

Rheology and yielding of charged vesicle gels: Experiments and simulations

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The behavior of charged vesicle suspensions, commonly encountered in biological and industrial contexts, is largely governed by screened electrostatic repulsions. However, the addition of depletants such as polymers can induce attractive interactions and lead to gel formation. Here, we investigate the rheology and yielding behavior of such a vesicle gel, relevant to a class of consumer products. The combination of experiments and Brownian dynamics simulations enables us to establish connections between macroscopic rheology and microstructural features. Oscillatory tests reveal a predominantly elastic response at small deformations, followed by yielding upon increasing the strain amplitude. With increasing shear rate, the flow curves feature a yield stress regime, followed by shear thinning and, eventually, a Newtonian-like response (viscosity plateau). We find that, in both oscillatory and shear-rate-controlled tests, the yielding transition is accompanied by nonmonotonic trends in structural heterogeneity. Fitting the flow curves with the recently introduced three-component model reveals that structural heterogeneity peaks near the crossover from the yield stress plateau to shear thinning, while homogeneity is recovered in the Newtonian-like regime. Numerical creep tests exhibit rich phenomenology, including Andrade-like deformation, delayed yielding, and resolidification, whose persistence even above the dynamic yield stress highlights the ductile nature of gels with competing attractive and repulsive interactions. Overall, our study highlights distinctive rheological and structural features of gels with competing attractive and repulsive interactions, providing insight into how microscopic heterogeneity controls yielding and flow.

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I. INTRODUCTION

Vesicles or liposomes are particles consisting of a liquid enclosed by self-assembled lipid bilayers [1,2]. They are widespread in nature and in biological fluids, especially in the cellular and extracellular environment [1]. Artificial vesicles are also massively exploited in technological and industrial applications, including drug release and vaccines [1,3,4]. For instance, aqueous suspensions of charged vesicles with added salts are at the base of many consumer goods, a popular example being liquid fabric softeners (LFS) [5,6]. As a matter of fact, the production process of LFS is well representative of the diverse behaviors exhibited by charged vesicle suspensions. Typically, an initial stage of the production of LFS is the so-called *white base*, where cationic spherical vesicles are simply suspended in water with an anionic salt [5–10]. The salt partially screens the vesicle charge leading to a (repulsive) electrostatic double layer (EDL) interaction, whose strength and range depend on salt concentration [11]. It has been recently shown, through Brownian dynamics (BD) simulations, that these systems tend to form Wigner glasses at

progressively smaller vesicle volume fraction on decreasing the anionic salt concentration (i.e., with increasing the EDL range and strength) [7]. Similar glassy behavior has recently been reported in ultrasoft charged colloids [12]. Interestingly, in vesicle suspensions, interaction ranges as small as a few percent of the particle diameter are sufficient to produce significant differences with respect to the hard-sphere case, which may explain some intriguing features of the white base behavior [7,10]. At a later stage of LFS production, nonabsorbing polymers are added to the white base to promote (attractive) depletion interactions, which compete with the EDL repulsion and, in an appropriate range of vesicle and polymer concentrations, can lead to gelation [8,13,14]. Hence, the onset of a vesicle network opens the way to use it as a scaffold to incorporate a variety of further ingredients (e.g., dyes and perfume capsules), keeping them quite homogeneously distributed across the sample. Of course, there are several critical issues related to the rheological properties, aging, and shelf life of these vesicle systems with a range of ensuing failures, such as phase separation, gel collapse, and cracks [8]. A fine control of the mechanical and dynamic properties of those materials is crucial to prevent the above-mentioned failures. Needless to say, smart and reliable numerical models that may complement experiments are highly on demand.

Depletion-induced gelation is commonly ascribed to an arrested phase separation mechanism [15–17]. Briefly, short-range attractions initially drive the dispersion to demix into two domains—a particle-rich and a particle-poor region—separated by a single interface. However, the particle-rich

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domain becomes dynamically arrested before phase separation is completed, freezing the system into a nonequilibrium, particle-rich network lying in a particle-poor background. Thermal fluctuations are typically strong enough to break and reform interparticle bonds, allowing the network to slowly rearrange over time. Previous studies on depletion gels focused on systems where the interactions are purely attractive apart from a hard-core repulsion, as modeled by the Asakura-Oosawa-Vrij (AOV) or Morse potential [16,18,19]. Popular experimental models of these *standard depletion gels* include suspensions of sterically stabilized poly(methyl methacrylate) or silica beads in liquid solvent with nonadsorbing polymers or micelles as depletants [16,18,20–26]. On the other hand, less attention has been devoted so far to gels formed in the presence of depletion attraction and EDL repulsion with comparable effective ranges. In fact, the competition between these forces can alter several gel properties, such as network morphology, stress transmission, and relaxation pathways, potentially leading to responses that differ qualitatively from those observed in standard depletion gels with purely attractive interactions.

In this paper, we contribute to filling this gap through a combined experimental and numerical study of the rheology of charged vesicle gels, with a perspective on the underlying structural features. The investigated experimental system is directly relevant for current industrial production of LFS. Our BD simulations have been designed to closely mimic experiments, accounting for both EDL repulsion and depletion attraction that characterize our vesicle suspension.

The paper is organized as follows. The experimental system and the simulated model are described in Secs. II A and II B, respectively, together with the performed tests and other methodological details. In Sec. III A, we begin our presentation of results with oscillatory rheology tests, both frequency- and amplitude-sweep measurements. Shear-rate-controlled tests, including flow curves, are discussed in Sec. III B. In Sec. III C, we illustrate results of numerical creep (stress-controlled) tests and compare the emerging scenario with that obtained under shear-rate-controlled conditions. Some closing remarks and outlooks are provided in Sec. IV.

II. MATERIALS AND METHODS

A. Experiments

1. Investigated system

The investigated samples consist of charged, polydisperse vesicles of mean radius $R = 150$ nm, suspended into a solution of water, salt, and polymer molecules. Initially, a 13% w/w aqueous dispersion of vesicles of a double-tailed cationic surfactant (diethylesterdimethyl ammonium chloride, diC18:0 DEEDMAC, mol wt = 697.5), in the presence of 450 ppm of calcium chloride, is prepared according to an extrusion process with an apparatus similar to the one described by Corominas *et al.* [27]. This mother dispersion is then isotonicly diluted in water down to 11% and 4% w/w of surfactant concentration to obtain the above-mentioned WBs. These samples correspond to vesicle volume fractions of $\phi = 0.55$ and $\phi = 0.40$, respectively, as measured according to the method described by Seth *et al.* [28]. Direct force

measurements demonstrated that vesicles in WBs interact through a purely repulsive, EDL potential [11,29] (see Sec. II B 1 for details on the interaction parameters). We further induce depletion attractions by adding a concentration $c_p = 1.6\%$ w/w of nonadsorbing linear polymer chains of polyacrylamide, with molecular weight $M_w = 150\,000$ g/mol and radius of gyration $R_g = 40$ nm. With these parameters, a rough estimation of the characteristic energy scale and range of the depletion interaction are $U_{\text{dep}}(2R) \simeq -15k_B T$ and $\xi = 2(R + R_g) = 380$ nm, respectively, as computed within the framework of the AOV model of depletion interaction [30].

