely on actual structural changes that can experimentally be measured.

In microstructural models, the shear stress is decomposed as a sum of an elastic σ_e and the hydrodynamic σ_h contribution, so that $\sigma = \sigma_e + \sigma_h$. The elastic stress originates from the network of percolated clusters and is typically treated as a constant, derived from the particle interactions and the cluster properties^{25,26}. The hydrodynamic stress σ_h is calculated by introducing an effective volume fraction of clusters ϕ_{eff} . The effective volume fraction ϕ_{eff} is the equivalent volume fraction of spheres, considering the fractal structure of clusters^{25–27}:

$$\phi_{\text{eff}} = \frac{\phi_{r_0}}{k} \left(\frac{\xi_c}{r_0} \right)^{3-d_f} \quad (5)$$

where ϕ_{r_0} is the volume fraction of primary particles and k is a scaling constant usually approximated as unity. Then, various models have been used to relate ϕ_{eff} with the viscosity of the dispersion η ^{14,28–30}. Assuming that the viscosity dependence on the volume fraction follows the one of dispersion of hard spheres, a generalized viscosity equation for concentrated regimes can be used^{31,32} such as the one proposed by Krieger and Dougherty³³:

$$\eta = \eta_f \left(1 - \frac{\phi_{\text{eff}}}{\phi_{\text{eff}}^M} \right)^{-2.5\phi_{\text{eff}}^M} \quad (6)$$

with ϕ_{eff}^M the maximum packing fraction of hard spheres, typically $\phi_{\text{eff}}^M \simeq 0.64$.

In summary, a significant body of work aimed to establish connections between the cluster properties and the viscosity of colloidal dispersions. However, few studies have probed both aspects simultaneously and structural characterizations are lacking. Consequently, the validity of microstructural models has not been thoroughly tested¹⁴ and some questions have still to be answered: How the cluster properties change with shear rate? Are cluster properties driven by stress or shear rate? Is the decomposition of the stress into an elastic and hydrodynamic contribution sufficient to model the flow curve?

To address these questions, we follow an experimental approach with carbon black (CB) dispersions in oil, chosen as study model. Such dispersions present peculiar and fundamental rheological properties^{34–36} including rheopecty^{37–39}, delayed yielding^{40,41}, fatigue^{42,43}, rheo-conductive properties⁴⁴, sensitivity to flow cessations^{45,46} and rheo-acoustic properties^{47,48}. Furthermore, CB dispersions directly find utility in numerous applications such as ink⁴⁹, cement⁵⁰ or semi-solid flow batteries⁵¹.

The paper is structured as follows. We initially characterize the flow properties of CB dispersions using rheology across a range of volume fractions spanning from 0.6% to 4.1%. Then, we examine the structural features of these dispersions under flow conditions using ultra small-angle X-ray scattering⁵². Finally, we establish a relationship between the shear-dependent viscosity of the dispersions and their structural parameters by employing microstructural models

II. MATERIAL AND METHODS

A. Carbon black dispersions

CB particles (Vulcan[®]PF, Cabot, density $d_{cb} = 2.26 \pm 0.03$) were dispersed in mineral oil (RTM17 Mineral Oil Rotational Viscometer Standard, Paragon Scientific, viscosity $\eta_f = 252.1$ mPa.s at $T = 25^\circ\text{C}$, density $d_{oil} = 0.871$) at mass fractions c_w ranging from 1.5 to 10 % (w/w)⁴⁵. The corresponding volume fractions of primary aggregates ϕ_{r_0} were calculated as $\phi_{r_0} = c_w / \left(c_w + \frac{d_{cb}}{d_{oil}} (1 - c_w) \right)$. After mixing, dispersions were sonicated during 2h in an ultrasonic bath (Ultrasonic cleaner, DK Sonic[®], United-Kingdom) to ensure that all particles are fully dispersed.

B. Rheology

Experiments were carried out with two stress controlled rheometers: (i) a Haake RS6000 (Thermo Scientific) and (ii) a MCR 301 (Anton Paar), both equipped with a Couette geometry composed of concentric polycarbonate cylinders (inner diameter 20 mm, outer diameter 22 mm and height 40 mm).

All rheological measurements were performed at 25°C . After loading the CB dispersion, a preshear, $\dot{\gamma} = 1000\text{s}^{-1}$, was first applied during 60 s to erase any shear history. Then, a flow curve test was performed by ramping downward from $\dot{\gamma} = 1000$ to 0.01 s^{-1} (10 pts per decade) with a duration $\Delta t = 1$ s/pts and measuring the resulting stress σ . A downward ramping of the shear rate was chosen to prevent heterogeneous flows (*e.g.* shear banding) usually observed for yield stress fluids in the vicinity of the yield stress⁵³. We varied Δt and probed 50 and 100 s/pts and found that the flow curves were identical down to $\dot{\gamma} \sim 1\text{ s}^{-1}$ (see Appendix, Fig. 8). At shear rate $\dot{\gamma} > 1\text{ s}^{-1}$ a stationary regime is thus found rapidly as also observed in⁴⁵. Below $\dot{\gamma} \sim 1\text{ s}^{-1}$, the rheology is not stationary, wall slip may occur.

It is noteworthy that Hipp et al.¹⁶ also performed flow curve tests on CB suspensions. They constructed "self-similar flow curve" through a series of rheological measurements, involving a pre-shear at 2500 s^{-1} , followed by a resting period to facilitate gel formation, and subsequent application of given shear rates. The stress extrapolated at $t = 0$ s from the last step is then used to construct the flow curve. Due to the thixotropic nature of CB dispersions, comparing our study with Hipp et al.'s may pose challenges, as their "self-similar flow curve" is anchored to a gel state, while ours is related to the fluid state resulting from the previous shear rate.

C. Ultra Small angle X-ray scattering (USAXS)

The microstructural characteristics of the CB dispersion were probed using rheo-USAXS measurements conducted at the ID02 beamline within the European Synchrotron Radiation Facility (ESRF) in Grenoble, France⁵⁵. The incident

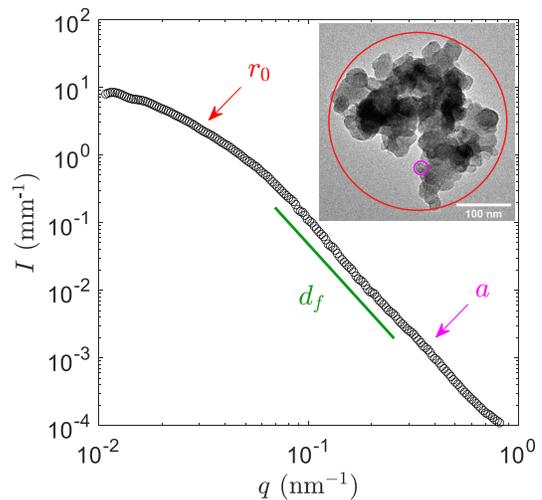


FIG. 1. Form factor of carbon black particles measured by USAXS for $\phi_{r_0} = 10^{-4}$. Carbon black particles are composed of nodules of radius a that are fused to form primary aggregates of radius r_0 . Inset displays a representative electron microscopy image of a primary aggregate. See Fig. 10 in appendix for a detailed analysis of the form factor.

X-ray beam, with a wavelength of 0.1 nm, was collimated to dimensions of $50\ \mu\text{m}$ vertically and $100\ \mu\text{m}$ horizontally. Utilizing an Eiger2 4M pixel array detector, two-dimensional scattering patterns were acquired. The subsequent data reduction process is detailed in⁵². The scattering intensity $I(q)$ was derived by subtracting the two-dimensional scattering profiles of the carbon black gel and the mineral oil. Importantly, the resulting scattering intensity remained isotropic throughout this study (see Appendix, Fig. 11) and an azimuthal average was performed to obtain a one-dimensional $I(q)$. Measurements were conducted in both radial and tangential configurations, yielding equivalent results due to the isotropic nature of the dispersions microstructure over the tested q -range.

D. Transmission electron microscopy

A diluted dispersion of CB in absolute ethanol ($c_w \approx 2 \cdot 10^{-5}$) was prepared and $5\ \mu\text{L}$ were deposited on a carbon grid (Carbon Film CF300-Cu, Electron Microscopy Science, England) and left to dry in a dust free environment. Individual CB particles were then imaged by transmission electron microscopy (TEM) using a JEOL JEM 1400 microscope. A representative set of CB particle images is displayed in Fig. 10 in Appendix.

