

Shear-induced clustering of Brownian colloids in associative polymer networks at moderate Péclet number

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We investigate shear-induced clustering and its impact on fluid rheology in polymer-colloid mixtures at moderate colloid volume fraction. By employing a thermoresponsive system that forms associative polymer-colloid networks, we present experiments of rheology and flow-induced microstructure on colloid-polymer mixtures in which the relative magnitudes of the time scales associated with relaxation of viscoelasticity and suspension microstructure are widely and controllably varied. In doing so, we explore several limits of relative magnitude of the relevant dimensionless shear rates, the Weissenberg number Wi and the Péclet number Pe . In all of these limits, we find that the fluid exhibits two distinct regimes of shear thinning at relatively low and high shear rates, in which the rheology collapses by scaling with Wi and Pe , respectively. Using three-dimensionally-resolved flow small-angle neutron scattering measurements, we observe clustering of the suspension above a critical shear rate corresponding to $Pe \sim 0.1$ over a wide range of fluid conditions, having anisotropy with projected orientation along both the vorticity and compressional axes of shear. The degree of anisotropy is shown to scale with Pe . From this we formulate an empirical model for the shear stress and viscosity, in which the viscoelastic network stress is augmented by an asymptotic shear thickening contribution due to hydrodynamic clustering. Overall, our results elucidate the significant role of hydrodynamic interactions in contributing to shear-induced clustering of Brownian suspensions in viscoelastic liquids.

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I. INTRODUCTION

Polymer nanocomposites have been widely used to enhance mechanical properties of polymeric materials [1]. Their properties and performance depend critically on the structure of the dispersed particle phase [2]. Thus, optimizing the final properties of nanocomposites requires careful control of particle dispersion and therefore rheology during processing. Since many nanocomposites are processed from solution [3], it is thus critically important to understand the influence of flow on polymer-particle interactions and suspension microstructure of colloidal suspensions in polymer liquids.

There have been many studies demonstrating shear-induced clustering of both Brownian and non-Brownian particles in polymer fluids. Although early studies of this phenomenon involved *ex situ* observations of solid composite structures, later work involved the direct observation of anisotropic clustering under flow. Interestingly, two significantly different anisotropic orientations of shear-induced clusters have been observed. In one case, Michele *et al.* [4] and Lyon *et al.* [5] observed stringlike particle clusters oriented along the flow direction in highly viscoelastic solutions under shear. However, vorticity-aligned clusters of particles have also been observed in attractive polymer-colloid mixtures [6,7]. More recently, Pasquino *et al.* observed a transition to vorticity-aligned clustering with decreasing particle size, suggesting that colloidal interactions and Brownian motion may be important in determining the mechanism and orientation of shear-induced particle clusters [8]. Also, Haddadi and Morris have shown that, using lattice-Boltzmann simulations, pair-sphere trajectories in finite inertia shear flow prefer vorticity alignment [9]. We note that similar

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clustering has also been observed in systems whose suspension microstructure is aggregated at rest [3], although it is not clear whether the same physics of clustering apply in these systems or whether the behavior is rather dominated by interparticle attractions. The mechanism of clustering in polymer-colloid mixtures also appears to be different from that observed in highly confined suspensions in Newtonian liquids, which is dominated by hydrodynamic effects of the confining walls [10,11].

From these studies, several hypotheses have been proposed for the mechanism of shear-induced clustering. Some groups have proposed that clustering is driven by the growth of polymer normal stresses at sufficiently high shear rates [12,13]. Others have argued that the formation of stringlike clusters is also influenced by the shear thinning viscosity of polymeric fluids [14,15]. However, more recent studies have cast some doubt on the role of elasticity in shear-induced clustering. Specifically, shear-induced particle clustering was not observed in a highly elastic Boger fluid for Weissenberg numbers Wi , exceeding 260, while in highly shear thinning polymeric fluids, the flow-induced clusters form only at low shear rates in which the observed rheology is uncorrelated with polymer elasticity [14]. Furthermore, in a recent study of non-Brownian particles in viscoelastic fluids by Snijkers *et al.*, the formation of particle pairs was shown in very weakly shear thinning Boger fluids [15].

In principle, the microstructure of suspensions in viscoelastic polymer solutions under shear flow is highly complex, due to the many coupled contributions to the total fluid stress. These include (i) viscoelastic stresses due to the effect of shear flow on the polymer network (typically shear thinning viscosity and positive first normal stress difference), (ii) hydrodynamic interactions arising from the coupling of flow disturbances due to the presence of particles and the suspending viscoelastic polymer flow, and (iii) Brownian stresses induced by deformation of the suspension microstructure away from its equilibrium configuration. Models for the former two contributions, and their effects on particle motion, have been extensively studied for the case of dilute non-Brownian suspensions in polymer solutions, primarily in the context of the second-order fluid (SOF) model. Early work found that isolated spheres in various shear flows of a SOF produce a secondary flow around the particle [16,17]. It was later found that such secondary flows result in significant normal stress disturbances in the vicinity of the particle and causes pairs of particles to rotate and align with the flow direction [18,19], and by extension cause chaining in dilute suspensions. Similar analysis has been used to predict the rheology of non-Brownian suspensions in a SOF [20,21]. It is notable that all of these theories predict shear-induced particle clusters aligned along the flow direction and not along the vorticity direction as observed in some experiments. As such, the propensity to form vorticity-aligned clusters is presumably due to either nondilute suspension effects or the effects of Brownian motion on the suspension and hydrodynamic stresses.

By comparison, the theory for nondilute Brownian suspensions in polymer solutions, including hydrodynamic interactions, is underdeveloped. Here it is important to distinguish between suspensions of Brownian and non-Brownian particles. In the former case, Brownian motion competes with hydrodynamic interactions to restore the suspension microstructure to its equilibrium state. These competing processes introduce competing time scales for the influence of polymer-particle and particle-particle interactions on the fluid microstructure and rheology. One of these is the viscoelastic relaxation time for the polymer network τ_r , which defines a characteristic dimensionless shear rate, the Weissenberg number $Wi = \tau_r \dot{\gamma}$, where $\dot{\gamma}$ is the applied shear rate. The other is the characteristic time scale for Brownian relaxation of the suspension microstructure τ_{Br} , which defines another characteristic dimensionless shear rate, the Péclet number $Pe = \tau_{Br} \dot{\gamma}$.

One can therefore anticipate a range of shear-induced microstructures depending on the relative magnitude of these two time scales. Unfortunately, systematic theoretical studies of flowing suspensions in viscoelastic solutions under various limits of Wi and Pe have yet to be made. However, there has been significant modeling of suspension microstructure in Newtonian fluids, to which some analogies might be made. For example, clustering due to an excess of particle pairs along the compressional axis has been demonstrated in shear flow by both experiment [22] and simulation [23]. Brady and Morris analyzed the influence of hydrodynamic interactions and Brownian diffusion

on such structural anisotropy at large Pe using Stokesian dynamic simulations [24]. However, it is currently unclear whether similar effects are dominant in viscoelastic suspending media and over what range of Wi they would apply.

Similarly, previous experimental studies of shear-induced clustering have yet to systematically explore the effects of competing viscoelastic and Brownian time scales. Recently, we developed a model system of nonaggregating, viscoelastic Brownian suspensions in polymer solutions in which such studies can be made [25]. The colloidal fluid is comprised of oil-in-water nanoemulsions in the presence of polyethylene glycol (PEG) and sodium dodecyl sulfate (SDS). These fluids form nonaggregating viscoelastic networks that can be considered to be rheologically similar to the materials previously studied by Belzung *et al.* in which vorticity-aligned clustering was observed in scattering measurements [26]. However, the present material system is advantageous in that it provides an unprecedented ability to fine-tune the characteristic time scales of viscoelasticity and shear-induced structuring. Specifically, in previous studies, we showed that these nanoemulsions exhibit strongly thermosensitive viscoelasticity at low temperatures, which was hypothesized to result from the formation of transient polymer-surfactant complexes that are physically cross-linked by the suspended colloids [25]. Specifically, polymer chains interact with surfactant on the surface of the droplets due to well-known ion-dipole interactions between PEG and ionic surfactants. The resulting polymer-surfactant complexes form a transient polymer network, in which a number of polymers are physically cross-linked by the droplets through weak adsorption to their surface. In this system, the viscoelastic relaxation time τ_r varies by several orders of magnitude with modest changes in temperature, even though the viscosity of the underlying suspension medium remains nearly constant. This provides a route by which Wi and Pe can be easily tuned relative to one another with temperature.