2. Rheological tests

Rheological tests are conducted at strain-controlled conditions, employing an Anton-Paar MCR302 rheometer with cone-plate geometry (50 mm and 0.01 rad angle). All experiments are carried out at $T = 20^\circ\text{C}$ using a Peltier system, while a solvent trap is utilized to prevent solvent evaporation during the measurements. The sample is loaded onto the rheometer plate, and a preshear of 1000 s^{-1} is applied to eliminate any residual stresses. Before starting any rheological test, a waiting time of about 1 min is adopted to allow for gel formation.

Frequency sweeps are performed at an amplitude of $\gamma_0 = 0.5\%$, with the frequency ramped down over an interval $\omega \in [0.1, 100]$ rad/s. Downward amplitude sweeps are carried out at a constant frequency of 1 rad/s for deformation amplitude γ_0 ranging in $[0.2\%, 500\%]$. The reported values of the viscoelastic moduli are measured after the attainment of a steady state.

In constant shear rate tests, the steady-state stress in response to distinct shear rates is measured to obtain the flow curves. The shear rate range is ramped down over an interval $\dot{\gamma} \in [0.001, 1000]\text{ s}^{-1}$.

B. Simulations

1. Numerical model

We perform BD simulations, by solving the Langevin equation in the inertialess limit, for polydisperse and neutrally buoyant beads immersed in a Newtonian solvent with viscosity η_s equal to that of water. The temperature and the particle volume fractions are the same as measured in the experiments ($T = 20^\circ\text{C}$, $\phi = 0.55$ and $\phi = 0.4$). Particle radii are generated according to a Gaussian distribution with mean equal to the experimental value $R = 150$ nm and a 7% variance. This polydispersity was introduced with the purpose of preventing crystallization [19]. Pair particle interaction $U(r)$ is described by the sum of two distinct contributions, i.e., $U(r) = U_{\text{EDL}}(r) + U_M(r)$, where U_{EDL} is the EDL potential, accounting for screened electrostatic repulsion, and U_M is the Morse potential, accounting for both an excluded-volume/hard-sphere-like repulsion and an attractive (depletionlike) interaction at separation slightly larger than the particle diameter. We adopt a superposition of an EDL and a Morse term, rather than a single effective potential, because the EDL contribution can be directly linked to independent experimental measurements on closely related vesicle systems [11].

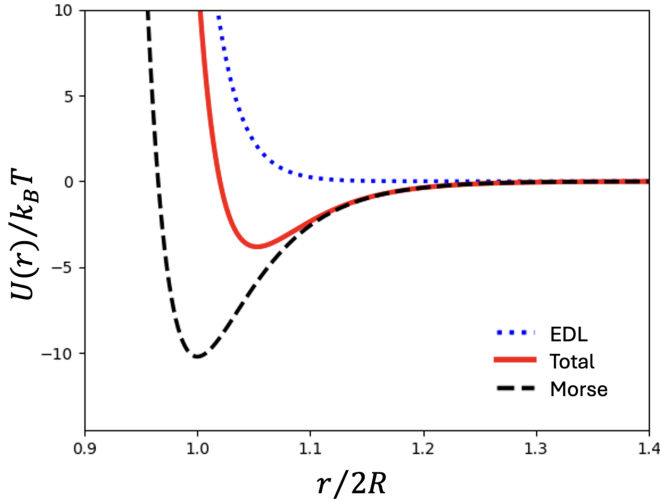


FIG. 1. Morse potential, EDL potential, and the total potential as a function of the nondimensional distance, $r/(2R)$, between two interacting particles, both having radius equal to the average value $R_i = R_j = R = 150$ nm.

Specifically, the EDL potential between two interacting particles reads

$$U_{\text{EDL}}(r) = \frac{A}{\kappa} e^{-\kappa[r-(R_i+R_j)]}, \quad (1)$$

where r is the center-to-center distance between two particles, R_i and R_j their radii, $A = 2\pi\epsilon_0\psi_0^2 \frac{R_i R_j}{R_i + R_j} \kappa$, ϵ the relative permittivity of the fluid medium, ϵ_0 the permittivity of free space, ψ_0 the surface potential, and κ the inverse of the Debye length. Both values of κ and ψ_0 were chosen according to previous experiments, where the screened electrostatic force between interacting surfactant bilayers was directly measured in similar systems [11]. Precisely, considering the salt concentration ($\text{CaCl}_2 = 450$ ppm) employed in our experiments, the values obtained by linear interpolation of the experimental data [11] are $\kappa^{-1} = 6.6$ nm and $\psi_0 = 11.37$ mV.

The Morse potential reads

$$U_M(r) = U_M^* (2e^{-\Delta[r-(R_i+R_j)]} - e^{-2\Delta[r-(R_i+R_j)]}), \quad (2)$$

where U_M^* is a characteristic energy setting the potential minimum and Δ^{-1} the interaction range. We choose $U_M^* = -10k_B T$ and $\Delta^{-1} = 15$ nm so that the attractive part of the total potential U used in simulations best approximates the one estimated for experiments.

The two potentials introduced in Eqs. (1) and (2), as well as their sum, are shown in Fig. 1 for two interacting particles of radius equal to the average value R . Compared to the Morse potential, the EDL contribution significantly weakens the attractive branch of the total interaction $U(r)$, reducing the depth of the potential well, U^* , by more than a factor of 2, i.e., $U^* = -4k_B T$. In addition, both the repulsive barrier and the minimum of the total potential are shifted away from the particle surface by a distance of order $0.1 R$. At larger distance $r \geq 2.2R$, the EDL force becomes negligible and it is $U(r) \simeq U_M(r)$. The total interaction has essentially vanished [i.e.,

$U(r)$ has attained its asymptotic plateau] around $r \simeq 2.6 R$. This value is consistent with the AOV model, which predicts that the depletion interaction vanishes at $r = 2(R + R_g)$. Interparticle hydrodynamic interactions are neglected.

The initial configuration is generated by randomly placing the particles into a cubic box with periodic boundary conditions. Energy minimization is performed to relax particle overlap. Brownian dynamics is then activated, allowing the gel to form and age quiescently for a duration of $400t_B$, $t_B = R^2/D$, with t_B and D being the characteristic Brownian time and self-diffusion coefficient, respectively. After this preparation protocol, the system is subject to several rheological tests, as described below. Most simulations were performed for a system size of $N = 50\,000$ particles. A larger system with $N = 500\,000$ particles was also simulated for very slow imposed flows and weak stresses, to reduce the noise in the measured mechanical response. However, no significant size effects were generally detected in both macroscopic and microscopic observables.