E. Characterization of carbon black particles

The CB particles were analyzed using TEM and USAXS. As shown in the TEM images in inset of Fig.1, CB particles are composed of nodules of radius a that are fused to form primary aggregates of radius r_0 ⁵⁶. These two length scales,

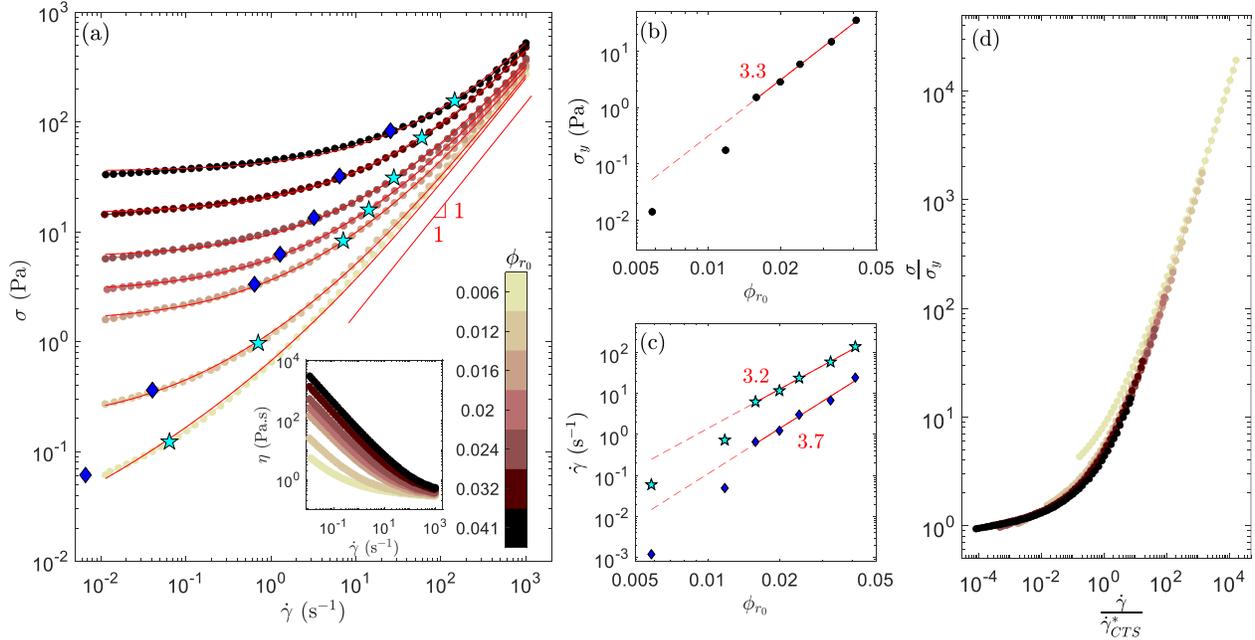


FIG. 2. Flow curve of the CB dispersions and the Cagioni-Trappe-Spicer (CTS) model⁵⁴. (a) Shear stress σ vs shear rate $\dot{\gamma}$ during fast flow curves of carbon black dispersions at various volume fractions of CB ϕ_{r0} . The red curves correspond to the best fits with the CTS model (eq. 7). Inset: viscosity η vs $\dot{\gamma}$. Evolution of the parameters of the CTS model with ϕ_{r0} : (b) Apparent yield stress σ_y ; (c) Critical shear rates $\dot{\gamma}_{CTS}^*$ (blue diamonds) and $\dot{\gamma}_{CTS}^p$ (cyan stars). $\dot{\gamma}_{CTS}^p$ is a "plastic" shear rate and $\dot{\gamma}_{CTS}^*$ is another critical shear rate obtained as $\dot{\gamma}_{CTS}^* = \sigma_y/\eta_0$, with η_0 the high shear viscosity. Red dash lines are the best power law fit of the data. (d) Normalized flow curves: σ/σ_y vs $\dot{\gamma}/\dot{\gamma}_{CTS}^*$.

$q_{r0} \approx 5.10^{-2}$ and $q_a \approx 4.10^{-1} \text{ nm}^{-1}$ are also identified on the form factor of the CB particles, measured on a diluted sample ($\phi_{r0} = 10^{-4}$) at rest (Fig.1). The power law scaling $I(q) \propto q^{d_f}$ at intermediate q is related to the fractal dimension of the primary aggregates d_{fr0} . Having tested different models to fit the USAXS data (see Fig. 10 in Appendix), we estimate $a \simeq 20 \text{ nm}$, $r_0 \simeq 85 \text{ nm}$ and $d_{fr0} \simeq 2.8$. Vulcan PF particles are therefore small and compact in comparison with other CB particles previously reported (e.g. $r_0 \simeq 180 \text{ nm}$ for Vulcan XC-72^{44,48}).

III. RESULTS AND DISCUSSION

A. Rheological properties of carbon black dispersions

We first examine the influence of the particles volume fraction ϕ_{r0} on the flow behavior of the CB dispersions. Fig. 2a displays the flow curves for dispersions with ϕ_{r0} ranging from 0.6 to 4.1%. In Fig. 2a, the flow curve exhibits a similar trend for all the tested volume fractions: a shear-thinning behavior at high shear rates and the presence of a dynamic yield stress σ_y at low shear rates. The dynamic yield stress σ_y decreases with increasing ϕ_{r0} (Fig. 2b) and its existence can even be debated at the lowest volume fraction ($\phi_{r0} = 0.006$). Dynamic oscillatory shear experiments indicate that the minimum par-

ticle volume fraction required to form a gel is $\phi_{r0}^{gel} \approx 0.01$, a value consistent across different pre-shear histories (data not presented).

To quantitatively assess the impact of ϕ_{r0} on the flow curves, two empirical models were employed: the Herschel-Bulkley²⁴ model and the Cagioni-Trappe-Spicer model⁵⁴. The Herschel-Bulkley model fit is not entirely satisfactory, especially for $\dot{\gamma} < 1 \text{ s}^{-1}$ (see Appendix, Fig. 9). Improved fits are obtained with the Cagioni-Trappe-Spicer model (CTS)⁵⁴:

$$\sigma = \sigma_y + \sigma_y \left(\frac{\dot{\gamma}}{\dot{\gamma}_{CTS}^*} \right)^{\frac{1}{2}} + \eta_0 \dot{\gamma} \quad (7)$$

where σ_y is the yield stress (Pa), $\dot{\gamma}_{CTS}^*$ a critical shear rate (s⁻¹) and η_0 a viscosity (Pa.s). In addition to taking into account the elastic component represented by the yield stress σ_y , this model incorporates a Newtonian viscous stress at high shear rates, $\eta_0 \dot{\gamma}$. Furthermore, it introduces a "plastic" dissipation mechanism, where the stress scales with the square root of the shear rate, serving as an intermediate regime between the purely viscous and purely elastic behaviors. The elastic and plastic regimes are separated by a critical shear rate $\dot{\gamma}_{CTS}^*$. A second critical shear rates $\dot{\gamma}_{CTS}^p$ can be obtained as $\dot{\gamma}_{CTS}^p = \sigma_y/\eta_0$. It corresponds to the point at which the stress contribution of the high shear viscosity equals the yield stress.⁵⁴ In Eq. 7, the high shear viscosity η_0 can be calculated with the Einstein's viscosity⁵⁷ $\eta_0 = \eta_f(1 + 2.5\phi_{r0})$, given that

both the fluid viscosity η_f and ϕ_{r_0} are known. This approximation is reasonable since all the values of ϕ_{r_0} under consideration remain low.

The CTS model yields a satisfactory fit with only two adjustable parameters, namely σ_y and $\dot{\gamma}_{CTS}^p$, displayed as function of ϕ_{r_0} in Fig 2b-c. In the case of gelling dispersions (*i.e.* $\phi_{r_0} > \phi_{r_0}^{gel}$), the yield stress follows a scaling law $\sigma_y \propto \phi_{r_0}^{3.3}$, consistent with findings in other colloidal gel systems⁵⁸. $\dot{\gamma}_{CTS}^*$ roughly follows the same power law, $\dot{\gamma}_{CTS}^* \propto \phi_{r_0}^{3.2}$. Using σ_y and $\dot{\gamma}_{CTS}^*$ as scaling factors for the y - and x -axes, the flow curves can be rescaled onto a single master curve (Fig. 2e), provided that $\phi_{r_0} > \phi_{r_0}^{gel}$. This master curve implies a consistent microstructural scenario along the entire flow curve for all volume fractions. Furthermore, the observed relationships $\sigma_y \sim \dot{\gamma}_{CTS}^* \sim \phi_{r_0}^3$ indicates that the initial volume fraction of primary particles completely accounts for both the horizontal and vertical shifts of the flow curves as the volume fraction varies. This is noteworthy given the structural complexity expected for attractive dispersions. In the next section, our objective is to characterize the structure of CB dispersions and to provide insights into how ϕ_{r_0} influences the flow characteristics of these dispersions.

B. Microstructure of the carbon black dispersions under shear

The structural analysis of CB dispersions was conducted using ultra small-angle X-ray scattering (USAXS) at three volume fractions, namely $\phi_{r_0} = 0.6, 1.2$ and 3.2% . We recorded the scattering intensity $I(q)$ as function of the scattering wave number q within the range of 1.10^{-3} to $2.10^{-1} \text{ nm}^{-1}$ during flow curve measurements. It is noteworthy that $I(q)$ exhibited isotropic behavior for all measurements (see appendix, Fig.11), ruling out any anisotropic structuring over the probed length scales. This isotropic behavior aligns with previous observations in CB dispersions^{16,45}. Consequently, our analysis focuses on the azimuthally averaged intensity $I(q)$.

Fig. 3a presents $I(q)$ at various shear rate values for $\phi_{r_0} = 0.032$. Similar scattering patterns were observed for dispersions at lower volume fractions, and they displayed the same shear rate dependence (see appendix, Fig. 12). Upon transitioning from high to low shear rates, the scattering curves exhibit two and then three distinct bumps. These features become more pronounced in the Kratky representation ($I(q)q^2$ vs q), where the bumps are transformed into peaks (Fig. 3b). At higher q values (*i.e.* $q \approx 5.10^{-2} \text{ nm}^{-1}$), the first bump corresponds to the form factor of the CB particles of size r_0 , as evidenced on Fig.1. Notably, the position of this bump is independent of the shear rate as shear does not alter the size of the primary aggregates.