In this study, we use this model system to perform rheological and three-dimensionally-resolved rheology–small-angle neutron scattering (rheo-SANS) measurements to explore shear-induced clustering in several limits of the relative magnitudes of the viscoelastic relaxation time and the Brownian relaxation time, i.e., $Wi \gg Pe$, $Wi \sim Pe$, and $Wi < Pe$. As will be shown later, an advantage of our thermoresponsive nanoemulsions is that all of these limits can be accessed within relatively narrow ranges of composition and temperature. These studies overcome several drawbacks of previous microstructural measurements involving direct visualization [6,27,28] and scattering [26,29–31]. First, the small size of the nanodroplets (<50 nm in radius) avoids the use of highly confined systems, as confinement alone is known to force structure formation in the vorticity direction [6,10,11]. Second, whereas most previous scattering studies have been by light scattering, SANS enables particle-scale examination of the structuring process. Finally, rheo-SANS measurements in multiple orthogonal projections allow for a fully-three-dimensional understanding of shear-induced clustering and its relation to macroscopic rheology and flow [32]. We note that similar combined studies involving light and x-ray measurements have elucidated the mechanisms of shear-induced structuring in aggregated colloidal suspensions [28,31]. However, it is not clear whether the phenomena examined in those studies can explain the clustering observed in a number of polymer-colloid systems that are nonaggregating at rest [26,33].

II. MATERIALS AND EXPERIMENTS

A. Nanoemulsion preparation

Oil-in-water nanoemulsions were prepared with polydimethylsiloxane (PDMS) (viscosity $\eta = 5$ mPa s at 25 °C, Sigma Aldrich) as the dispersed phase. Dihydroxy-polyethylene glycol (molecular weight $M_w \sim 600$ g mol⁻¹, Sigma Aldrich), SDS, deionized water, and deuterium oxide (D₂O) (99.9%, Cambridge Isotope Laboratories) were used as a continuous phase. The nanoemulsions were prepared using a high-pressure homogenization method (Avestin Emulsiflex-C5) following a procedure described previously [25]. Dynamic light scattering (DLS) (Brookhaven Instrument BI-200SM) was used to characterize the size distribution of the nanoemulsion droplets.

TABLE I. Viscosity of continuous phase at different temperatures.

Suspending medium fluid	Suspending medium viscosity η_m (mPa s)					
	5 °C	10 °C	15 °C	20 °C	25 °C	30 °C
33 vol% PEG with 48 mM SDS	12.48	10.03	8.19	6.79	5.69	4.84
36 vol% PEG with 41 mM SDS	15.26	12.17	9.85	8.09	6.76	5.70
40 vol% PEG with 50 mM SDS	21.82	17.09	13.66	11.09	9.15	7.64

The nanoemulsions used in this study contains a volume fraction $\phi_o = 0.33$ of PDMS oil nanodroplets in an aqueous continuous phase containing 120 mM SDS and various volume fractions of PEG ($\phi_p = 0.33, 0.36$, and 0.40). This surfactant concentration was chosen in order to produce viscoelasticity in the nanoemulsions at low temperature [25]. For rheo-SANS measurements, the nanoemulsion was prepared in 82/18 (vol%) $\text{H}_2\text{O}/\text{D}_2\text{O}$ in order to match the scattering length density of the solvent to that of the polymer and reduce multiple scattering from the droplets [34]. The average radius of droplets measured by DLS depends on the sample-to-sample difference ($\langle a \rangle = 34.6$ nm for $\phi_p = 0.33$, $\langle a \rangle = 31.7$ nm for $\phi_p = 0.36$, and $\langle a \rangle = 35.4$ nm for $\phi_p = 0.40$). Given the overall surfactant concentration and the size of the nanodroplets, we estimate that the nanoemulsions contain approximately 40–50 mM “free” SDS in the continuous phase, with the remainder at the oil-water interface of the nanodroplets. The viscosity of the continuous phase at this SDS concentration was measured using a falling ball capillary viscometer (Anton Paar Lovis) at temperatures ranging from 5 °C to 30 °C. The resulting measured viscosities are listed in Table I.

B. Rheology

Rheological measurements were performed using a stress-controlled rheometer (TA Instruments AR-G2). For time-temperature superposition measurements of linear viscoelasticity, the dynamic shear moduli were measured using a 60-mm, 2° upper cone geometry and a Peltier temperature-controlled lower-plate geometry. Samples were presheared at 10 rad s^{-1} for 60 s. Frequency sweeps were performed over a range of $0.02\text{--}200 \text{ rad s}^{-1}$ at 1% strain amplitude and equilibrated temperatures ranging between 5 °C and 30 °C. Above this temperature range, the linear viscoelasticity becomes immeasurable [see Supplemental Material (SM) [35]]. For steady-state shear rheology measurements, the steady shear stress was measured using a Peltier temperature-controlled Couette geometry (inner radius, 14.0 mm; outer radius, 15.2 mm) at equilibrate temperatures ranging between 5 °C and 30 °C. The shear rate sweeps were performed over a range of $0.01\text{--}2000 \text{ s}^{-1}$ with steady-state sensing for 30 s at 5% tolerance. We found that there is no history dependence of the steady shear rheology using forward-backward shear rate sweep measurements to test for hysteresis (see SM [35]). Furthermore, since the particle-scale Reynolds number $\text{Re} = \rho_m \dot{\gamma} a^2 / \eta_m$, where ρ_m is the density of the suspending medium, is less than $O(10^{-7})$ for all shear rates and temperatures, particle inertia effects can be safely neglected for all experiments.

C. Rheo-SANS measurements

Small-angle neutron scattering measurements were performed using the NG7 30m and NGB 10m SANS instruments at the National Institute of Standards and Technology Center for Neutron Research (Gaithersburg, MD). A schematic depiction of the rheo-SANS measurements is shown in Fig. 1. For measurements in the flow-vorticity projection (1-3 plane), samples were loaded in a 50-mm optical quartz outer cylinder with a 48-mm titanium inner cylinder and measured at a sample to detector distances of 13 and 4.6 m. For measurements in the flow-gradient projection (1-2 plane), a short-gap Couette shear cell with inner and outer radii of 25.1 and 26.5 mm, respectively, was used. Samples were measured at a sample to detector distance of 15.3 m. Details of the shear cell and its operation are described elsewhere [36,37]. The temperature of the sample was left to

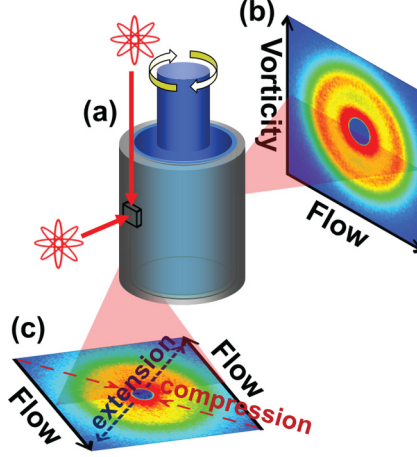


FIG. 1. (a) Schematic diagram of the Couette shear cell for the 2D flow-SANS scattering. Also shown are 2D scattering projections for the (b) flow-vorticity (1-3) plane and (c) flow-gradient (1-2) plane.

equilibrate in the relevant sample environments for at least 30 min prior to measurement. Steady shear flow-SANS measurements were performed at several shear rates ranging from 0 to 2000 s^{-1} . For each measurement, at least 3 min are waited to reach steady state. In the 1-2 shear cell measurements, the flow-SANS was measured at center of the gap due to spatial inhomogeneity at different gap positions (see SM [35]). Also, we measured flow-SANS under both forward and backward shear directions to check for reversibility. The resulting data were reduced using the IGOR software package provided by National Institute of Standards and Technology using standard protocols [38].