2. Rheological tests

To perform rheological tests, a shear flow is imposed on the system using the Lee-Edwards boundary conditions. Shear flow occurs along the x direction, with the velocity gradient oriented along the y direction. Two different shear protocols are applied: constant shear rate, defined by $\dot{\gamma}(t) = \text{const}$, and oscillatory shear tests, described by $\dot{\gamma}(t) = \dot{\gamma}_0 \cos(\omega t)$, utilized in both frequency and amplitude sweeps. The investigated dimensional shear rates and frequencies as well as the amplitudes span ranges comparable to those probed experimentally. The mechanical response of the system is analyzed after steady-state conditions have been attained.

While experimental measurements are limited to strain-controlled tests, simulations also include creep tests, where a constant stress σ is applied and the deformation simultaneously monitored, starting from a time t_0 . To simulate the effect of a constant shear stress, we adopt the stress control method described in Ref. [31].

3. Structural characterization

Structural characterization of the simulated systems includes statistics of the coordination number Z (i.e., the number of contacts per particle) and direct visualization of the microstructure.

The coordination number is defined by considering two particles to be “in contact” (or bonded) if their center-to-center distance, r , in the considered frame is smaller than $2.6R$, a threshold indicative of the position where $U(r)$ attains its asymptotic plateau. The mean value and the square fluctuations of the coordination number are computed at steady-state conditions by averaging over all particles in the system and over different times.

For direct visualization, we focus on the largest investigated system size $N = 500\,000$ and on the smallest volume fraction $\phi = 0.40$, where the structure appears neater with respect to the most crowded systems. The snapshots represent a slab parallel to the flow-gradient plane with a thickness of $10R$ along the vorticity direction. Under quiescent condition,

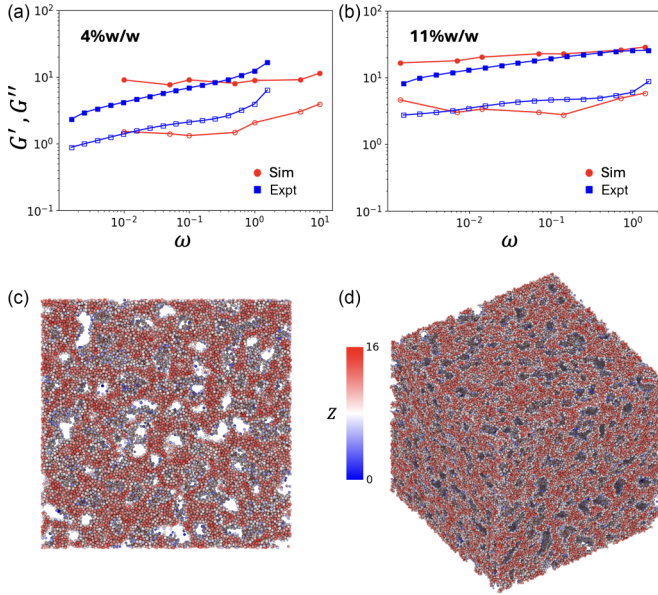


FIG. 2. Storage G' (closed symbols) and loss moduli G'' (open symbols) as a function of the frequency ω , for systems at $\rho = 4\%w/w$ [panel (a)] and $11\%w/w$ [panel (b)], at strain amplitude $\gamma_0 = 0.5\%$. Circles and squares correspond to numerical and experimental results, respectively. (c) Snapshot of a slab of the simulated system at $\rho = 4\%w/w$ under quiescent conditions. (d) Snapshot of the same system as in panel (c) from a three-dimensional perspective. Here and in all other snapshots, particles are colored according to their coordination number, using the reported color scale.

a three-dimensional perspective of the system is also shown in Fig. 2(d). In each frame, particles are colored according to their coordination number. For all snapshots, we adopt the color scale reported in Fig. 2, spanning from blue to red as the coordination number increases.

C. Dimensionless quantities

All quantities reported in this study are plotted in a nondimensional version, by adopting the following strategy: Stress and viscoelastic moduli are expressed in terms of the “Brownian stress” $\frac{k_B T}{R^3}$, while its inverse is used for the creep compliance. To properly compare experiments and simulations, times are expressed in terms of a generalized Brownian time $\hat{t}_B$: It is $\hat{t}_B = t_B \equiv R^2/D$ for experiments, while for simulations $\hat{t}_B = h(\phi)t_B$, with $h(\phi)$ being a volume fraction dependent factor. This factor has been introduced following recent works [18,24] to roughly account for the missing hydrodynamics in simulations. In fact, particle diffusion is expected to be somewhat slower in experiments due to hydrodynamic interactions [32]. Accordingly, $h(\phi) > 1$ is expected. To estimate $h(\phi)$, we focus on the flow curve of Figs. 4(a) and 4(b) and identify the horizontal shifting factor to best collapse the numerical data over the experimental ones, especially in the high shear rate regime. By doing so, we find $h = 38.5$ and 7 for $\phi = 0.40$ and 0.55 , respectively. Frequency and shear rate are expressed in terms of $\frac{1}{\hat{t}_B}$.

III. RESULTS AND DISCUSSION

A. Oscillatory rheology

1. Frequency sweep

We start by describing oscillatory shear tests in the linear regime, as probed by small amplitude frequency sweeps. Figure 2 shows the storage and loss moduli, G' and G'' , as a function of the frequency ω . Panels (a) and (b) refer to the systems at concentration $\rho = 4\%w/w$ and $11\%w/w$, respectively, including both experimental and numerical results. Generally, G' exceeds G'' over the whole frequency range. The two moduli show mild frequency dependence and remain closely parallel, differing by less than one order of magnitude. It is also worth noticing that, in panel (b), the moduli are somewhat larger than in panel (a), suggesting a stiffening of the system with increasing the vesicle volume fraction. Thus, the system can be regarded as primarily solidlike, as expected for a well-formed gel network. Indeed, Figs. 2(c) and 2(d), two snapshots of the structure at quiescent conditions, clearly illustrate the presence of a well-established gel network with qualitative features typical of an arrested phase separation.

Concerning the comparison between numerical and experimental data, we can appreciate that our simulations finely reproduce the experimental results. Although the moduli from simulations show a slightly weaker frequency dependence compared to experiments, the magnitude of the moduli remains always closely comparable. Such an agreement is noteworthy, especially considering that the uncertainties inherent to the experimental parameters and the approximation used in the numerical model may be an intrinsic source of discrepancies between experiments and simulations.