As previously stated, the scattering curves exhibit two characteristic lengths at high shear rates, denoted as r_0 and ξ_c (Fig. 3c-d), and an intermediate length scale, ξ_s , becomes apparent at lower shear rates (approximately $\dot{\gamma} < 75 \text{ s}^{-1}$). For a precise and empirical determination ξ_c and ξ_s and their relationship with $\dot{\gamma}$, we conducted fitting procedures on the peaks

observed in the Kratky representation (Fig. 3c-d). These fittings were carried out using a log-normal function⁵⁹:

$$G_i(q) = \frac{A_i}{\sqrt{2\pi}\sigma_i q} \exp\left(-\frac{\ln\left(\frac{q}{q_i}\right)^2}{2\sigma_i^2}\right) \quad (8)$$

where $G_i(q)$ describes a log-normal function of average position q_i , width σ_i and amplitude A_i . The estimated radius ($\xi_i = \pi/q_i$) are displayed for $\phi_{r_0} = 0.006, 0.012$ and 0.032 in Fig. 15b in appendix.

The size ξ_c is attributed to the form factor of clusters, formed through the aggregation of primary particles. Let us first focus on $\phi_{r_0} = 0.032$. At high shear rates, ξ_c is inversely proportional to the shear rate according to $\xi_c = B\dot{\gamma}^{-m}$, where $B \simeq 10^4 \text{ nm/s}^m$ and $m \simeq 0.44$ (inset of Fig. 3e). Below a critical shear rate of about 50 s^{-1} , ξ_c becomes constant with a critical value close to $2 \mu\text{m}$. This behavior coincides well with the simulation of Varga et al.¹⁵ where a similar scaling with $\dot{\gamma}$ and $m = 1/2$ was found. The evolution of ξ_c at lower volume fractions ($\phi_{r_0} = 0.006$ and 0.012) is similar to the one observed at $\phi_{r_0} = 0.032$. At high shear rates, the data even superimpose. However, at lower shear rates, data are lacking because the peak in $I(q)$ corresponding to ξ_c shifts to values lower than the minimum q accessible in the USAXS experiments. Based on simulations studies¹⁵, for $\phi_{r_0} = 0.006$ and 0.012 , one can expect that the scaling $\xi_c = A\dot{\gamma}^{-m}$ holds down to a critical shear rate lower than 50 s^{-1} and that the cluster size converges to values much larger than $2 \mu\text{m}$. For $\phi_{r_0} = 0.006$ and 0.012 , extrapolations of ξ_c vs $\dot{\gamma}$ (Fig. 3e) will be justified during the microstructural analysis developed in the next section.

So far, the present results show that the cluster size is governed by the background fluid stress, $\sigma_f = \eta_f \dot{\gamma}$ in agreement with^{11,15}. This is in contrast to the proposition in^{16,46}, where the dispersion stress was proposed as the determining factor (see appendix, Fig. 13 for an evolution of ξ_c vs σ). Hipp et al.¹⁶ reported a scaling of ξ_c with the dispersion stress and $m \approx 1$ ¹⁶. In this study, "self-similar" flow curves were generated through a series of rheological measurements, involving a resting period before application of a given shear rate. The resulting pre-shear history differs with our protocol, and the values of m are hardly comparable.

ξ_s is found to be independent of the shear rate and slightly diminishes as ϕ_{r_0} increases (see appendix, Fig.15). The exact interpretation of ξ_s remains uncertain. In the context of CB gels at rest, ξ_s had previously been considered either as the separation distance between two neighboring clusters, with the idea that clusters interpenetrate due to the fact that $\xi_c > \xi_s$ ⁴⁵, or as an intermediate cluster size contributing to the construction of clusters with a size of ξ_c ⁶⁰. Alternatively, as proposed in the context of colloidal gelation under quiescent conditions, ξ_s could represent the distance over which particles are transported to the growing cluster. In this case, ξ_s is attributed to a correlation hole corresponding to the size of the depleted region surrounding the clusters^{61,62}.

To extract the fractal dimension of clusters, the scattering data were fitted with a modified two-level Beaucage

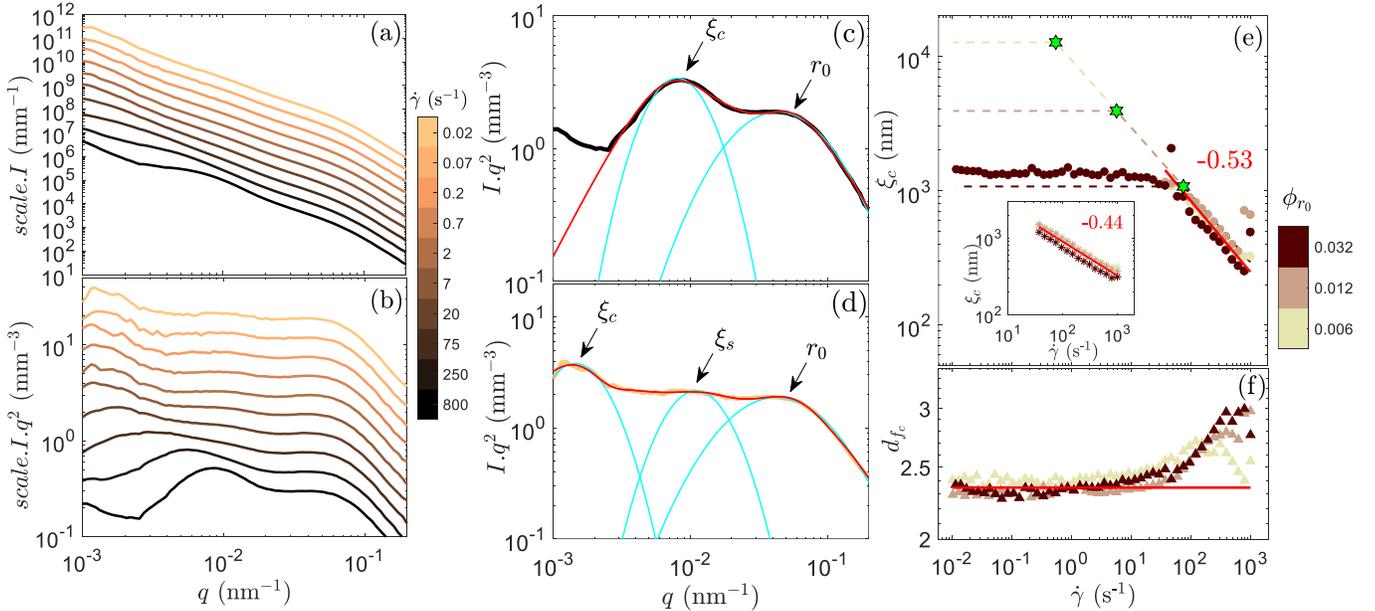


FIG. 3. Structure of the carbon black dispersion at $\phi_{r_0} = 0.032$ during a flow curve test. (a) Scattered intensity $I(q)$ vs the wave vector q . (b) Kratky representation, Iq^2 vs q , of the data in (a). The curves are shifted along the y-axis for better visualization. (c)-(d) Typical scattering curves in Kratky representation obtained at high ($\dot{\gamma} = 800$ s $^{-1}$) and low shear ($\dot{\gamma} = 0.02$ s $^{-1}$), respectively. The cyan lines show the fit of the peak positions using Eq. 8. The red lines are the modified Beaucage fits using Eq. 10. (e) Evolution of the cluster size ξ_c with the shear rate $\dot{\gamma}$ for three different ϕ_{r_0} , determined with the Beaucage model (Eq. 10). Note that for $\phi_{r_0} = 0.006$ and 0.012 , the cluster size increases beyond the resolution of the USAXS experiments at low $\dot{\gamma}$. Dash lines are extrapolated cluster sizes and green stars correspond to the cluster size at percolation ξ^* , determined using the microstructural model (See Fig. 4). Red line is the best power law fit for $5 \cdot 10^2 < \dot{\gamma} < 10^3$ s $^{-1}$. Inset: ξ_c vs $\dot{\gamma}$ determined with the model-free analysis (Eq. 8). (f) Fractal dimension of the cluster d_f obtained from the modified Beaucage fit. The red line indicates $d_f = 2.35$, the mean value of d_f for $10^{-2} < \dot{\gamma} < 10^1$ s $^{-1}$.

model^{45,63}, accounting for the scattering of the particles r_0 and of the clusters ξ_c (see appendix, section V E). To account for the intermediate level ξ_s , the cluster-level term was multiplied by an empirical structure factor to account for some correlated region⁶³. The modified Beaucage model provides a good fit of the experimental data for all volume fractions (Fig. 3c-d and Fig. 12 in appendix). Fig. 3e-f display the cluster sizes and fractal dimensions as function of the shear rate. The cluster sizes ξ_c obtained from the modified Beaucage model correspond well with the values obtained from the model free analysis, also displayed in Fig. 3e. The power law fit of ξ_c vs $\dot{\gamma}$ yields $m \simeq 0.53$, confirming that the value of the breaking exponent is about 0.5. In Fig. 3f, the fractal dimension shows a non-monotonic evolution with the shear rate. Overall, d_f is close to 3 at high shear rates and tends toward a constant value $d_f = 2.35$ when $\dot{\gamma}$ decreases. Determining d_f at high shear rates presents notable challenges for two primary reasons. First, in $I(q)$, d_f is determined by the power-law relationship $I(q) \sim q^{-d_f}$ observed between the bumps associated with r_0 and ξ_c . At high shear rates, where r_0 and ξ_c are in close proximity, this power-law behavior extends over a relatively limited range, resulting in insufficient statistical data for accurate determination of d_f . Secondly, when examining the structure factor (see appendix, Fig. 14), an anticorrelation peak is observed at $q \approx 0.03$ nm $^{-1}$ resulting from

attractive interactions among the CB particles. This anticorrelation peak is not accounted by the modified Beaucage model, which leads to an overestimation of d_f . At low shear rate, the extended distance between the bumps associated to r_0 and to ξ_c allows for a more reliable determination of d_f . Moving forward, we disregards the values of d_f obtained at high shear. The fractal dimension is assumed to remain constant and equal to $d_f = 2.35$ across the entire range of shear rates ($10^{-2} < \dot{\gamma} < 10^3$ s $^{-1}$), a value which aligns with values predicted by theoretical models^{12,64} and those obtained through other experimental determinations^{11,16}.