III. RESULTS

A. Characteristic time scales

The nanoemulsions exhibit viscoelasticity at low temperature and obey time-temperature superposition (TTS), in agreement with previous work [25]. To demonstrate this, we measured the frequency-dependent linear viscoelastic spectra for the nanoemulsions at temperatures ranging from 5 $^{\circ}\text{C}$ to 30 $^{\circ}\text{C}$. Figures 2(a), 2(c), and 2(e) show the linear viscoelastic master curves obtained by shifting G' and G'' to the reference temperature $T = 15^{\circ}\text{C}$ for each of the samples studied. From this we obtain the temperature-dependent viscoelastic relaxation time $\tau_r(T)$, which corresponds to the time scale for dynamic formation and breakage of a network structure comprised of polymer-nanodroplet junctions [25]. Specifically, the TTS master curve is first used to determine $\tau_r(T_{\text{ref}})$ for a particular sample at the reference temperature, which is equal to the inverse of the frequency at crossover between G' and G'' . The remaining values of τ_r at all other temperatures for that sample are then computed from the horizontal shift factors by $\tau_r(T) = \tau_r(T_{\text{ref}})/a_T(T)$. Here τ_r decreases with increasing temperature by as much as two orders of magnitude over the range of temperature studied. In what follows we will use τ_r to scale the shear rate to construct the Weissenberg number Wi . We also computed the Brownian relaxation time for the suspension microstructure. In principle, τ_{Br} is most closely related to the time scale associated with the long-time diffusivity of the suspension (which depends on the volume fraction) by $\tau_{\text{Br}} = a^2/D_{\infty}(\phi_o)$. However, in the present system, the long-time dynamics exhibit subdiffusive behavior due to the collective dynamics of the polymer-droplet network [25], preventing quantification of $D_{\infty}(\phi_o)$. Therefore, we resort to replacing the long-time diffusivity of the suspension with self-diffusivity of an isolated sphere such that $\tau_{\text{Br}} = 6\pi a^3 \eta_m / k_B T$. Here a is the average droplet radius, η_m is the suspending medium viscosity, k_B is the Boltzmann constant, and T is the temperature. A more realistic treatment

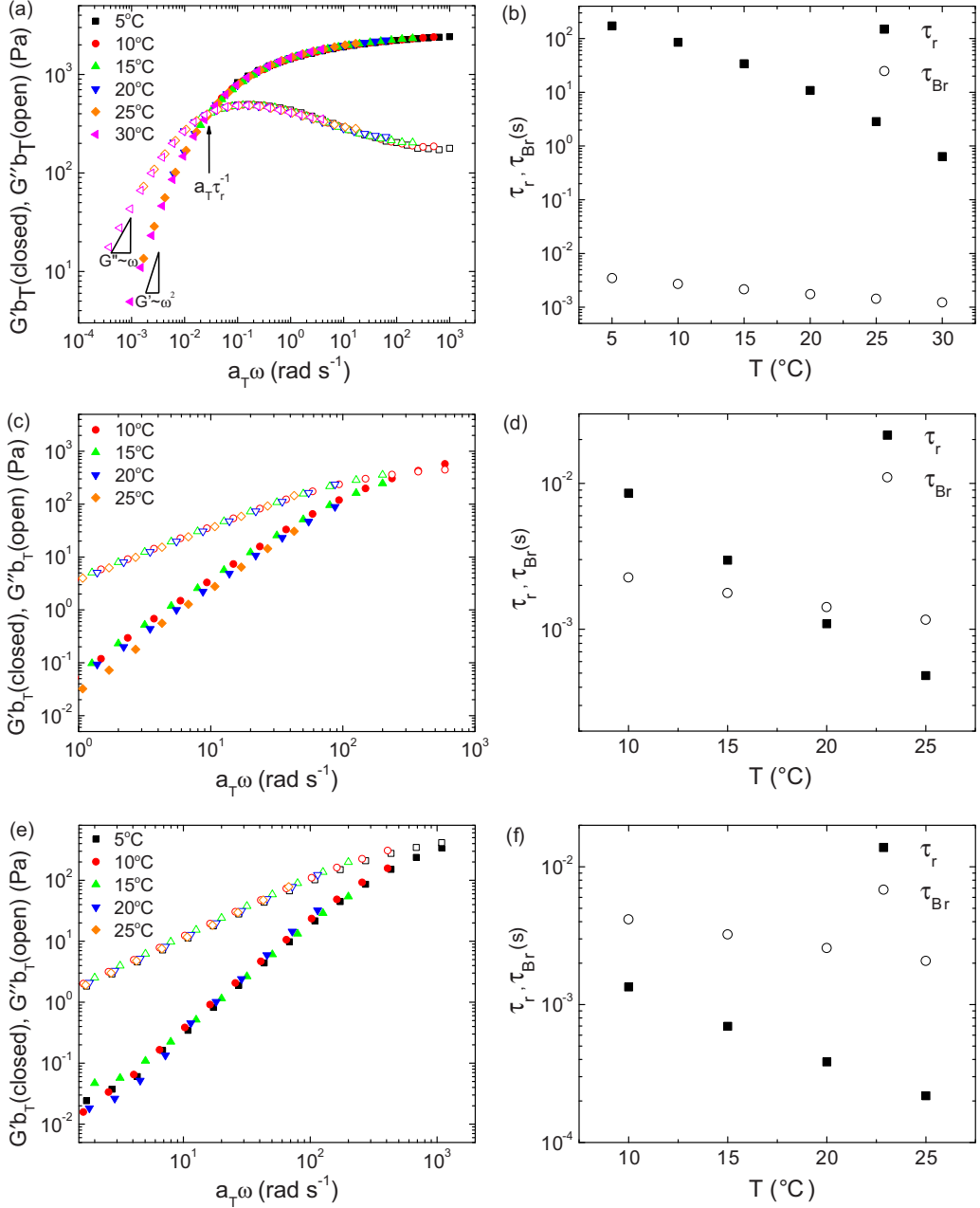


FIG. 2. TTS master curves and characteristic time scales. Nanoemulsions contain $\phi_o = 0.33$ PDMS droplets with PEG and $C_s = 120$ mM SDS, with (a) and (b) $\langle a \rangle = 34.6$ nm and $\phi_p = 0.33$, (c) and (d) $\langle a \rangle = 31.7$ nm and $\phi_p = 0.36$, and (e) and (f) $\langle a \rangle = 35.4$ nm and $\phi_p = 0.40$. The reference temperature is 15 °C. (See SM [35] for the horizontal and vertical shifting factors.)

for τ_{Br} would include hindered diffusion due to interactions between droplets at the relatively large concentrations studied here. Thus, this choice of τ_{Br} serves as a lower bound such that the actual value of Pe for a fixed shear rate will be larger than we report.

Figures 2(b), 2(d), and 2(f) show the temperature dependence of the relative magnitudes of τ_r and τ_{Br} for the three samples studied. We find that each sample lies in a different limit of these time scales. For the sample depicted in Fig. 2(b), we find that $\tau_r \gg \tau_{Br}$ over the entire temperature range, i.e., the suspension microstructure relaxes significantly faster than the viscoelastic polymer network. Thus, for this sample, $Wi \gg Pe$. For the sample in Fig. 2(d), we see that τ_r and τ_{Br} are of similar magnitude and in fact the two time scales cross over in the measured temperature range so that $Wi \sim Pe$. Finally, for the sample depicted in Fig. 2(f), $\tau_r \ll \tau_{Br}$ over the measured temperature range such that $Wi \ll Pe$. Thus, these three samples are convenient for examining how the relative magnitude and Wi and Pe influence the process of shear-induced clustering and as we will show later help to identify its dominant mechanism. One might expect to be able to probe these different regimes in the same sample by performing measurements at elevated temperatures. However, for all samples studied, the viscoelasticity becomes immeasurable for temperatures larger than 35 °C, preventing a clear quantification of τ_r .

B. Steady shear rheology

To investigate the nonlinear shear rheology, we performed steady shear measurements at temperatures spanning the same range as that for linear viscoelastic measurements. Figure 3(a) shows the steady shear stress and viscosity of the three samples whose linear viscoelasticity is shown in Fig. 2. The polymer concentration and droplet size were previously shown to significantly affect the linear viscoelastic rheology; specifically, the viscoelasticity decreases with increasing droplet size and exhibits a complex nonmonotonic dependence on polymer concentration due to the thermodynamics of polymer-surfactant complexation [25]. In all cases, the material exhibits significant shear thinning over a range of shear rates. At sufficiently low temperatures [e.g., in Fig. 2(a)], this shear thinning resembles a near plateau in the shear stress with increasing shear rate. In some systems, such a plateau is interpreted as reflecting a yield stress in the material. However, given the remarkable collapse of the linear viscoelastic data by time-temperature superposition, we interpret this feature not as a yield stress, but simply as a failure to achieve low enough shear rates to probe the low-shear-rate pseudo-Newtonian regime of the fluid.