2. Amplitude sweep

Next, still within the framework of oscillatory rheology, we probe the system response beyond the linear regime by measuring the moduli at increasing strain amplitudes γ_0 . Figures 3(a) and 3(c) show the amplitude dependence of G' and G'' for simulations and experiments, respectively, at $\rho = 4\%w/w$. At small amplitude, the moduli display a plateau with $G' > G''$, indicative of a solidlike, elastic regime, in agreement with the frequency-sweep tests in the linear regime. Instead, at larger amplitudes, decreasing trends are observed and G' becomes smaller than G'' . The crossover point of the moduli is indicative of an incipient yielding process, with an ensuing solid-to-liquid-like transition. Notably, also in this case, there is a good agreement between experiments and simulations, with the crossover point falling at the same strain amplitude of about 10%, as indicated by the vertical dashed lines. To have a qualitative overview of the structural changes accompanying these behaviors, four snapshots from simulations at different strain amplitudes are shown in Fig. 3(e). For γ_0 values corresponding to the small amplitude plateau (i), the structure appears to be similar to that of the system at rest [see Fig. 2(c)]. Instead, after the moduli crossover [(ii) and (iii)], structural heterogeneities become more pronounced with increasing the strain amplitude. In particular, the structure appears to become more coarse and features larger voids. However, this trend changes as the strain amplitude increases

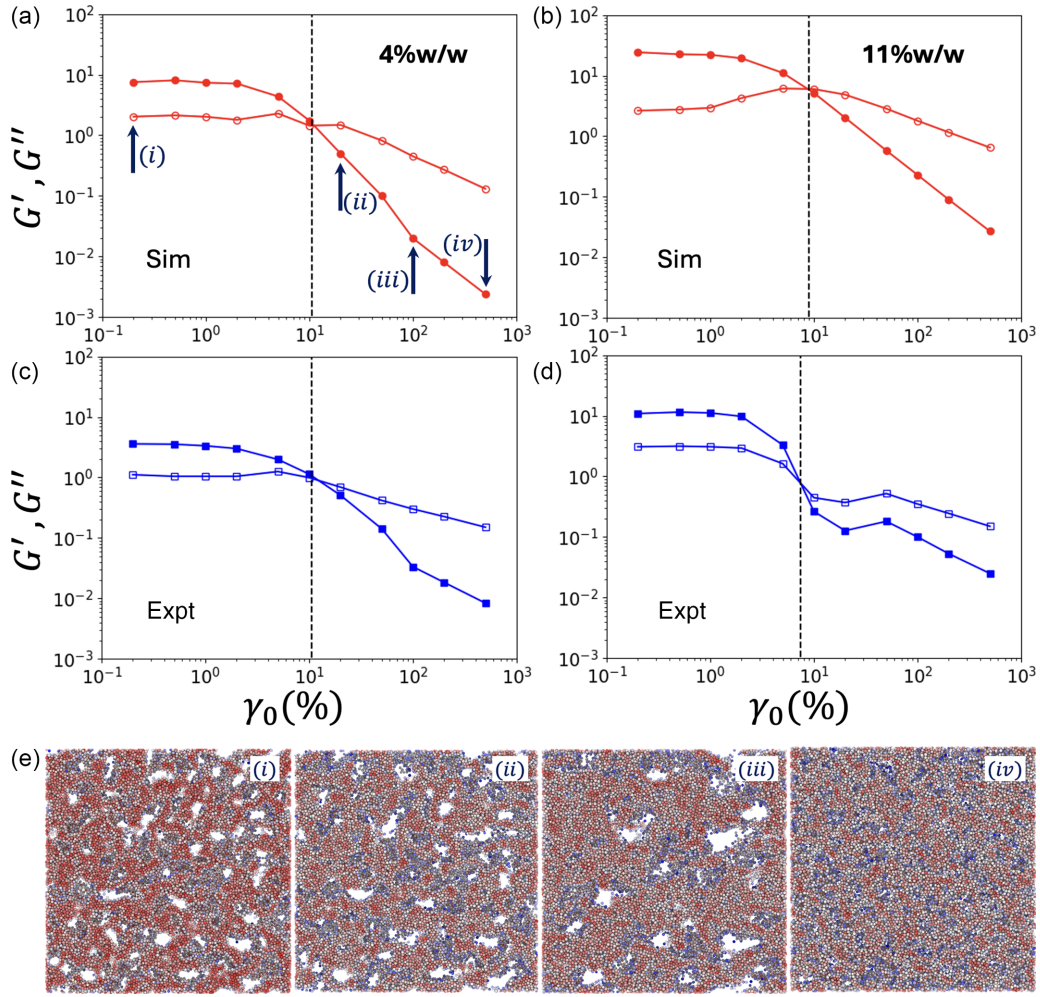


FIG. 3. Storage (G' , closed symbols) and loss (G'' , open symbols) moduli as a function of strain amplitude from simulations (red) and experiments (blue) on systems at $\rho = 4\%$ w/w [panels (a) and (c)] and 11% w/w [panels (b) and (d)], respectively, as indicated. The vertical dashed lines denote the amplitude where the moduli cross over, indicative of a yielding transition. (e) Snapshots of the gel microstructure at $\rho = 4\%$ w/w for different strain amplitudes, taken at zero crossing of the strain oscillations. Italic letters indicate the correspondence between snapshots and panel (a).

further, and, in fact, at the largest strains investigated, the system displays a quite homogeneous structure (iv).

The same type of plots are shown at concentration $\rho = 11\%$ w/w in Figs. 3(b) and 3(d). The results are qualitatively similar to those at $\rho = 4\%$ w/w. The only noticeable difference is the appearance, in both G' and G'' , of a mild local minimum just beyond the crossover point of the moduli, which is observed in the experimental dataset but not in simulations. A similar local minimum near the crossover point has also been reported in previous experiments on standard depletion gels [24], where, interestingly, the behavior was likewise absent in simulations. At this stage, it is difficult to determine whether such feature arises from experimental artifacts or from some intrinsic effect that simulations are not able to capture. However, also in this case, the crossover point occurs with close correspondence between experiments and simulations at $\gamma_0 \simeq 8\%$, a value slightly smaller than that at the lower concentration, as expected for a stiffer sample.

B. Shear-rate-controlled tests

1. Flow curves

Now, we turn to discuss the flow curves of the measured shear stress σ as a function of the applied shear rate $\dot{\gamma}$, under steady-state conditions. Figures 4(a) and 4(b) include both numerical and experimental data for the systems at concentration $\rho = 4\%$ w/w [panel (a)] and 11% w/w [panel (b)], respectively. Once again, an overall good agreement is found between experiments and simulations. Some discrepancy emerges for small $\dot{\gamma}$ at $\rho = 4\%$ w/w: A possible explanation is wall slip effects typically occurring in experimental measurements at low shear rates [33–35].

The flow curves generally exhibit three different regimes: At low shear rate, the stress tends to a plateau, whose value identifies the dynamic yield stress. At intermediate shear rate, a shear thinning regime is found, where the stress leaves the plateau with a sublinear growth with increasing $\dot{\gamma}$. Such a behavior is known to be a common feature of yield-stress soft