C. Modeling the hydrodynamic regime of the flow curve based on the cluster structure.

In the previous section, rheo-USAXS measurements have shown that the CB dispersions undergo an hydrodynamic regime at high shear rates. In this regime, for all ϕ_{r_0} , the cluster size scales as $\xi_c \propto \dot{\gamma}^{-m}$ with $m \approx 0.5$ and their fractal dimension remains constant at $d_f \approx 2.35$. For the lowest volume fractions, due to experimental limitations, the cluster size cannot be measured beyond 2 μ m and the extent of the hydrodynamic regime is not directly accessible. To address this limitation, the cluster size is extrapolated based on the re-

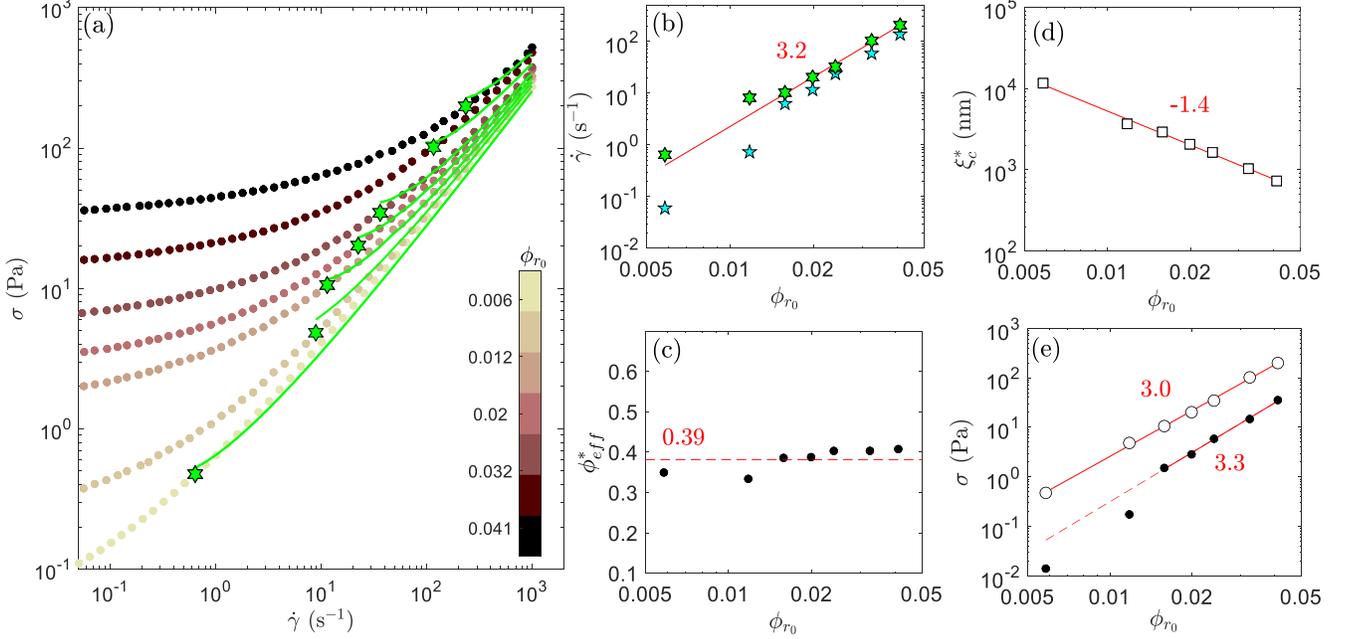


FIG. 4. Microstructural modeling of the hydrodynamic stress of the flow curve. (a) Comparison between the experimental flow curves (circles) and σ_h (green line) determined using Eq. 5 and 6 and the structural parameters of CB dispersions measured by USAXS. Stars are points of coordinate $(\dot{\gamma}^*, \sigma^*)$ such that $\sigma_h \approx \sigma$, interpreted as the dynamic percolation of clusters and $\dot{\gamma}_{CTS}^*$ (cyan pentagrams) as a function of the volume fraction of primary aggregates ϕ_{r0} . (b) Comparison between $\dot{\gamma}^*$ (green hexagrams) and $\dot{\gamma}_{CTS}^*$ (cyan pentagrams) as function of ϕ_{r0} . Dash line indicates the mean value of $\phi_{eff}^* \approx 0.39$. (d) Cluster length ξ_c^* at percolation displayed as a function of ϕ_{r0} . Red line indicates the best power fit. (e) Comparison between the stress at percolation σ^* (empty circles) and the apparent yields stress σ_y (solid circles) as a function of ϕ_{r0} . Red line indicates the best power law fit.

relationship $\xi_c \propto \dot{\gamma}^{-m}$ observed in Fig. 3e. Using the measured and extrapolated microstructural parameters of the CB dispersions, an hydrodynamic stress $\sigma_h = \eta(\phi_{eff})/\dot{\gamma}$ is calculated using Eq. 5 for ϕ_{eff} and Eq. 6 for η . The scaling factor k in Eq. 5 was calculated⁶⁵ as $k \approx 4.46d_f^{-2.08}$ leading to $k \approx 0.75$.

As reported in Fig. 4a, σ_h captures well the flow curves down to a critical shear rate $\dot{\gamma}^*$, identified when σ_h becomes larger than the dispersion stress σ . Indeed, extrapolation of the cluster size ξ_c leads to an increase of σ_h up to $\sigma_h \geq \sigma$. This point is interpreted as a percolation point where clusters growth becomes restricted by percolation into a dynamic network, with an effective volume fraction ϕ_{eff}^* and an effective yield stress σ^* . Consequently, for $\dot{\gamma} \leq \dot{\gamma}^*$, the cluster size is assumed to become constant and equals at ξ_c^* , as depicted in Fig. 3e where $\dot{\gamma}^*$ is pointed out by stars. This analysis is consistent with the scattering data at $\phi_{r0} = 0.032$, where the cluster sizes at low shear rates are available. Fig. 5b displays the dispersion viscosity η vs ϕ_{eff} , the effective volume fraction of clusters. The collapse of viscosity onto a master curve confirms that the rheology of the CB dispersions depends on the shear dependent volume fraction of clusters. The Krieger-Dougherty fit (red line) accurately describes the dispersions behavior up to approximately $\phi_{eff}^* \simeq 0.4$, which sets the upper limit in effective volume fraction of the hydrodynamic regime.

D. Properties of the percolation point $(\dot{\gamma}^*, \sigma^*)$.

The values of $\dot{\gamma}^*$, ξ_c^* , σ^* and ϕ_{eff}^* are plotted as function of ϕ_{r0} in Fig. 4b-e. As mentioned in the previous section, these parameters relate to the structure of dispersions when clusters are assumed to percolate into a dynamic network.

In Fig. 4b, $\dot{\gamma}^*$, obtained from the microstructural approach and $\dot{\gamma}_{CTS}^*$, obtained from the CTS model, are overlaid for $\phi_{r0} > \phi_{r0}^{gel}$. Thus, $\dot{\gamma}_{CTS}^*$, used to rescale the flow curves in Fig. 2, is now identified as the shear rate at which clusters percolate. In Fig. 4c, $\phi_{eff}^* \approx 0.39$ is constant for all ϕ_{r0} . This value is lower than the random close packing fraction of hard spheres, as illustrated on Fig. 5. Percolation below random close packing has been previously reported for non-Brownian dispersions with adhesive constraints at an "adhesive close packing" fraction $\phi_{acp} = 0.55$ ⁶⁶. Varga et al.¹⁵ have proposed that a critical Mn value for a percolated network could be obtained as $Mn_c \propto \phi_{r0}^{2/(3-d_f)}$. Assuming that $Mn \propto \dot{\gamma}$, the critical shear rate $\dot{\gamma}^*$ should scale with ϕ_{r0} with a power exponent $2/(3-d_f) \simeq 3.1$ given that $d_f = 2.35$. This is consistent with the observed scaling $\dot{\gamma}^* \propto \phi_{r0}^{3.2}$ observed in Fig. 4b.