In all cases, the material exhibits two distinct regimes of shear thinning. This could be because, in these systems, there are two dominant contributions to the dynamics of the fluid as mentioned earlier, i.e., there will be one time scale for breakage and reformation of the viscoelastic network and another related to the relaxation of the suspension microstructure through Brownian motion. In order to test this hypothesis, we computed the Weissenberg number $Wi = \tau_r \dot{\gamma}$ and the Péclet number $Pe = 6\pi a^3 \eta_m \dot{\gamma} / k_B T$. The steady shear rheology data were then scaled by these dimensionless groups to test their ability to describe the observed regimes of shear thinning. Figure 3 shows the data rescaled by Wi [Figs. 4(a)–4(c)] and Pe [Figs. 4(d) and 4(e)]. To account for a small temperature dependence of the linear elastic modulus, the stress is scaled by the vertical shifting factor b_T from the time-temperature superposition measurements. Furthermore, the steady shear viscosity is scaled by the dimensionless shear rate (for dimensional consistency) and b_T (for the same reason just described).

We find that, for all sample compositions and temperatures, the rheology data for each composition collapse by scaling with Wi for low shear rates corresponding to the first shear thinning regime. This suggests that the initial shear thinning is dominated by the viscoelastic relaxation of the transient network and the nonlinear disruption thereof. However, the data at individual temperatures deviate from this collapse at significantly high shear rates, the onset of which depends on the composition and temperature of the material. In this range of shear rates, the high-shear rheology collapses by scaling with Pe , suggesting that second shear thinning is dominated by disruption of the equilibrium suspension microstructure due to the hydrodynamic interactions between droplets (this will be tested using the SANS measurements to follow). Furthermore, we find that the onset of this collapse of the second shear thinning regime, which occurs at $Pe \sim 0.1$, coincides precisely with the shear rates at

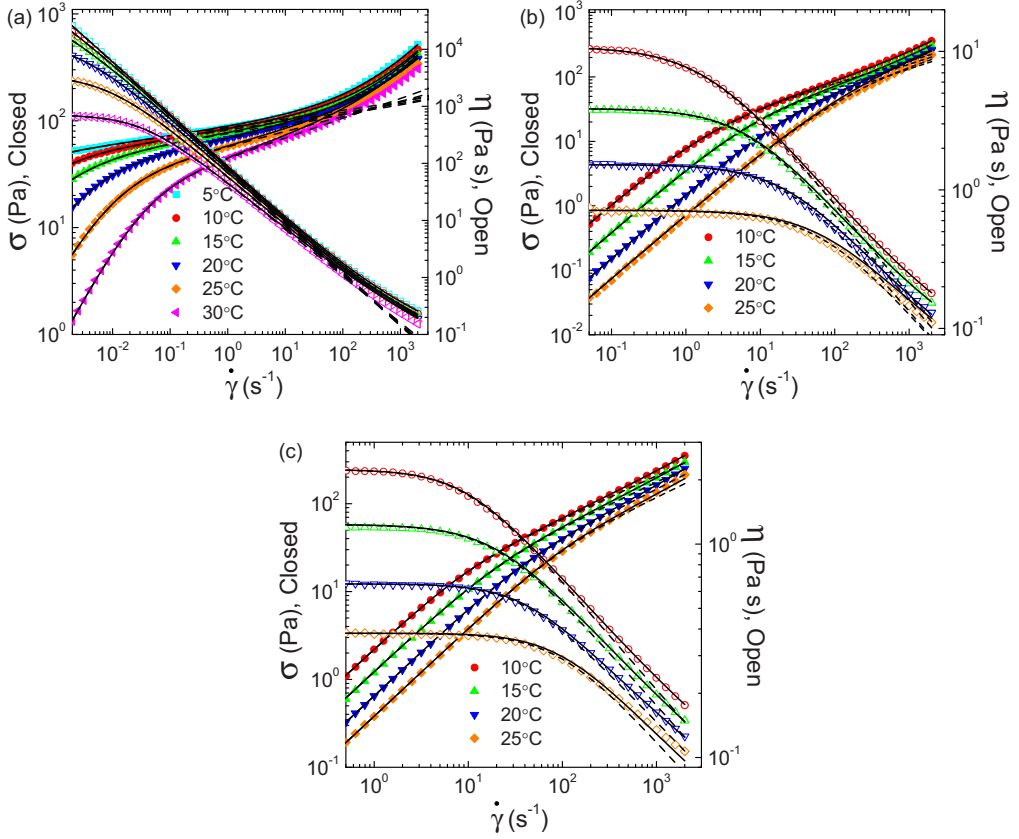


FIG. 3. Steady shear rheology for several nanoemulsions at the indicated temperatures. Nanoemulsions contain $\phi_o = 0.33$ PDMS droplets with PEG and $C_s = 120$ mM SDS, with (a) $\langle a \rangle = 34.6$ nm and $\phi_p = 0.33$, (b) $\langle a \rangle = 31.7$ nm and $\phi_p = 0.36$, and (c) $\langle a \rangle = 35.4$ nm and $\phi_p = 0.40$. Dashed lines represent the Carreau-Yasuda model fitting at low shear rates and solid lines represent the fitting result proposed by the perturbation model (4).

which the steady shear rheology begins to deviate from the Wi scaling of the low-shear-rate rheology [Fig. 4(a)].

It is surprising to find that the collapse of these two shear thinning regimes, one at low shear rates with Wi and one at high shear rates with Pe, occurs regardless of whether $Wi \gg Pe$, $Wi \sim Pe$, or $Wi < Pe$. Note, however, that for samples corresponding to the latter two cases [i.e., Figs. 4(c) and 4(f)] the Pe scaling of the steady shear rheology begins to become inadequate to collapse the data at high shear rates. We anticipate that this is due to the emergence of a new limiting behavior when $Wi < Pe$. This hypothesis will be further tested using the perturbative rheological model to follow.

C. Shear-induced microstructure

To further understand how these phenomena relate to the shear-induced structuring of the polymer-colloid mixture, we performed flow-SANS measurements in a Taylor-Couette geometry both in the 1-3 (flow-vorticity) and 1-2 (flow-gradient) projections. The measurements are performed under contrast-matched conditions for the polymer such that only the suspension microstructure is observed. Figure 5(a) shows reduced 2D-flow SANS patterns with heat plots of the absolute intensity for both shear planes at various values of Pe for the sample with $Wi \gg Pe$. In order to emphasize