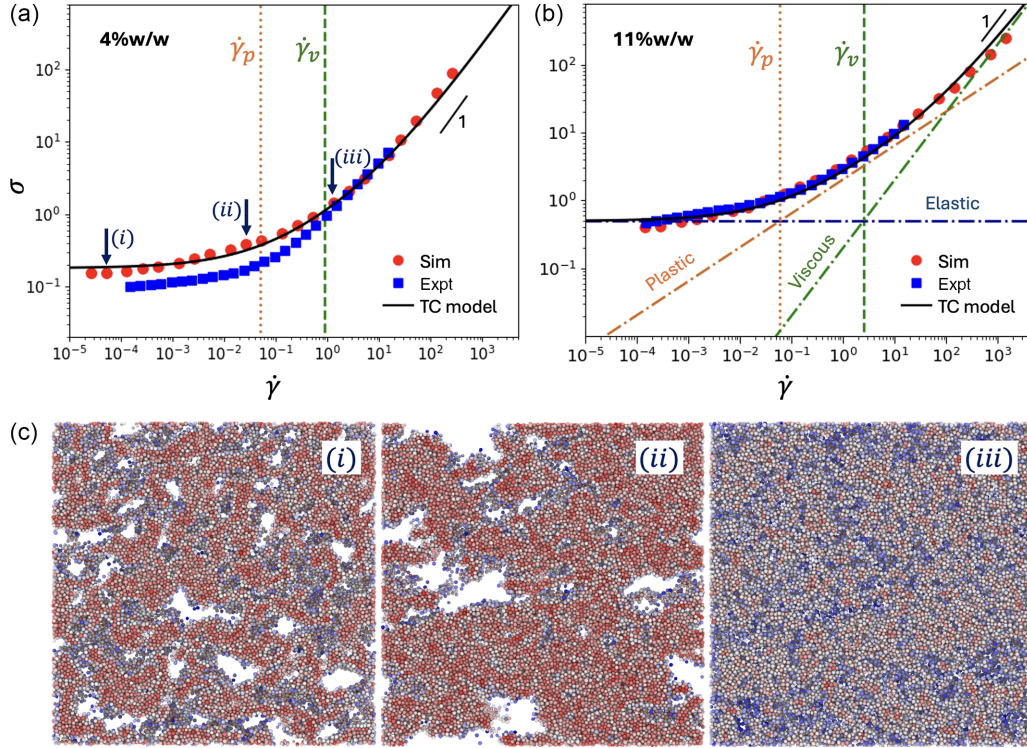


FIG. 4. Flow curves from simulations (circles) and experiments (squares) for systems at $\rho = 4\%$ w/w [panel (a)] and 11% w/w [panel (b)], as indicated. The solid lines are fits of the simulation data to the TC model [Eq. (3)]; in both panels, the vertical lines mark the position of the shear rates, $\dot{\gamma}_p$ (dotted) and $\dot{\gamma}_v$ (dashed). Panel (b) also includes dash-dotted lines illustrating the separate stress contributions entering the TC model. (c) Snapshots of the gel microstructure at $\rho = 4\%$ w/w for different shear rate values. Italic letters indicate the correspondence between snapshots and panel (a).

materials and is indeed described by the popular Herschel-Bulkley (HB) model [36–38]. At higher shear rates, however, a linear increase of the stress is attained, which is fully manifested on the broader $\dot{\gamma}$ range covered by simulations. Although not captured by the HB model, such a Newtonian-like regime is frequently observed in soft glassy materials, particularly in studies spanning extended $\dot{\gamma}$ ranges [18,35].

To describe the flow curve over the entire investigated $\dot{\gamma}$ range, we adopt the recently introduced three-component (TC) model [35], obtained by combining the Bingham model [39] and the model proposed by Bocquet and coworkers [40]. We present the TC model in a form that is slightly different from that used in Ref. [35], and best suited to our purposes:

$$\sigma = \sigma_y \left[1 + \left(\frac{\dot{\gamma}}{\dot{\gamma}_p} \right)^{1/2} + \left(\frac{\dot{\gamma}}{\dot{\gamma}_v} \right) \right]. \quad (3)$$

The TC model in Eq. (3) includes three fitting parameters, namely, the dynamic yield stress σ_y and two characteristic shear rates, $\dot{\gamma}_p$ and $\dot{\gamma}_v$. The three terms on the right-hand side account for different contributions to stress dissipation, namely, elastic, plastic, and viscous dissipation, which are associated with the low (yield stress), intermediate (shear thinning), and large (Newtonian-like) shear rate regime, respectively. Indicative boundaries between these three regimes are given by $\dot{\gamma}_p$ and $\dot{\gamma}_v$, which identify the shear rates where plastic and viscous dissipation, respectively, equal the elastic one (i.e., the yield stress). We adopt the form of the TC

model given in Eq. (3) in order to emphasize the presence of two characteristic shear rates, $\dot{\gamma}_p$ and $\dot{\gamma}_v$, and to analyze how the system behavior changes upon crossing them. We also remark that $\dot{\gamma}_v$ is not meant to identify the point where viscous dissipation becomes the largest contribution overall, which occurs only at larger shear rates; rather, it marks the shear rate at which the viscous contribution becomes comparable to the elastic one and starts to play a relevant role in the flow response. We also note that the exponent $1/2$ characterizing the shear-rate dependence of the plastic term in Eq. (3) can be understood in the framework of a mean-field model [40,41], as well as in elastoplastic models [38,42], where plastic and irreversible rearrangements determine the local mechanism for stress dissipation close to yielding. TC fits to the flow curves from simulations (whose $\dot{\gamma}$ range is larger compared to experiments) are shown in Figs. 4(a) and 4(b) as solid lines, while the vertical dashed lines mark the positions of the characteristic shear rates $\dot{\gamma}_p$ and $\dot{\gamma}_v$. In addition, Fig. 4(b) also shows, as dash-dotted lines, the separate stress contributions entering the TC model in order to further clarify the meaning of the characteristic shear rates.

The complete set of fitting parameters is reported in Table I.

In agreement with our frequency-sweep tests, the flow curves point to a hardening of the materials with increasing the vesicle concentration: Indeed, the estimated yield stress is $\sigma_y \simeq 0.2$ at $\rho = 4\%$ w/w and $\sigma_y \simeq 0.5$ at $\rho = 11\%$ w/w. It is worth noting in this regard that our vesicle gels are softer than the standard depletion gels investigated in Ref. [18], where

TABLE I. TC model fitting parameters.

ρ (% w/w)	$\sigma_y (k_B T / R^3)$	$\dot{\gamma}_p (\hat{t}_B^{-1})$	$\dot{\gamma}_v (\hat{t}_B^{-1})$
4	$0.18 \pm 1e^{-2}$	$0.05 \pm 5e^{-3}$	$0.90 \pm 8e^{-2}$
11	$0.50 \pm 3e^{-2}$	$0.06 \pm 7e^{-3}$	$2.50 \pm 2e^{-1}$

$\sigma_y > 1$ was reported. Such a difference is fully consistent with the potential energy well being about four times deeper in that system than in ours.