As shown in Fig. 4d, the cluster size at percolation ξ_c^* decreases with ϕ_{r0} as ϕ_{eff}^* is reached at higher shear for the high-

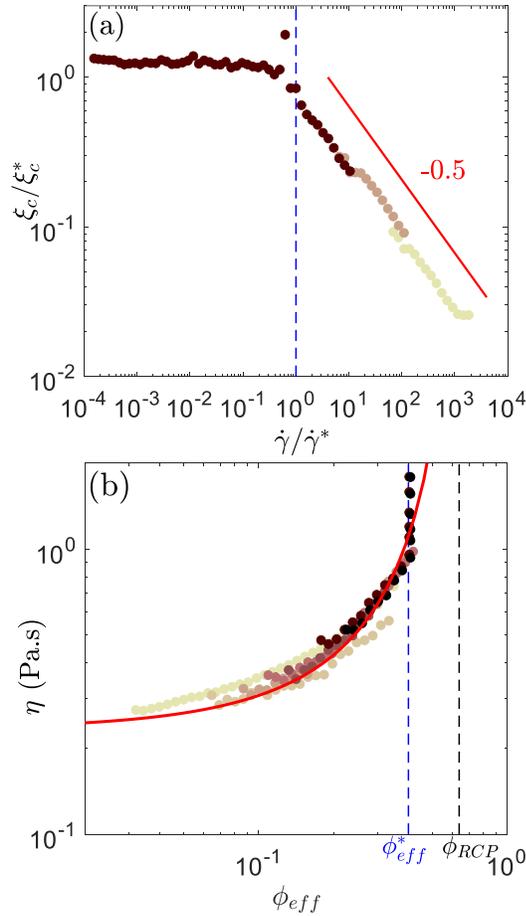


FIG. 5. Transition between the hydrodynamic regime and dynamic percolation. (a) Normalized cluster size ξ_c/ξ_c^* as a function of the normalized shear rate $\dot{\gamma}/\dot{\gamma}^*$. ξ_c^* and $\dot{\gamma}^*$ are the cluster size and shear rate at percolation, respectively. (b) Viscosity η of the CB dispersions as a function of the effective volume fraction of clusters ϕ_{eff} using Eq. 5. The red line is the viscosity issued from the Krieger-Dougherty model with $\eta_f = 0.234$ Pa.s and $\phi_{eff}^M = 0.64$. Blue and black dotted lines indicate the volume fraction of clusters at percolation ϕ_{eff}^M and at ϕ_{eff}^M , respectively.

est volume fractions. In fractal aggregation theories^{67,68}, it is assumed that the gel network is built of closely packed clusters at $\phi_{eff}^* = 1$ which directly yields $\xi_c \propto \phi_{r_0}^{1/(d_f-3)}$. For CB dispersions, $\phi_{eff}^* \neq 1$ but ϕ_{eff}^* is constant and the observed scaling $\xi_c^* \propto \phi_{r_0}^{-1.4}$ aligns well with $1/(d_f-3) \approx -1.5$ given that $d_f = 2.35$ (Fig. 4d). Fig. 4e compares the dependency of σ_y , measured in the zero shear rate limit, and σ^* on ϕ_{r_0} . Interestingly, both quantities exhibit a similar scaling pattern with respect to ϕ_{r_0} . This observation supports the idea that the value of σ_y is a direct outcome of the percolation point. Indeed, when σ_y is plotted against ξ_c^* (Fig. 6), it is found that $\sigma_y \propto \xi_c^{*-2.2}$ a close match to what one would expect¹⁷: $\sigma_y \propto \xi_c^{-2}$ for a network of characteristic size ξ_c . It is worth mentioning that, when the measuring time Δt of the flow curve

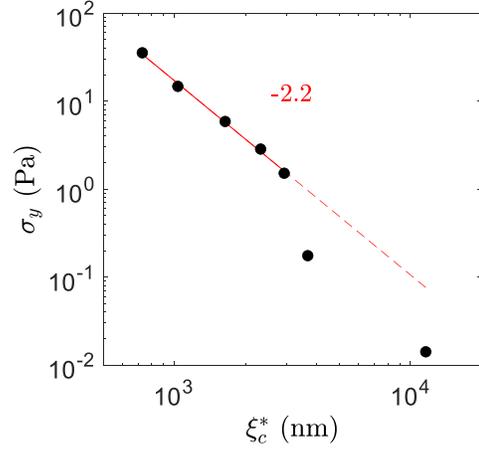


FIG. 6. Yield stress σ_y as a function of the cluster size at percolation ξ_c^* for dispersions with different volume fractions of carbon black particles. The red line represents the best-fitting power law.

increases (see Fig. 8 in appendix), this direct dependence between σ_y and ξ_c^* is probably lost as structural rearrangements may occur at low shear rates.

To sum up, in Fig. 2 the flow curve σ vs $\dot{\gamma}$ of CB dispersions at various ϕ_{r_0} have been rescaled using a critical shear rate $\dot{\gamma}_{CTS}^*$ and σ_y as scaling factors for the x - and y -axis, respectively. Now, the origin of this scaling can be understood on a microstructural basis. The critical shear rate $\dot{\gamma}_{CTS}^*$ corresponds to the dynamic percolation of clusters at $\phi_{eff}^* \simeq 0.39$. The decrease of the cluster size ξ_c^* at percolation is then responsible for the increase of σ_y with ϕ_{r_0} , as the network structure in the zero shear limit is inherited from the percolation point. When ϕ_{r_0} approaches $\phi_{r_0}^{gel}$, dispersions no longer displays a yield stress and the structuring at low shear is somewhat different. The percolation point, defined by $\dot{\gamma}^*$, ξ_c^* , σ^* , and ϕ_{eff}^* , holds significant importance in understanding the flow behavior of CB particles, being the transition point between the hydrodynamic regime and the dynamic percolation of clusters. In Fig. 5a, ξ_c vs $\dot{\gamma}$ at various ϕ_{r_0} can be normalized onto a master curve linking using the percolation point, $\dot{\gamma}^*$ and ξ_c^* as scaling factors for the x and y axis, respectively. The experimental results display on Fig. 5a are fully consistent with simulations performed in¹⁵.

IV. CONCLUSION AND PERSPECTIVES

A series of rheo-USAXS experiments was conducted on CB dispersions with $\phi_{r_0} \in [0.006, 0.041]$ to investigate the response of attractive colloidal dispersions to mechanical shear. These experiments involved rapidly changing the shear rate from high to low values, revealing a microstructural scenario depicted in Fig. 7.

In the hydrodynamic regime, attractive CB particles assemble into clusters with a fractal dimension of $d_f = 2.35$, and their size inversely scales with the shear rate as $\xi_c \propto \dot{\gamma}^{-m}$,

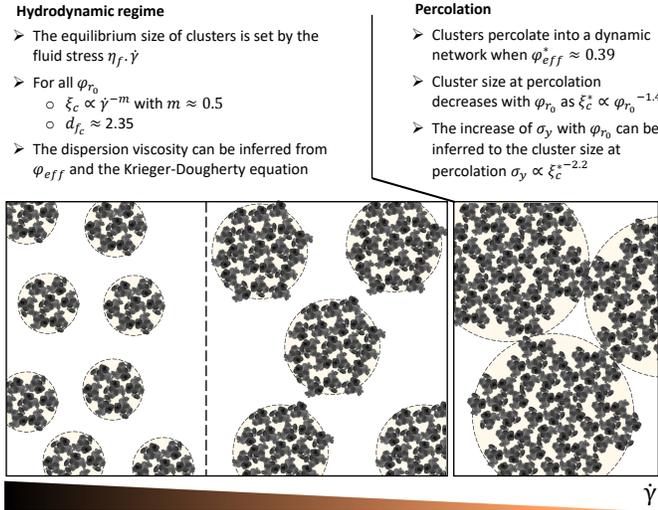


FIG. 7. Schematic of the evolution of the CB dispersions microstructure with the shear rate $\dot{\gamma}$.

where m is approximately equal to 0.5. The size of these clusters is primarily determined by the fluid stress, represented by $\sigma = \eta_f \dot{\gamma}$, where η_f is the fluid background viscosity. The viscous contribution of the clusters can be approximated to the one of a hard sphere suspension and the viscosity of CB dispersions could be calculated using the Krieger-Dougherty equation, provided we replace the CB particle volume fraction ϕ_{r0} by an effective volume fraction of clusters ϕ_{eff} . This hydrodynamic regime persists down to a critical point characterized by coordinates $(\dot{\gamma}^*, \sigma^*)$.

At this juncture, the clusters growth stops and their effective volume fraction stabilizes at $\phi_{eff}^* \approx 0.39$, irrespective of ϕ_{r0} . We propose that at ϕ_{eff}^* , clusters percolate into a dynamic network. This hypothesis gains support from the observation that σ^* closely tracks variations in the dynamical yield stress σ_y . When ϕ_{r0} increases, the clusters size at percolation decreases, leading to a higher σ_y . In essence, the properties of dispersions in the limit where $\dot{\gamma} = 0$ are inherited from the percolation point. To sum up, the dynamic percolation point is a key parameter to explain the mechanical response of CB dispersions under shear. While the cluster growth in the hydrodynamic regime proceeds independently of the volume fraction, the percolation of clusters at a constant ϕ_{eff}^* determines both the critical shear rate and the yield stress of the flow curve.