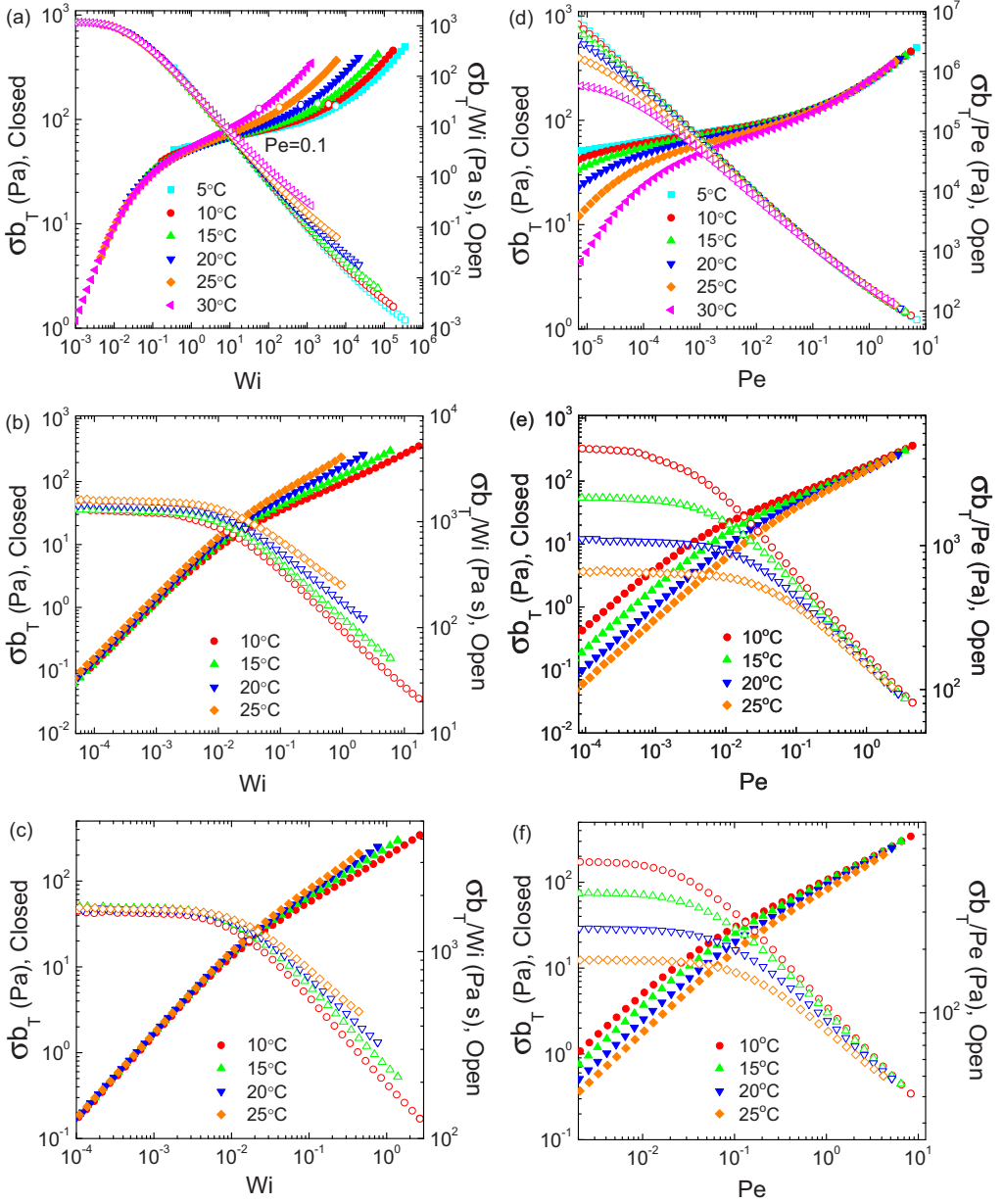


FIG. 4. Scaled steady shear rheology. (a)–(c) Weissenberg number scaling. (d)–(f) Péclet number scaling. Nanoemulsions contain $\phi_o = 0.33$ PDMS droplets with PEG and $C_s = 120$ mM SDS. (a) and (d) $\langle a \rangle = 34.6$ nm and $\phi_p = 0.33$. (b) and (e) $\langle a \rangle = 31.7$ nm and $\phi_p = 0.36$. (c) and (f) $\langle a \rangle = 35.4$ nm and $\phi_p = 0.40$.

the effect of shear on the suspension microstructure, we also show a representation of the scattering in which the absolute scattering intensity at zero shear rate is subtracted from the data [Fig. 5(b)].

At vanishingly small Péclet number ($Pe = 6.88 \times 10^{-5}$), the two-dimensional (2D) SANS patterns exhibit isotropic scattering, with a correlation peak at $q = 0.015 \text{ \AA}^{-1}$ due to droplet-droplet correlations in the suspension microstructure. We note that this correlation peak is diminished in the 1-2 plane measurements, possibly due to the corrupting effects of multiple scattering, which are

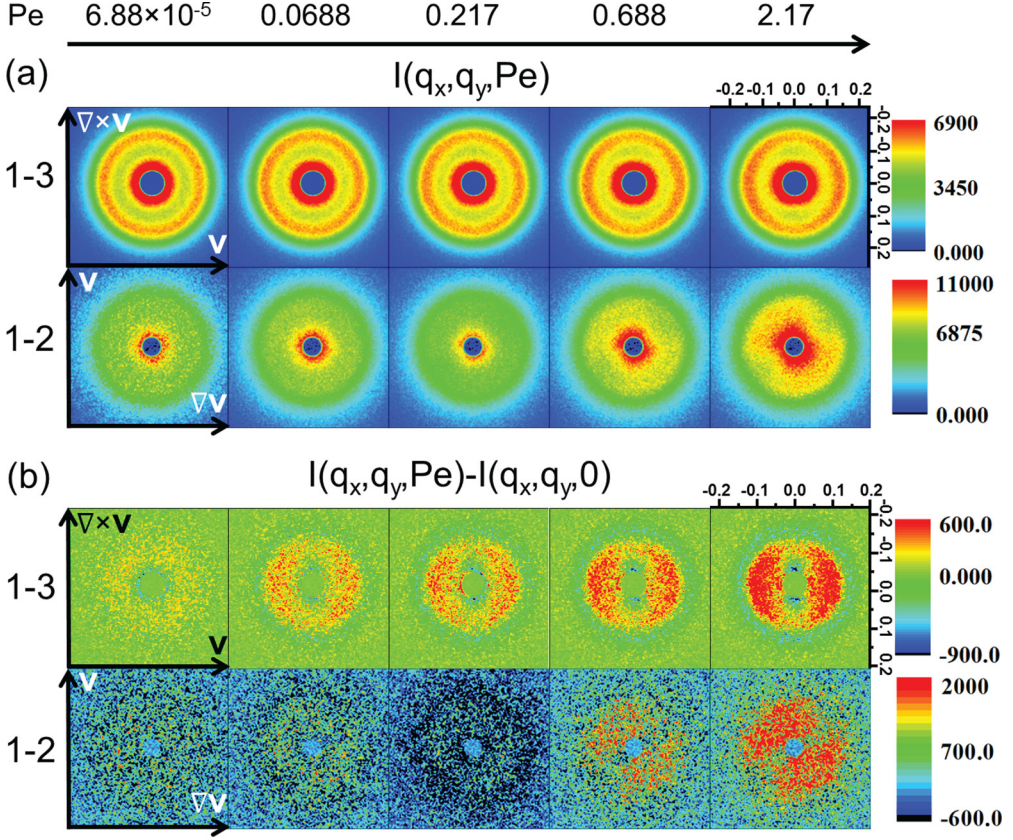


FIG. 5. 2D flow-SANS scattering patterns showing heat plots of absolute intensity (a) before and (b) after subtracting the intensity at zero shear rate in both 1-3 (flow-vorticity) and 1-2 (flow-gradient) planes at the Péclet numbers indicated. Data are for the nanoemulsion containing $\phi_o = 0.33$ PDMS droplets ($\langle a \rangle = 34.6$ nm) with $\phi_p = 0.33$ PEG and $C_s = 120$ mM SDS. Scale tick labels represent values of q_x and q_y in nm^{-1} and the color intensity scales represent the absolute scattering intensity in cm^{-1} .

enhanced by the longer sample path length. Nevertheless, the scattering at vanishingly small shear rates is consistent with a concentrated dispersion of nonaggregated droplets interacting primarily through repulsive (excluded volume and electrostatic) interactions, in agreement with previous work on these materials [25].

At $Pe \sim 1$, we find that the fluid develops a so-called butterfly scattering pattern, i.e., an anisotropic scattering pattern with lobes of excess scattering oriented along a preferred direction. The degree of anisotropy appears to increase with increasing Pe . We note that the q values associated with the observed anisotropy in the scattering patterns encompass a range of $0.15 < qa/2\pi < 0.65$ such that we can associate it with pairs or small groups of suspended particles. This is different from previous scattering studies that were performed at much smaller q values [3,26] and will be important in the interpretation of the data to follow.

In the 1-3 (flow-vorticity) plane, the excess scattering is oriented along the flow direction, suggesting that there is an excess of particle pairs along the vorticity direction. In the 1-2 (flow-gradient) plane, we also find butterfly scattering, however with lobes of excess scattering oriented along the extensional axis of shear (i.e., at 45° with respect to the flow direction). This suggests that there is also an excess of particle pairs oriented along the compressional axis of deformation. As further proof of this anisotropy in the 1-2 plane, we confirmed that the flow-induced anisotropy

is reversible with respect to the direction of the shear (see SM [35]). We note that the droplets are essentially undeformable under the measurement conditions due to the small dimension of the droplets, i.e., the estimated maximum capillary number at the highest shear rates probed is less than 10^{-4} [39]. Thus, it is highly unlikely that the observed scattering anisotropy is caused by the deformability of individual droplets.

The observed anisotropy indicates shear-induced clustering in the fluid, consistent with previous observations of Brownian suspensions in viscoelastic liquids [7,8]. However, we note that our measurements, which include measurements in all of the orthogonal directions (flow, gradient, and vorticity), suggest a clustered microstructure that is qualitatively different from what was inferred from previous studies of scattering in the 1-3 (flow-vorticity) plane alone at smaller q values [3,26]. Specifically, those studies hypothesized the formation of chains of particles whose long dimension is oriented along the vorticity axis. However, our measurements show that this clearly cannot be the case for the present materials, since the scattering indicates preferred orientation of particle pairs along both the vorticity (in the 1-3 projection) and compressional (in the 1-2 projection) axes of flow. Our studies therefore highlight the need for structural measurements in multiple shear projections and suggest that the mechanism for shear-induced clustering (at least in the present fluids) is different from what was hypothesized based on measurements in the 1-3 plane alone.