Concerning the structure, Fig. 4(c) shows a nonmonotonic trend of heterogeneity with increasing the shear rate, resembling the behavior observed as a function of γ_0 for the amplitude-sweep tests. At small shear rate $\dot{\gamma} \ll \dot{\gamma}_p$ (i), where the flow curve is close to the yield stress plateau, the structure resembles that of the quiescent gel. Then, as the stress escapes the plateau (ii), structural heterogeneity increases (e.g., voids enlarge). In this regime, aggregation leads to a sharp coexistence of dense, particle-rich regions and large low-density voids. These structural heterogeneities evolve dynamically, as the imposed shear rate tends to push voids outside of dense regions and merge them into larger, elongated domains, in line with recent observations on attractive colloidal suspensions [43]. However, in the well-established shear thinning regime, $\dot{\gamma} > \dot{\gamma}_p$, the increasing shear rate leads to a decrease of heterogeneity. Eventually, in the Newtonian-like regime $\dot{\gamma} > \dot{\gamma}_v$ (iii), the imposed flow is so strong that it fully breaks the attractive bonds and produces a quite homogeneous configuration, closely resembling that of a hard-sphere system. It has been proposed that, for standard depletion gels with strong interparticle attraction, an indicative shear rate for bond breaking can be estimated by equating the characteristic shear force $F_{\text{shear}} = 12\pi\eta_s R R_p \dot{\gamma}$ to the attractive one $F_{\text{attr}} = U^*/(2R_p)$ [18]. Estimating this shear rate for our system yields a nondimensional value $\dot{\gamma} \simeq 14.2$, which is significantly larger than the measured values of $\dot{\gamma}_v$. This discrepancy is likely due to the presence of repulsive EDL interactions in our system, which effectively weaken the net attractive forces. In addition, the estimate of Ref. [18] is based on simple two-body arguments and does not account for crowding effects, which may be relevant for our system.

2. Coordination number

To have a more quantitative perspective on the structure, we now focus on the coordination number Z , monitored at steady-state conditions for the same simulations illustrated in Fig. 4(c). Figure 5(a) shows that the particle- and time-averaged coordination number, $\langle Z \rangle$, exhibits a sigmoidal shape as a function of the shear rate. Quantitatively, we find that the decay of $\langle Z \rangle$ is well described by a stretched exponential function [solid line in Fig. 5(a)]:

$$\langle Z(\dot{\gamma}) \rangle - Z_\infty = A \exp \left[- \left(\frac{\dot{\gamma}}{\dot{\gamma}_z} \right)^\beta \right], \quad (4)$$

with best-fit values $Z_\infty = 7.0 \pm 1e^{-1}$, $A = 3.5 \pm 4e^{-2}$, $\dot{\gamma}_z = 0.075 \pm 3e^{-3}$, and $\beta = 0.39 \pm 1e^{-2}$. The characteristic shear rate associated with decay of this function can be estimated as $\langle \dot{\gamma}_z \rangle = \frac{\dot{\gamma}_z}{\beta} \Gamma(\frac{1}{\beta}) \simeq 0.27$, where Γ denotes the Gamma

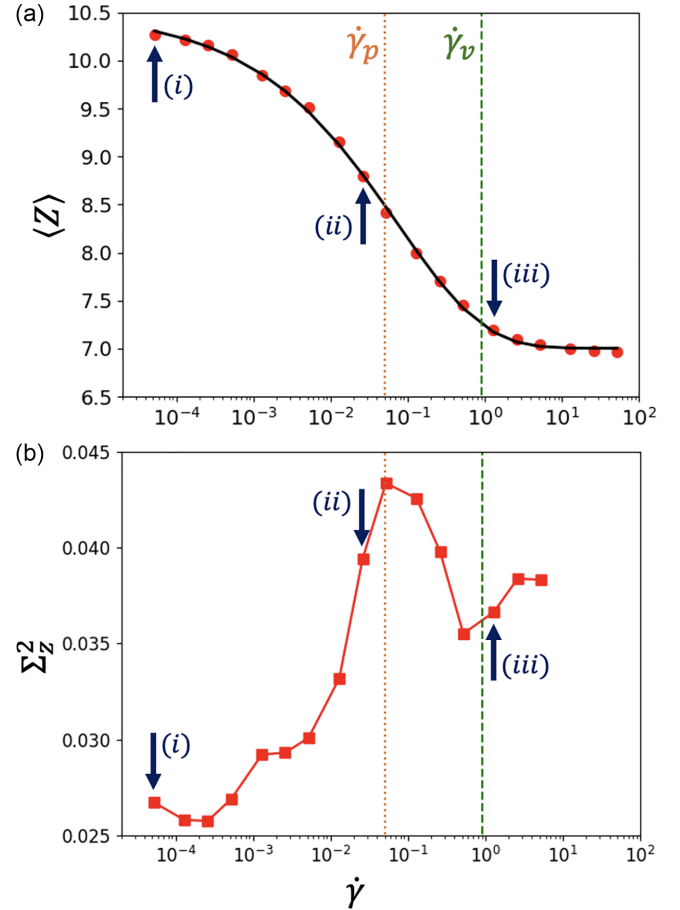


FIG. 5. For shear-rate-controlled simulations at $\rho = 4\%$ w/w: (a) average coordination number $\langle Z \rangle$ as a function of $\dot{\gamma}$. The solid line is a fit to the stretched exponential function in Eq. (4). (b) Relative fluctuations Σ_Z^2 as a function of the shear rate $\dot{\gamma}$. In both panels, the vertical lines mark the position of the shear rates, $\dot{\gamma}_p$ and $\dot{\gamma}_v$. Italic letters indicate the correspondence with Figs. 4(a) and 4(c).

function. Accordingly, at small shear rate $\dot{\gamma} \ll \dot{\gamma}_z$ [snapshot (i) in Fig. 4(c)], the coordination number tends to a plateau $Z_\infty + A$, corresponding to the quiescent state. Then, $\langle Z \rangle$ monotonically decreases, with increasing the shear rate over a range, which fully includes the shear thinning regime of the flow curve (ii). Finally, at large shear rates, $\langle Z \rangle$ saturates to a smaller plateau Z_∞ . Interestingly, we find that the characteristic shear rate $\dot{\gamma}_v$, associated with the emergence of a relevant viscous contribution and with the incipient Newtonian-like part of the flow curve, is larger but of the same order of magnitude as the characteristic shear rate for the decay of the coordination number: $\dot{\gamma}_v \simeq 3\langle \dot{\gamma}_z \rangle$. Thus, saturation is essentially attained at a shear rate around $\dot{\gamma}_v$, and the low plateau Z_∞ can be associated with the homogeneous state observed in the Newtonian-like regime (iii).

The monotonic behavior found for $\langle Z \rangle$ provides an average characterization of the structure. On the other hand, the main structural feature visually emerging from the snapshots of Fig. 4(c) is a nonmonotonic trend of heterogeneity. Dealing with heterogeneity, in fact, fluctuations rather than averages are generally expected to be a more relevant indicator.