Microstructural models have traditionally partitioned the stress response of attractive dispersions into hydrodynamic and elastic contributions^{25,26}. A robust and self-consistent comprehension of these two regimes has been established for CB dispersions. However, in Fig. 4a, it is clear that the hydrodynamic regime does not extent to low shear rates, in the vicinity of σ_y , and that an additional contribution is required to model the flow curve at intermediate shear rates ($\dot{\gamma} < \dot{\gamma}^*$). Previously, we have stressed that the cluster size at percolation was maintained when $\dot{\gamma}$ is further decreased. It pictures the idea that, during the intermediate regime, the structure of the suspension is shear-independent and composed of large

and crowded clusters, comparable with the flow of adhesive non-Brownian suspensions. Based on the phenomenological model of Wyart and Cates⁶⁹, constraint-based rheology was shown to successfully model all flow curve types⁷⁰. In this approach, particle sliding and rolling are constrained by adhesive and/or frictional contacts that are accounted by a shear-dependent jamming point ϕ_m . For adhesive non-Brownian suspensions, experimental results⁷¹ highlight the coupling between adhesion and friction to account for the shear-thinning and yield stress of the suspensions. In the case of attractive Brownian suspensions, for $\dot{\gamma} < \dot{\gamma}^*$, the flow of sticky clusters may be successfully modeled using constraint-based rheology. The challenge probably lies in rationalizing the contribution of adhesion and friction in these systems.

Additional research is needed to characterize the intermediate regime. Colloidal systems that are optically transparent would be particularly advantageous, as they would allow for the characterization of mesoscopic structures (with $\xi > 2\mu m$) using optical microscopy or dynamic light scattering. An alternative method for modeling this plastic regime would involve describing the elastic stress contribution of the dynamic network with a network percolation loss rate that decreases with respect to a characteristic time of $1/\dot{\gamma}$. Finally, it would be beneficial to validate the approach used in this paper and compare our findings with those from other attractive colloidal systems subjected to flow.

AUTHOR CONTRIBUTIONS

JB and TG carried out the experiments. JB analysed the data. TG, LVB and AP helped JB analyzing the data. TG and JB wrote the paper. TG designed and managed the project.

CONFLICTS OF INTEREST

There are no conflicts to declare.

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V. APPENDIX

A. Effect of the duration on the flow curve

As shown in Fig. 8, the shape of the flow curve depends on the shear duration Δt applied to measure each point. Two regimes can be distinguished depending on the shear rate: at high shear rate ($\dot{\gamma} > 1 \text{ s}^{-1}$), the stress response is independent on Δt while at low shear rate ($\dot{\gamma} < 1 \text{ s}^{-1}$) and for high volume fractions of primary particles ϕ_{r_0} , a drop of the stress can be observed. The drop is all the more important that Δt is large.

B. Herschel-Bulkley model

In Fig. 9, the Herschel-Bulkley model provides an acceptable fit of the data. However the Herschel-Bulkley model is less efficient than the CTS model to capture the data at intermediate shear rate, around $\dot{\gamma} \approx 1 \text{ s}^{-1}$. Notably, the critical shear rate $\dot{\gamma}_{HB}^*$ shows a different scaling with ϕ_{r_0} in comparison with $\dot{\gamma}^*$ obtained from the CTS model (Fig. 9c). As pointed in⁵⁴, the CTS model gets rid of the nonphysical power exponent n (Fig. 9d) by introducing a high shear viscosity η_0 (Eq. 7).

C. Form factor

The form factor of the CB particles was measured with SAXS on a diluted sample ($\phi_{r_0} = 10^{-4}$) at rest and fitted using different models.

In Fig. 10a, the form factor described as a combination of a particle form factor $P(q)$, accounting for the nodules, and

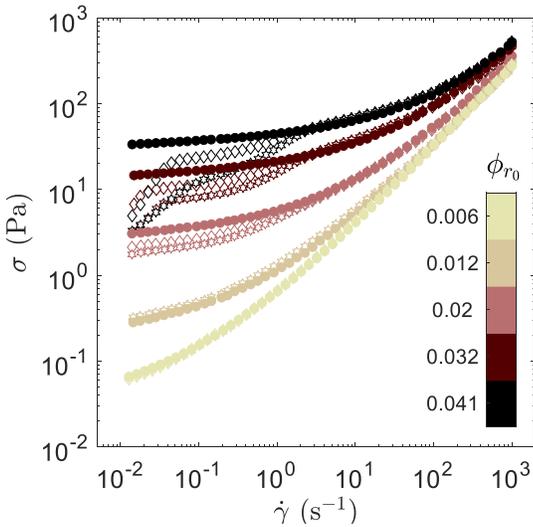


FIG. 8. Flow curve of carbon black dispersions at various volume fraction ϕ_{r_0} . The ramp was conducted with $\Delta t = 1$ (circle), 50 (diamond) and 100 (star) s/pts.

a fractal structure factor $S(q)$, accounting for the primary aggregates, with $I(q) \propto P(q)S(q)$. $P(q)$ is modeled as the form factor of polydisperse spheres with a log-normal distribution⁷² and $S(q)$ is modeled as a mass fractal structure factor⁷³. The fit yields $a = 3 \text{ nm}$, $r_0 = 33 \text{ nm}$, $d_{f,r_0} = 2.85$. The radius of gyration of a fractal aggregate is given by⁷³: $r_0^2 = \frac{d_f(d_f+1)\xi_s^2}{2}$ which yields $r_0 = 76 \text{ nm}$.

In Fig. 10b, the form factor is modeled using a two-level Beaucage model. The first level models the particles of size $a = 20 \text{ nm}$. The second level models the primary cluster of size $\xi_{r_0} = 85 \text{ nm}$ and fractal dimension $d_{f,r_0} = 2.78$.

In both cases, the fit results compares well with the primary aggregates TEM images in Fig. 10c. The characterization of the Vulcan PF particles presented here confirms that these particles are small and compact in comparison with other CB particles previously reported (e.g. $R_g \approx 180 \text{ nm}$ for Vulcan XC-72^{44,48}).

D. Anisotropy

Fig. 11 displays the scattering curves of CB dispersions, azimuthally averaged either in the flow direction or in the vorticity direction. For the blue-green curves, corresponding to the vorticity direction, the low q region is reduced because of the rectangular shape of the beamstop used. At all shear rates, the superimposition of the curves in both directions indicates the absence of anisotropic structure, also reported by¹⁶ for CB dispersions in oil.

E. Modified Beaucage model

The intensity spectrum $I(q)$ may be fitted by a modified two-level Beaucage model^{45,46,63,74,75} through:

$$I(q) = I_c(q)S_s(q) + I_{r_0}(q) \quad (9)$$

with

$$\begin{cases} I_c(q) = G_c e^{-\frac{q^2 \xi_c^2}{3}} + B_c e^{-\frac{q^2 r_0^2}{3}} \text{erf}\left(\frac{q \xi_c}{\sqrt{6}}\right)^{-3d_f} q^{-d_f} \\ S_s(q) = 1 + C_s \left(\left(\frac{q \xi_s}{2\pi}\right)^2 + \left(\frac{2\pi}{q \xi_s}\right)^2 \right)^{-1} \\ I_{r_0}(q) = G_{r_0} e^{-\frac{q^2 r_0^2}{3}} + B_{r_0} \text{erf}\left(\frac{q r_0}{\sqrt{6}}\right)^{-3d_{r_0}} q^{-d_{r_0}} \end{cases} \quad (10)$$

This model accounts for the presence of three distinct bumps observed in $I(q)$ corresponding to the length scales r_0 , ξ_s , and ξ_c arranged in ascending order. The two-level Beaucage model combines the scattering contribution $I_c(q)$ from the clusters with a size ξ_c and a fractal dimension d_f with the contribution $I_{r_0}(q)$ from the primary aggregates with a size r_0 . To account for the intermediate length scale ξ_s , revealed at low shear rate, the cluster intensity $I_c(q)$ is multiplied by an ad-hoc structure factor $S_s(q)$, resulting in an increase in