To further understand the anisotropic structure under shear, we compute the anisotropy factor [40], given by

$$A_f(q) = -\frac{\int_0^{2\pi} I(q, \phi) \cos[2(\phi - \phi_0)] d\phi}{\int_0^{2\pi} I(q, \phi) d\phi}. \quad (1)$$

To perform this calculation, we use an annular average of the 2D scattering intensity $I(q, \phi)$ with an average q value of $0.007 \text{ \AA}^{-1}$ and Δq of $0.004 \text{ \AA}^{-1}$ for both scattering projections. This particular q range corresponds to the location of the maximum intensity in the butterfly pattern. In Eq. (1) the weighting term $\cos[2(\phi - \phi_0)]$ assumes twofold symmetry of the scattering pattern and accounts for the possibility of average orientation away from the flow direction along an angle ϕ_0 , which may be different in the different flow projections. In order to account for any nonuniformities in the neutron detector, the value of A_f measured at rest was subtracted from each data set so that $A_f = 0$ corresponds to isotropic structures and A_f increases with increasing degree of anisotropy.

Figure 6(a) shows values for A_f across all samples and shear rates measured, including the projections in both the 1-2 and 1-3 planes of shear. From this we find that the anisotropy factor increases systematically with increasing shear rate, but to a different extent depending upon the sample. However, due to the differences in composition, temperature, and particle size, the samples also have widely varying values of the characteristic time scales τ_r and τ_{Br} . Therefore, to test whether these data collapse considering the characteristic time scales of the fluid, we rescaled the data by Pe . We find that all of the data nearly collapse onto a single master curve over two decades in the Péclet number [Fig. 6(b)], whereas scaling of the shear rate by Wi does not collapse the data. We note that this plot includes data from both projections of the structure and values of the viscoelastic relaxation time τ_r spanning four orders of magnitude. In all cases, the anisotropy factor is immeasurably small until $Pe \sim 0.1$ and increases with increasing Pe thereafter. Interestingly, this threshold value of $Pe \sim 0.1$ for the onset of anisotropy is quantitatively similar to that for the onset of the second shear thinning regime in steady shear rheology.

These results suggest that hydrodynamic interactions between suspended particles, and not viscoelasticity of the polymer network, dominate the formation of anisotropic cluster structure. Interestingly, we furthermore find that the anisotropy factor follows a power law at high Pe , with $A_f \sim Pe^{0.34 \pm 0.026}$. This suggests that, at length scales corresponding to individual particles, the average degree of anisotropy of particle pairs increases according to the strength of interparticle hydrodynamic interactions.

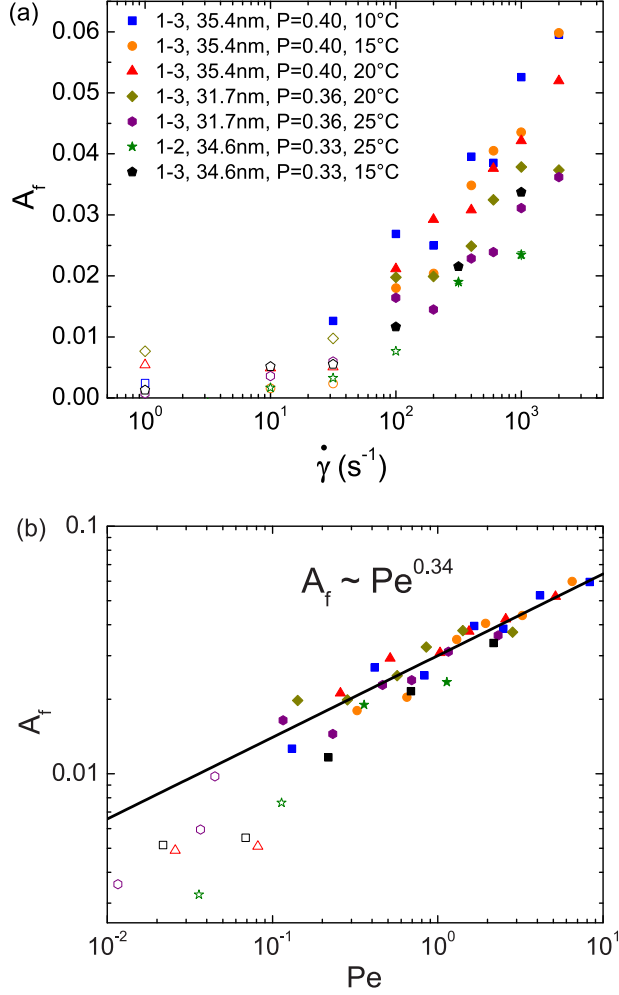


FIG. 6. Anisotropy factors as a function of (a) shear rate and (b) Pe with power-law scaling. The power-law exponent is 0.34 ± 0.026 . Legend represents scattering plane, average radius of droplets, concentration of polymer, and temperatures. Open symbols represent values that represent unresolvable anisotropy.

IV. DISCUSSION

We have presented rheology and flow-SANS measurements to understand the mechanism of shear-induced clustering of nanoparticles in viscoelastic polymer-colloid mixtures and its dependence on the characteristic time scales of viscoelasticity and Brownian motion. In all the dynamical limits we study (i.e., $Wi \gg Pe$, $Wi \sim Pe$, and $Wi < Pe$), our thermoresponsive nanoemulsions exhibit two regimes of shear thinning: one at low shear rates where the rheology collapses by scaling with Wi and one at high shear rates where the rheology collapses by scaling with Pe . The transition between these regimes occurs when $Pe \sim O(0.1)$. Furthermore, we find evidence of shear-induced clustering, in which anisotropic butterfly scattering develops in both the 1-3 and 1-2 shear planes for $Pe > 0.1$, with a degree of alignment that scales as $A_f \sim Pe^{0.34 \pm 0.026}$. Most significantly, the average projected orientation of the local clustering lies along both the vorticity (in the 1-3 plane) and the compressional (in the 1-2 plane) directions of shear. This is significantly different from what was hypothesized in previous studies on similar systems, where complete vorticity alignment

was inferred from measurements in the 1-3 plane [7,8]. Interestingly, Eberle *et. al.* showed similar anisotropic scattering in colloidal gels in Newtonian fluids that are aggregated at rest, where the shear stress was found to scale with the degree of anisotropy of particle clusters [41]. However, since our fluids are not significantly aggregated and do not possess a yield stress, it is impossible to directly compare the results. Nevertheless, it is remarkable that we find that both the rheology and shear-induced anisotropy exhibit the same scaling, regardless of the relative magnitudes of Wi and Pe . Combined with the fact that the anisotropy is dominated by scaling with Pe , this strongly suggests that hydrodynamic interactions, which act to deform the suspension microstructure from its equilibrium state, are primarily responsible for shear-induced clustering in the system.

We rationalize these results by analogy to the shear-induced structure and rheology of Brownian suspensions in Newtonian fluids. Specifically, Wagner and Ackerson showed that the Brownian and hydrodynamic contributions to the stress for creeping flows are proportional to the degree of anisotropy of particle pairs through a spherical harmonic expansion of the nonequilibrium suspension microstructure [37]. For suspensions in Newtonian fluids, it follows that the shear stress scales as a power law with respect to Pe . More recently, this analysis was found to explain how the emergence of hydrodynamically induced clusters at high Pe served as the basis for shear thickening of model near hard-sphere suspensions [42]. Therefore, by analogy one might expect the effect of anisotropic suspension microstructure and clustering on the total stress in a non-Newtonian suspending fluid should arise from a contribution through the Brownian and hydrodynamic suspension stress, proportional to the degree of anisotropy, which in this case also follows a power-law behavior with respect to Pe . What is not known, however, is the degree to which the non-Newtonian behavior of the suspending fluid affects this contribution.

There are three contributions to the total stress affected by the non-Newtonian behavior of the suspending fluid: (i) the viscoelastic shear thinning of the polymer network stress due to the combined shearing flow and disturbance flow around the equilibrium suspension microstructure, (ii) the effect of non-Newtonian viscosity on particle-particle hydrodynamic interactions (which drive the deformation of the suspension microstructure), and (iii) the effect of deformation of the suspension microstructure on the shear thinning of the fluid. Since our experiments are performed mostly in a regime where $Wi \gg 1$, the shear thinning will contribute negligibly to the background viscosity of the suspending medium in this limit. Therefore, we anticipate that (iii) will be vanishingly small and so the primary effect of suspension anisotropy on the total stress will be due to interparticle hydrodynamic forces (ii). Furthermore, for $Pe \sim O(1)$, we expect that (ii) will be non-negligible, but still small relative to (i).