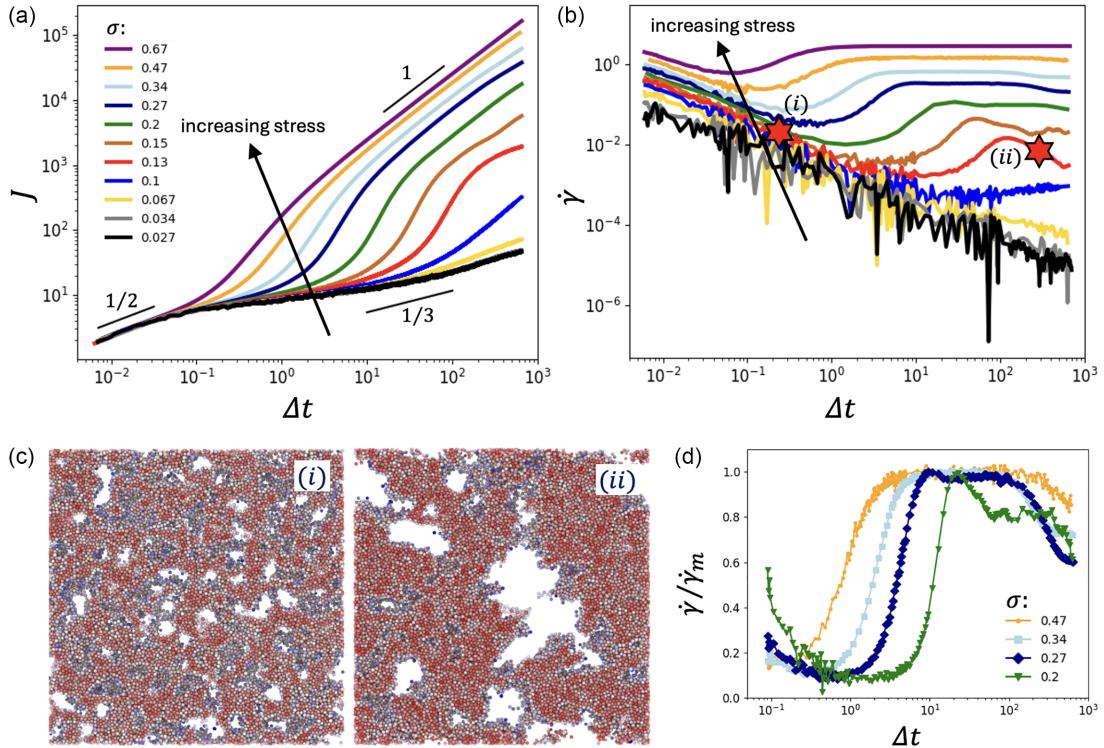


FIG. 6. For simulations of creep tests at $\rho = 4\%$ w/w and different applied shear stress σ , as indicated: (a) compliance $J(\Delta t)$ and (b) shear rate $\dot{\gamma}(\Delta t)$ as a function of the lag time Δt . Arrows in panels (a) and (b) indicate increasing stress. Color codes in panel (b) are the same as in panel (a). (c) For $\sigma = 0.13$, snapshots of the system for two lag times are presented, corresponding to the preyield gel and resolidified gel, respectively. Italic letters indicate the correspondence between snapshots and panel (b). (d) Long-time shear rates corresponding to stresses $0.20 \leq \sigma \leq 0.47$ are plotted in a semilogarithmic scale, after rescaling the ordinates of each curve with its maximum $\dot{\gamma}_m$, to highlight the features of weak resolidification.

Accordingly, we compute the normalized fluctuation of the coordination number $\Sigma_Z^2 = \frac{\langle Z^2 \rangle - \langle Z \rangle^2}{\langle Z \rangle^2}$, which is shown in Fig. 5(b) as a function of $\dot{\gamma}$. This fluctuation displays a non-monotonic behavior with a distinct maximum at intermediate shear rates. Notably, the position of the maximum closely corresponds to the characteristic shear for the onset of shear thinning $\dot{\gamma}_p$, supporting the picture that the most heterogeneous structures are formed around that shear rate value.

C. Creep tests

Finally, we discuss the results of creep tests conducted for simulations at $\rho = 4\%$ w/w. In such tests, a constant shear stress σ is applied at time $t = t_0$ and the ensuing deformation is monitored as a function of the lag time $\Delta t = t - t_0$. In the following, we focus on the compliance $J(\Delta t) = \frac{\gamma(\Delta t)}{\sigma}$, defined as the ratio between the time-dependent shear strain and the applied stress. Accordingly, an increasing trend of the compliance points to deviations from an ideal solidlike behavior due to softening of the sample.

Figure 6(a) shows the lag-time dependence of the compliance for different values of shear stress. At early times, a common behavior $J(\Delta t) \propto \Delta t^{1/2}$ is observed at any value of σ . Such a power-law trend has been previously reported for simulations of standard depletion gels [31] and ascribed to a high-frequency viscoelastic response, where modest structural deformations interplay with Brownian motion within the local cages typical of gels and glasses [19,44]. We notice as an

aside that, in experiments, this short-time response is typically masked by an initial superlinear increase of the compliance, $J(\Delta t) \propto \Delta t^2$, due to the rheometer inertia [45].

After the common $J(\Delta t) \propto \Delta t^{1/2}$ regime, the compliance keeps being stress independent only up to a given value of the stress. The threshold for the onset of a stress-dependent compliance is commonly used to define the so-called *creep yield stress*, σ_c [31,45]. It is worth mentioning, however, that the identification of σ_c may depend on the observation time and that the very existence of a finite creep yield stress for ideal, infinitely lasting experiments on gels is disputable [46]. As a matter of fact, here, we estimate $\sigma_c = 0.067$, as the stress value where a dependence of J on the shear stress is first detected.

For $\sigma \leq \sigma_c$, the compliance tends to increase slowly, resembling Andrade's creep, $J(\Delta t) \propto \Delta t^{1/3}$, a phenomenon originally reported for metallic solids [47]. More recently, similar trends have been observed also for many soft materials [31,38,43,48–50] and associated with localized energy releases and minor structural changes (e.g., bond stretching or distortion [43]). As a matter of fact, our simulations at $\sigma \leq \sigma_c$ do not exhibit clear-cut signatures of yielding transition up to the longest investigated time, in analogy with previous creep experiments on soft glassy materials [51,52].

Conversely, for larger stresses $\sigma > \sigma_c$, we do observe, at intermediate times, a sharp increase of the compliance, which is indicative of the onset of a yielding process. Notably, the yielding is found to occur earlier and earlier with increasing

the applied stress, a phenomenon known as *delayed yielding* [31,46].

Focusing on long times, Fig. 6(a) also shows that a linear increase of the compliance is attained at the largest stresses, which is indicative of a steady-state, viscous flow. At intermediate stress, however, a more complex behavior is apparent, where $J(\Delta t)$ seems to increase with a nonmonotonic rate. This latter feature is more clearly manifested in the shear rate $\dot{\gamma}(\Delta t)$ that is in fact proportional to the time derivative of the compliance. Figure 6(b) indeed demonstrates the presence of a nonmonotonic time dependence of the postyield shear rate that is especially manifested at $\sigma = 0.13$ (red curve). After yielding, $\dot{\gamma}(\Delta t)$ reaches a maximum but then drops quickly to a value comparable to the preyield minimum. A similar behavior has been previously observed in standard depletion gels and ascribed to the so-called *resolidification* or *reentrant solid* regime [31,45]. According to this picture, after the (first) yielding point, there is a transient flow during which a new, possibly stronger, solidlike state is formed. As a matter of fact, from the snapshots shown in Fig. 6(c) for the simulations at $\sigma = 0.13$, it is clear that the gel reformed after yielding (ii) features evident structural differences, in particular, a much more coarsened morphology, compared to the initial network (i).