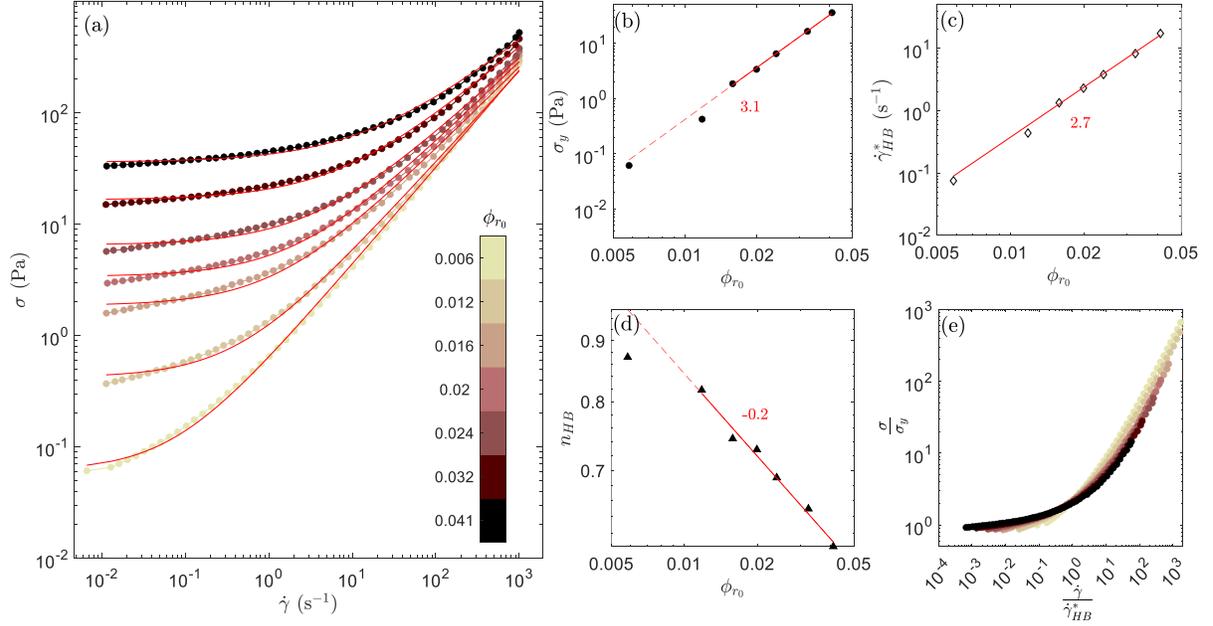


FIG. 9. Herschel-Bulkley model of the CB flow curves. (a) Shear stress σ vs shear rate $\dot{\gamma}$ during fast flow curves of carbon black dispersions at various volume fraction of primary aggregates ϕ_{r_0} . Inset displays the dynamic viscosity η vs $\dot{\gamma}$. The red curves correspond to the best fits with the Herschel-Bulkley component model (eq. 4). (b)-(d) Evolution of the parameters of the Herschel-Bulkley model with ϕ_{r_0} . σ_y is the apparent yield stress, $\dot{\gamma}_{HB}^*$ is a critical shear rate and n is the power exponent. Red lines are the best power law fit of the data. (e) Normalized flow curves: σ/σ_y vs $\dot{\gamma}/\dot{\gamma}_{HB}^*$.

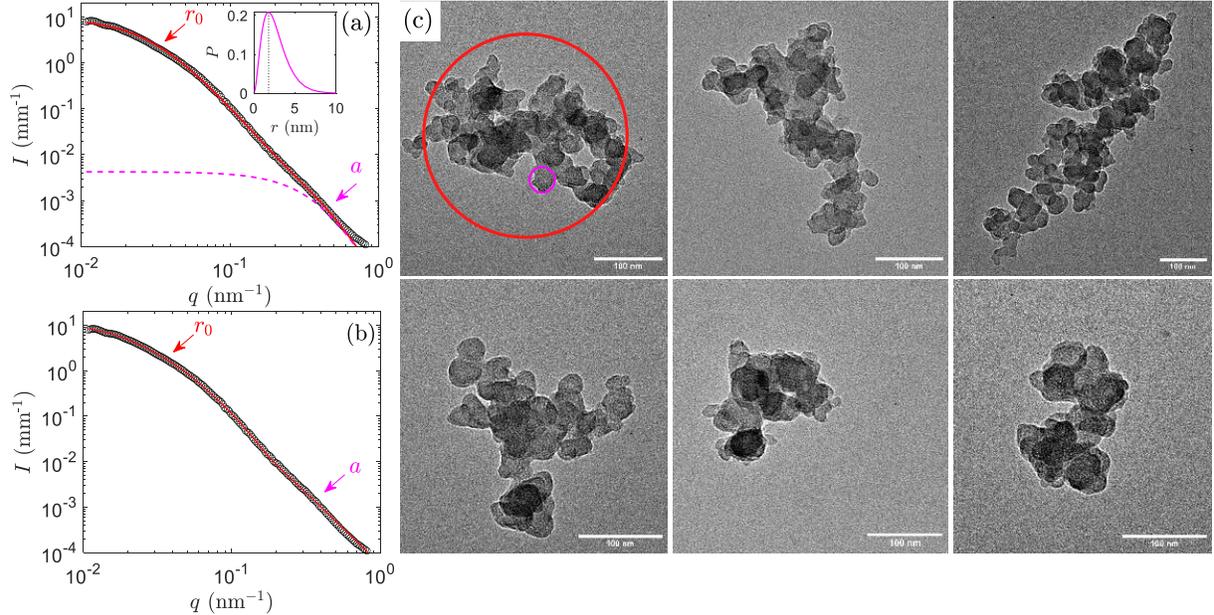


FIG. 10. Characterization of the Vulcan[®] PF carbon black particles. (a) Fit of the CB form factor using a mass fractal model. Inset: log-normal distribution of a . (b) Fit of the CB form factor using a Beaucage model. Form factor of the carbon black particles measured by SAXS for $\phi_{r_0} = 10^{-4}$. Carbon black particles are composed of nodules of radius a that are fused to form primary aggregates of radius r_0 . (c) Representative set of TEM images of individual carbon black particles.

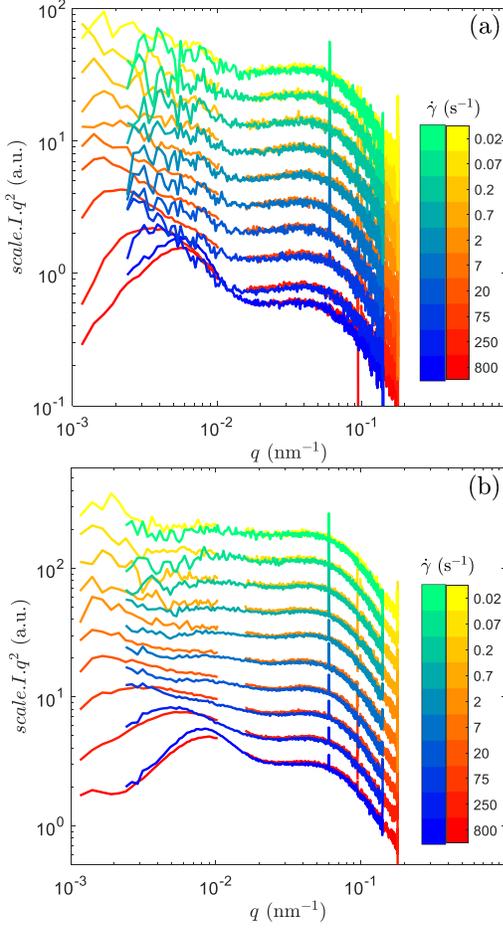


FIG. 11. Comparison of the scattering intensity between the flow direction (red-yellow) and the vorticity direction (blue-green) at $\phi_{r0} = 0.006$ (a) and 0.032 (b). The color gradients code for the shear rate.

scattering at intermediate q . This structure factor $S_s(q)$ is a function that exhibits a peak at $q_s = 2\pi/\xi_s$ and reaches a maximum value of $1 + C_s/2$. Away from $q_s = 2\pi/\xi_s$, it gradually converges to 1. While this choice of $S_s(q)$ is straightforward, it is not entirely satisfactory as it fails to meet thermodynamic limits. Specifically, $S_s(q \rightarrow 0)$ equals 1, whereas it should be proportional to the isothermal compressibility. In Fig. 12, we show the fit of the scattering intensity of the CB dispersions using the modified two-level Beaucage model.

F. Evolution of ξ_c with σ

In Fig. 13, we observe that ξ_c does not scale with σ .

G. Structure factor

The structure factor of the CB dispersion $S(q, \phi_{r0}) = \frac{I(q, \phi_{r0})}{P(q)} \frac{\phi_{r0}^P}{\phi_{r0}}$ is obtained by dividing the the scattering intensity

of the CB dispersion at ϕ_{r0} by the primary aggregates form factor measured at $\phi_{r0}^P = 10^{-4}$ as shown in Fig 10. $S(q)$ displays an anticorrelation peak at $q \sim 0.03 \text{ nm}^{-1}$, associated with attractive interactions among the CB particles the background oil.

H. Evolution of ξ_s and ξ_c with ϕ_{r0} and $\dot{\gamma}$

The dependence of the length scales ξ_s and ξ_c with ϕ_{r0} and $\dot{\gamma}$ was investigated using (i) a model free analysis (Eq. 8) and (ii) a two-level modified Beaucage model (Eq. 10). ξ_s and ξ_c are displayed as function of $\dot{\gamma}$ on Fig. 15b-c. Both approaches show that for $\dot{\gamma} > 50 \text{ s}^{-1}$, ξ_c increases with $\dot{\gamma}$ as $\xi_c \propto \dot{\gamma}^{-m}$ with $m \approx 0.5$, highlighting the robustness of this result. Below $\dot{\gamma} = 50 \text{ s}^{-1}$, ξ_c is found to be constant ($1 < \xi_c < 2 \mu\text{m}$) at $\phi_{r0} = 0.032$. For lower volume fraction we believe the cluster size increases beyond the range of length scales that can be probed by the SAXS set-up. In the microstructural analysis developed in section III for the Fig. 4, we have extrapolated the values of ξ_c using $\xi_c \propto \dot{\gamma}^{-m}$ up to the limit when $\sigma_h > \sigma$.