We therefore hypothesize that the total stress in the limit of $Pe \sim O(1)$ can be captured by a modification of the viscoelastic polymer stress that includes a small correction term due to the suspension anisotropy and its associated dependence on Pe :

$$\sigma_{\text{total}}(\dot{\gamma}) = \sigma_{\text{viscoelastic}}(\dot{\gamma})(1 + cPe^x), \quad (2)$$

where $\sigma_{\text{viscoelastic}}(\dot{\gamma})$ corresponds to (i), the viscoelastic polymer network contribution to the total stress (which includes both linear and nonlinear features). Equation (2) is expected to be approximately valid only in the case where the characteristic relaxation time scales for the viscoelastic and suspension hydrodynamic contributions to the total fluid stress are well separated and the perturbative stress due to the suspension anisotropy is small compared to the background viscoelastic stress. The coefficient c is such that $c > 0$ corresponds to a shear thickening contribution of (ii) and $c < 0$ corresponds to a shear-thinning contribution of (ii). We already see that, because the shear thinning exponent for $Pe > 1$ is larger than that for $Pe < 1$ (Fig. 4), the coefficient c is positive and therefore the suspension anisotropy exerts a shear thickening response on the fluid. We recall that Brownian particles in a Newtonian suspending medium also exhibit a shear thickening contribution to the stress [24]. It is interesting to note that, in the case of a Newtonian suspending medium, the critical shear rates for the onset of shear thickening in the hydrodynamic stress are typically when $Pe \sim 1$ [43], which is similar to where we find the onset of anisotropic clustering. This suggests that

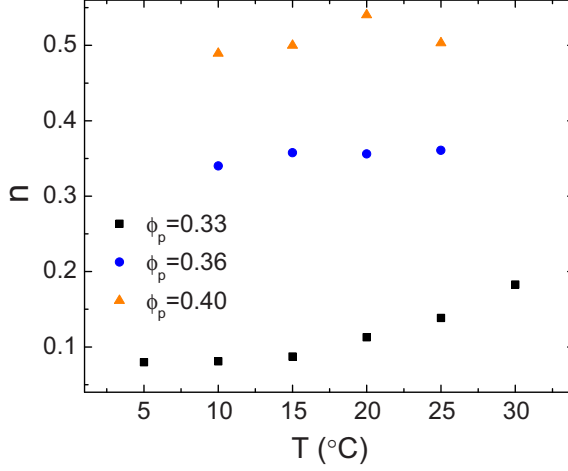


FIG. 7. Temperature dependence of the Carreau-Yasuda power-law slope for the samples indicated, obtained by fits to shear rates in the low-Wi regime.

the contribution of suspension hydrodynamics to structuring and bulk rheology for suspensions in viscoelastic fluids at high Wi may be similar to that for suspensions in Newtonian fluids.

We test the applicability of Eq. (2) by applying it to the steady shear rheology of the system (Fig. 3). We note that the intent here is not to devise a wholly accurate model for the rheology of the system, but rather to test whether the rheological behavior of the system at moderate Pe can be explained by a consistent underlying behavior, and that the mechanism for the behavior is consistent with the observed anisotropic clustering of the suspension. As such, since we do not currently have a detailed constitutive model for $\sigma_{\text{viscoelastic}}(\dot{\gamma})$ for the system under study, we empirically capture the viscoelastic shear thinning (i.e., the shear thinning regime at low shear rates) of the polymer network by fitting the rheological data at $\text{Pe} \ll 1$ to the Carreau-Yasuda model

$$\sigma_{\text{viscoelastic}}(\dot{\gamma}) = \left[\eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{\{1 + (\lambda\dot{\gamma})^b\}^{1-n/b}} \right] \dot{\gamma}. \quad (3)$$

The zero shear rate viscosity η_0 is treated as an adjustable parameter and we further assume that the high-shear viscosity η_{∞} at an infinite shear rate is the viscosity of water due to the limited range of shear rates in this initial shear thinning regime. Here $1/\lambda$ is the critical shear rate at which viscosity begins to decrease and n is the asymptotic power-law slope for shear thinning at large shear rates (but still small Pe). The parameter b sets the width of the transition region between η_0 and the power-law regime.

To fit this initial shear thinning, we only use the shear rates corresponding to $\text{Pe} < 0.01$, where presumably the hydrodynamic interactions between droplets is insufficient to produce a nonequilibrium suspension stress. The corresponding fits to the Carreau-Yasuda model are presented in Fig. 2 as the dashed lines. From this fitting, we find that the power-law slope n increases monotonically with increasing temperature (Fig. 7) and this dependence becomes more significant at relatively small polymer concentrations and large temperatures. In previous work we showed that the time scale for the transient network decreases with increasing polymer concentration and temperature at fixed surfactant concentration [25].

As expected, we find that the Carreau-Yasuda model cannot describe the second regime of shear thinning that occurs in the limit of $\text{Wi} \gg \text{Pe}$ and $\text{Pe} \sim O(1)$ (Fig. 3, dotted lines). Instead, we fit the empirical asymptotic relationship given by Eq. (2). To do so, we first attempt to extract the perturbative stress contribution arising from hydrodynamic interactions between droplets, i.e., $\sigma_{\text{total}}(\dot{\gamma})/\sigma_{\text{viscoelastic}}(\dot{\gamma}) - 1 = c\text{Pe}^x$. The results are shown in Fig. 8. As hypothesized, we find that the

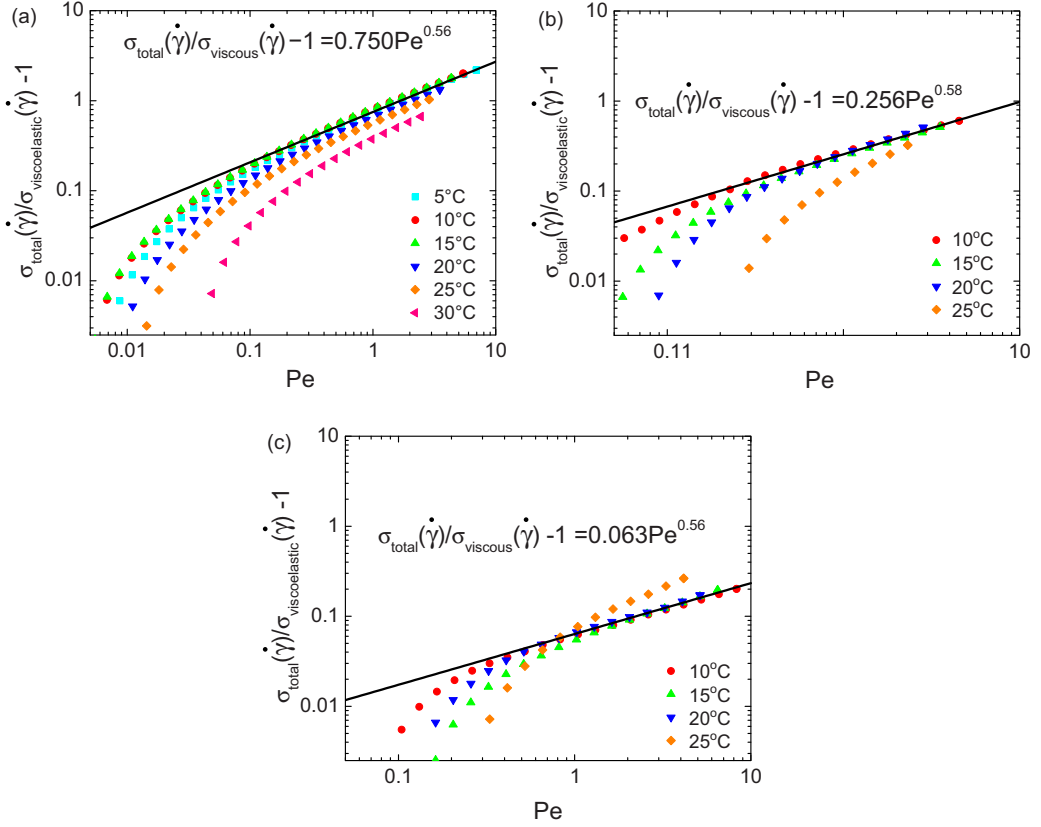


FIG. 8. $\sigma_{\text{total}}(\dot{\gamma})/\sigma_{\text{viscoelastic}}(\dot{\gamma}) - 1$ as a function of Pe for the nanoemulsions containing (a) $\phi_p = 0.33$, (b) $\phi_p = 0.36$, and (c) $\phi_p = 0.40$.

proposed equation (2) collapses nearly all of the experimental data at sufficiently high Pe , suggesting that the second regime of shear thinning can indeed be captured by an extra contribution involving Pe alone. A notable exception is the data at relatively high temperatures. However, as discussed previously, these temperatures correspond to relatively short values of τ_r such that the asymptotic approximation $Wi > Pe$ will be invalid for these conditions.