In Fig. 15b-c, ξ_s is found to be independent of the shear rate and slightly diminishes as ϕ_{r0} increases. The dependence of ξ_s with ϕ_{r0} is also illustrated in Fig. 15a.

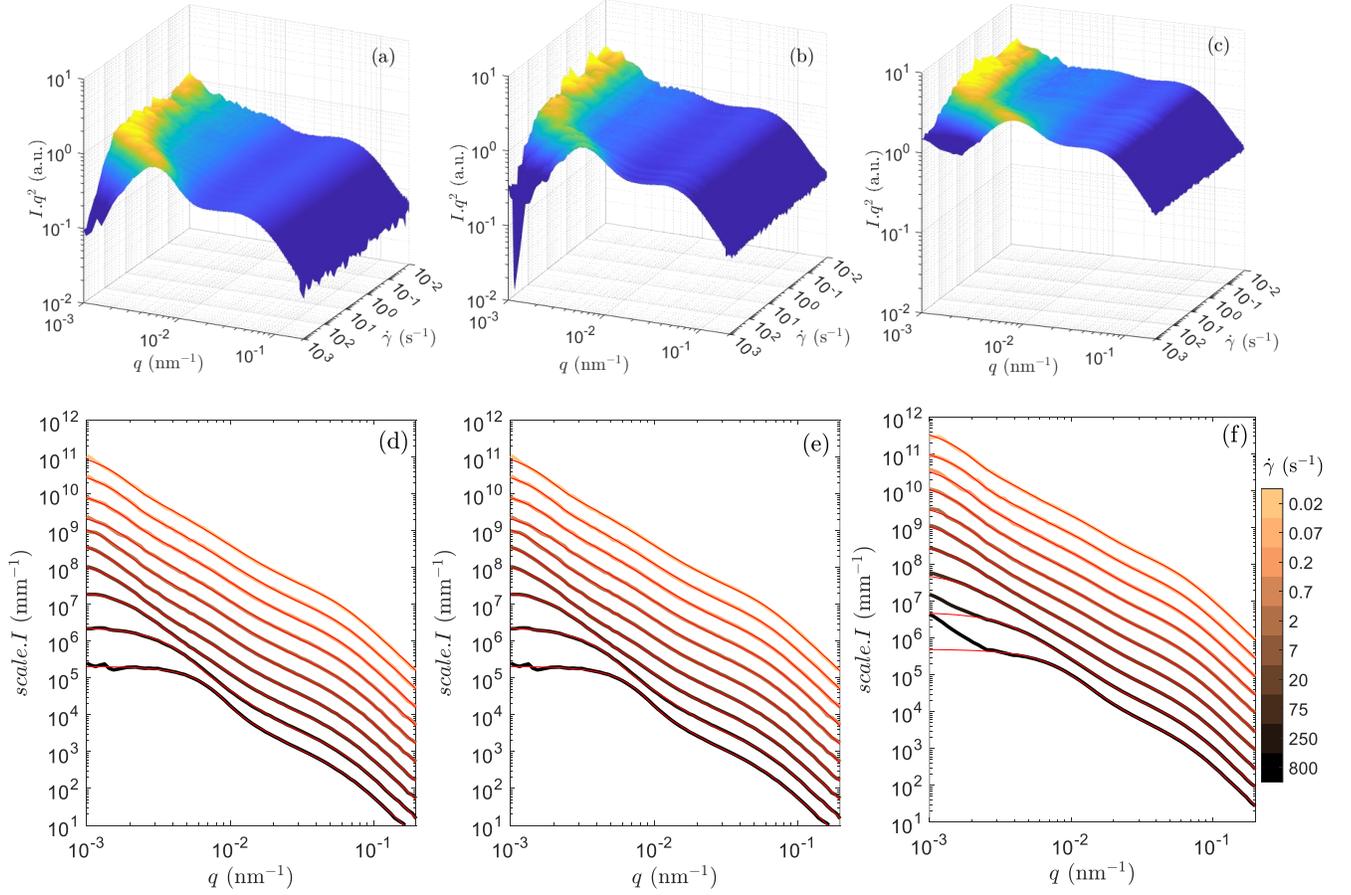


FIG. 12. (a)-(c) 3D visualization of the shear dependence of the scattering intensity in Kratky representation Iq^2 vs q for the volume fractions $\phi_{r0} = 0.006$ (a), 0.012 (b) and 0.032 (c). The color gradient codes for the intensity of Iq^2 . (d)-(f) $I(q)$ and their fit (red lines) using the modified Beaucage model (Eq. 10) for the volume fractions $\phi_{r0} = 0.006$ (d), 0.012 (e) and 0.032 (f). The color gradient from light orange to black codes for the shear rate. $I(q)$ are shifted along the y-axis for better visualization.

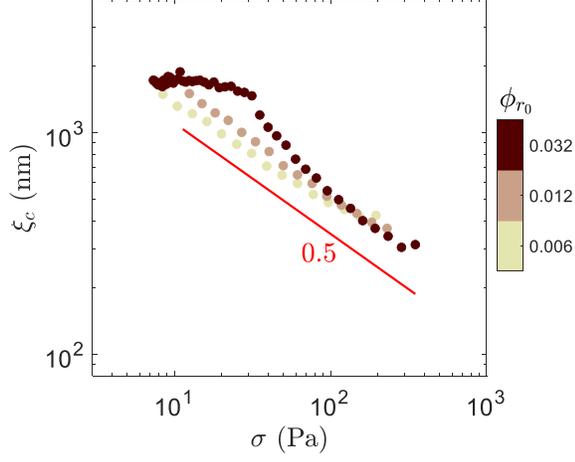


FIG. 13. Evolution of ξ_c with σ for $\phi_{r_0} = 0.006, 0.012$ and 0.032 . Red line is a power law $\xi \propto \sigma^{-0.5}$ displayed for comparison.

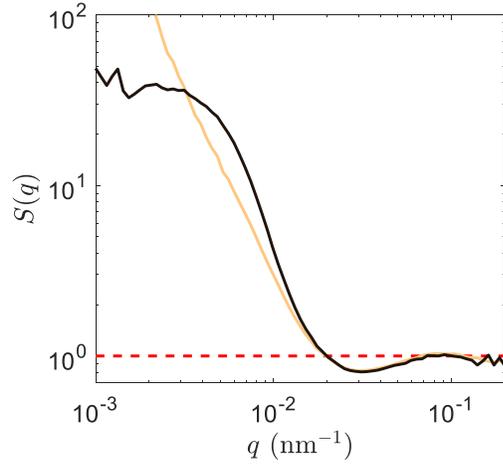


FIG. 14. Comparison of the structure factor $S(q)$ of the CB dispersion at $\phi_{r_0} = 0.006$ at $\dot{\gamma} = 800$ (black) and 0.02 s^{-1} (light orange).

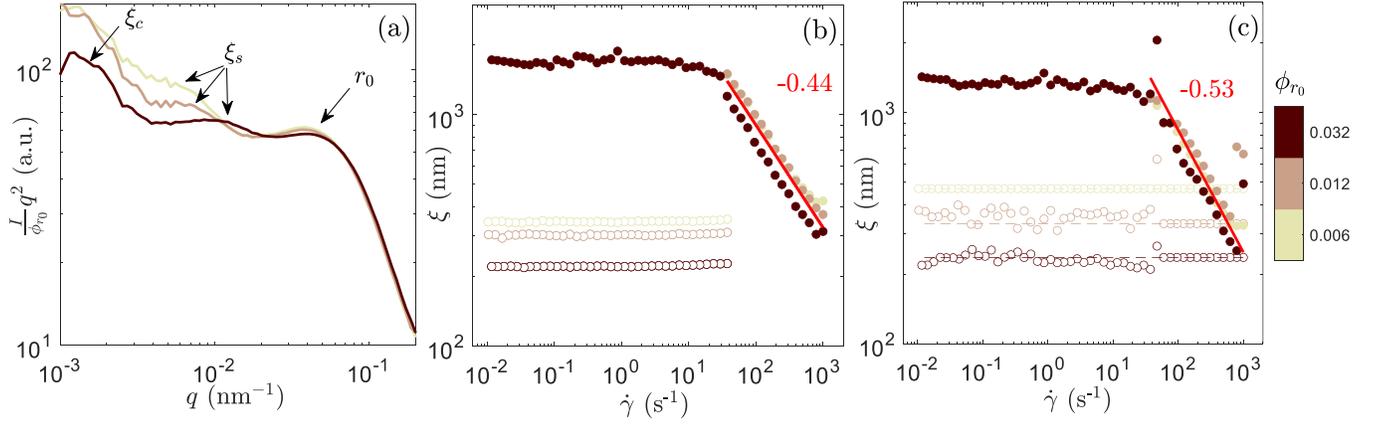


FIG. 15. (a) Rescaled scattering curve $I(q)/\phi r_0$ vs q measured under low shear rate at $\dot{\gamma} = 0.02 \text{ s}^{-1}$ for $\phi r_0 = 0.006, 0.012$ and 0.032 . (b)-(c) Cluster size ξ_c (solid circles) and intermediary length ξ_s (empty circles) as function of the shear $\dot{\gamma}$ determined from the model-free analysis (b) and the modified two-level Beaucage model (c). Red lines are the best power law fit of ξ_c vs $\dot{\gamma}$ for $\dot{\gamma} > 50 \text{ s}^{-1}$.