In the region of data collapse in Fig. 8, we find that all of the data, regardless of polymer concentration, exhibit power-law behavior as anticipated by Eq. (2). We further assume that the scaling exponent x is independent of the details of the material and that c depends only on the composition (and not the temperature). A global fit of the power-law exponent x to all of the data results in an exponent $x = 0.57 \pm 0.011$ at high shear rate ($Pe > 1$). The values of the coefficient c are fit to each distinct sample composition, from which we find values of c ranging from 0.06 to 0.75. Since c is always positive, we see that the hydrodynamic interactions produce a shear thickening contribution to the overall shear thinning of the fluid.

From these results, we expect that the rheology of Brownian suspensions in viscoelastic fluids in the limit of $Wi > Pe$ and $Pe \sim O(1)$ can be adequately described by Eq. (2). To test this, we combine fits of the first shear thinning regime using the Carreau-Yasuda model (3) with the additional power-law correction due to hydrodynamic interactions at moderate Péclet number,

$$\sigma_{\text{total}}(\dot{\gamma}) = \sigma_{\text{viscoelastic}}(\dot{\gamma})(1 + cPe^x) = \left[\eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{\{1 + (\lambda\dot{\gamma})^b\}^{1-n/b}} \right] \dot{\gamma}(1 + cPe^x), \quad (4)$$

where all of the model parameters are now fixed as described above. The resulting comparisons to the steady-state shear stress and viscosity data (with no adjustable parameters) are represented by the solid lines in Fig. 3. We find excellent quantitative agreement between the model and experimental data, except for at relatively high temperatures (and correspondingly short τ_r) when $Wi < Pe$, where modest deviations are observed at sufficiently high shear rates. Presumably, this is due to the failure of the limit $Wi > Pe$ assumed in the model. We thus conclude that the proposed empirical correction term is successful at capturing the additional contribution of hydrodynamic interactions on the total fluid stress when Wi is sufficiently large compared to Pe .

Having established the effect of shear-induced clustering on the macroscopic rheology of the fluid, we turn our attention to the microscopic mechanism of clustering in the limit where $Wi \gg Pe$. Again, due to the negligible influence of the shear thinning on interparticle hydrodynamic forces in this limit, we draw analogy to the shear-induced microstructure of Brownian suspensions in Newtonian fluids. We find that our SANS results are qualitatively similar to Stokesian dynamics simulations of the pair-probability distribution in flow-gradient and flow-vorticity planes for suspensions in Newtonian fluids [44,45]. Specifically, at sufficiently high Péclet number, deformation of the suspension microstructure away from equilibrium results in anisotropic hydrodynamic forces. Initially, this results in a shear thinning contribution to the shear stress, which saturates at moderate Pe . In the present experiments, we hypothesize that this shear thinning of the suspension stress is very small compared to the polymeric stress at the corresponding shear rates and so it will have a minor contribution to the viscoelastic shear stress fit by Eq. (3). At higher Pe , however, the contribution of short-range hydrodynamic forces on the microstructure becomes dominant due to the very thin boundary layer of the nearest-neighbor particles [45]. This results in excess and depleted particle fluxes along the compressional and extensional axes, respectively, as the Brownian forces attempt to restore particles to their equilibrium configuration. As such, one would expect to observe anisotropic scattering in the 1-2 plane indicating the shear-induced clustering oriented along the compressional axes, which is precisely what we find in the present system involving Brownian suspensions in viscoelastic liquids. Note that this discussion ignores frictional forces between particles in contact as well as elastohydrodynamic deformation of particles, which are known to play a significant role in shear thickening at sufficiently high shear rates [46,47]. However, we believe such effects to be negligibly small in the present system, since in the former case the oil-water interface is molecularly smooth and contact would cause coalescence of nanodroplets, and in the latter case the capillary number, which sets the relative deformation of droplets [48], is less than 10^{-4} for all conditions studied.

From this discussion, we hypothesize that the excess of particle fluxes along the compressional and vorticity axes due to short-range hydrodynamic forces gives rise to the shear-induced clustering in our Brownian suspensions in viscoelastic fluids when $Wi > Pe$. This is corroborated by the collapse of the scattering anisotropy in both shear projections as well as the high-shear rate rheology by scaling with Pe . It is also corroborated by the fact that clustering in the present system produces a shear-thickening contribution to the total shear stress, similar to the formation of so-called hydroclusters observed at large Pe for suspensions in Newtonian fluids [49,50]. However, it is interesting to find that, in these viscoelastic fluids, a shear thickening contribution to the stress is found even when $Pe \sim O(0.1)$, which is significantly smaller than that typically predicted and observed for the continuous shear thickening of Brownian suspensions in Newtonian fluids [42,45]. One possible explanation is the choice of the single-particle self-diffusivity as a choice for τ_{Br} , which underestimates the Péclet number.

V. CONCLUSION

We identified the relationship between rheology and microstructure for nonaggregating, viscoelastic, and Brownian suspensions in associative polymer solutions. The steady shear behavior is governed by two competing time scales: the relaxation time of the transient network (and associated shear rate scale Wi) and the time scale for the Brownian motion (and associated shear rate scale Pe). The present work covers several limits including $Wi \gg Pe$, $Wi \sim Pe$, and $Wi < Pe$.

Remarkably, the same qualitative behavior is observed in all of these limits. At low Pe , where interparticle hydrodynamic interactions are negligible, the shear thinning of the fluid is dominated by polymer viscoelasticity, which is collapsed by Wi . At $Pe > 0.1$, however, the steady shear rheology is collapsed by Pe due to suspension hydrodynamic contributions to the stress. In this regime, rheo-SANS measurements reveal that anisotropic scattering patterns develop and become enhanced with increasing Pe in both the flow-vorticity (1-3) and flow-gradient (1-2) planes. The orientation of the anisotropic scattering indicates concentration fluctuations oriented along both the vorticity and compressional axes of shear. The degree of anisotropy over a wide range of material parameters and shear rates collapse onto a master curve, which follows a scaling of $A_f \sim Pe^{1/3}$. Here we have reported such a power-law scaling of pair correlation anisotropy with Péclet number in polymer-colloid mixtures. From this, we proposed and validated a simple empirical model to capture the steady shear rheology of the fluid, in which the clustering of particles imparts a perturbative contribution to the shear stress that modifies the underlying viscoelastic shear stress. We found that this clustering contribution to the shear stress is shear thickening, which is reminiscent of the hydrocluster-driven shear thickening of suspensions in Newtonian fluids, but occurs at significantly smaller Pe .

Our results provide clear evidence for the role of interparticle hydrodynamic interactions in the formation of anisotropic particle clusters in viscoelastic fluids and that this clustering is responsible for modified shear thinning at high Pe . The influence of hydrodynamic interactions also suggests the possibility that the clusters may in fact be dynamic structures, rather than the persistent chains inferred from previous measurements. However, we caution that it is unknown whether the structures and interactions identified here also dominate in viscoelastic fluids other than associative polymer-colloid networks (such as entangled solutions with negligible polymer-colloid interactions). Nevertheless, our results highlight the importance of using simultaneous structural and rheological measurements, and fully-three-dimensionally-resolved structural measurements in particular, to elucidate the mechanisms of shear-induced clustering of suspensions in non-Newtonian fluids. We note that the rheological description of the system in terms of viscoelastic and hydrodynamic stresses proposed here is merely an attempt to capture the dominant physics of clustering and hope that our work will motivate further theoretical modeling of nondilute suspension microstructure in viscoelastic liquids where polymeric, Brownian, and hydrodynamic contributions all contribute to the behavior of the fluid. Ultimately, such studies should provide a more rational basis to control the rheology and microstructure of polymer-colloid mixtures.

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