In Fig. 6(b), postyield nonmonotonic trends of $\dot{\gamma}(\Delta t)$ persist, becoming progressively milder, in a range of larger stresses up to $\sigma_u = 0.47$, which we take as an upper boundary for resolidification. However, for high stress $\sigma \geq 0.2$, resolidification only involves relatively small drops of $\dot{\gamma}$ to values quite higher than the minimum attained before the “first” yielding and can interplay with temporary plateau. To properly highlight these behaviors, Fig. 6(d) shows $\dot{\gamma}(\Delta t)$ over the relevant range of stress and lag time, after rescaling each dataset by its postyield maximum, $\dot{\gamma}_m$. From now on, we will conventionally refer to these features as *weak resolidification*, to distinguish them from the *strong resolidification* observed at smaller shear stresses, such as that discussed for $\sigma = 0.13$. Nonmonotonic behaviors are definitely no longer present at the largest stress, $\sigma = 0.67$ included in Fig. 6(b), where a fully developed viscous plateau is manifested at long time.

Overall, the smooth shape of the curves in Fig. 6 indicates that yielding and resolidification are quite “ductile” processes and suggests that thermal motion plays an important role also at large lag times. More “brittle” features have been instead observed for creep tests on standard depletion gels with stronger attractive interactions [45]. As a further remark, we notice that it is generally hard to draw a definitive conclusion on the asymptotic, long-time behavior of the shear rate. For example, for stress slightly larger than σ_c , the first yielding is not clearly manifested within the simulated time window. For systems undergoing resolidification, it remains an open issue whether $\dot{\gamma}(\Delta t)$ approaches a plateau in the long-time limit or is characterized by some types of reiterated transitions. In other words, the question is whether nonmonotonic behaviors go on indefinitely or not. In fact, the long-time fate of gels after resolidification has been recognized as an open issue, with the intriguing possibility of continuously alternating liquid- and solidlike states [45]. However, the necessity of covering very large timescales makes this problem challenging both experimentally and numerically.

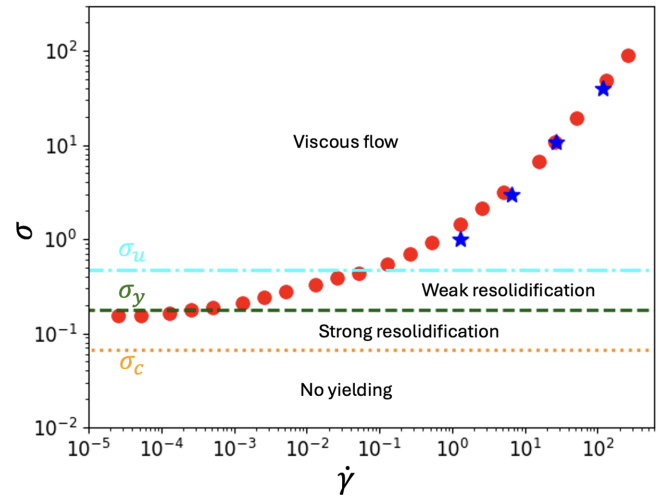


FIG. 7. For simulations at $\rho = 4\%$ w/w, shear-rate-controlled flow curve as in Fig. 4(a) (circles) and stress-controlled flow curve (stars), as measured in creep tests, provided that the shear rate attains a long-time plateau. The dashed line marks the position of the dynamic yield stress σ_y measured in shear-rate-controlled tests. The dashed and dotted-dashed lines indicate the positions of the creep yield stress σ_c and of the upper boundary of the creep yield stress σ_u , respectively, as measured in creep tests.

1. A comparison with shear-rate-controlled tests

For the system at $\rho = 4\%$ w/w, Fig. 7 shows, as circles, the shear stress measured at constant shear rate under steady-state conditions [i.e., the flow curve already shown in Fig. 4(a)] and, as stars, the shear rate measured in stress-controlled (i.e., creep) tests, provided that a steady-state flow (i.e., $\dot{\gamma}(\Delta t) = \text{const}$) is fully attained at long times.

The dashed and dotted horizontal lines mark the position of the dynamic and creep yield stress, σ_y and σ_c , as measured in shear-rate- and stress-controlled tests, respectively. We find σ_y to be somewhat larger than σ_c (by a factor of about 3). This result is consistent with the idea that an applied stress $\sigma \geq \sigma_c$ is strong enough to induce a yielding transition, whereas a postyield constant shear rate regime can be established only if σ also exceeds the dynamic yield stress σ_y . However, as already shown in Fig. 6, a constant shear rate regime is fully attained only above an even larger threshold, $\sigma_u > \sigma_y$ (dashed-dotted line in Fig. 7), at least within the time window covered by our creep tests. Accordingly, stress-controlled data in Fig. 7 start from a stress value above σ_u . For $\sigma < \sigma_u$, stress-controlled measurements are not available (i.e., ill-defined), as a clear-cut plateau of $\dot{\gamma}(\Delta t)$ is not attained and signatures of weak resolidification are still detectable. In the limited range where stress-controlled measurements are possible, data appear to be closely overlapped with the shear-rate-controlled ones, pointing to a viscous regime that is independent of the control parameter.

As a final remark, we notice that resolidification (including both strong and weak resolidification) occurs in creep tests for $\sigma_c < \sigma < \sigma_u$. However, σ_c and σ_u should only be considered as a lower and an upper boundary of the resolidification region. The sharp signatures characterizing strong resolidification are limited to a narrow stress window close

to σ_y . In a previous work on standard depletion gels [45], resolidification in creep tests has been reported to occur only between the creep yield stress and the dynamic yield stress. This picture is consistent with the common assumption that stress-controlled steady states at long time, corresponding to a flat shear rate $\dot{\gamma}(\Delta t) = \text{const}$, are achieved only for $\sigma \geq \sigma_y$ (the smallest steady stress measured under strain-rate-controlled conditions), but it definitely prevents the possibility that one such state may occur after resolidification (as the resolidification region is located below the dynamic yield stress). In our vesicle gels, the upper boundary for resolidification instead lies well above the dynamic yield stress. This observation raises the possibility that, on timescales longer than those accessed in our simulations, stress-controlled steady states with a constant shear rate may be reached after resolidification, in analogy with shear-rate-controlled tests, where a steady stress is attained after an initial overshoot.

IV. CONCLUSIONS

In this paper, we have studied the rheology of gels formed by charged vesicles, suspended in water-polymer solutions, by means of experiments and BD simulations. Oscillatory frequency sweeps in the linear regime display a predominantly elastic response, with the storage modulus exceeding the loss modulus and only a weak frequency dependence. Amplitude sweeps, instead, point to a yielding transition upon increasing the deformation amplitude. Shear-rate-controlled tests show that flow curves include three different regimes, namely, a dynamic yield stress plateau at small $\dot{\gamma}$, followed by shear thinning and eventually by a Newtonian-like regime. The largest structural heterogeneity appears to be associated with the yielding transition in both oscillatory and shear-rate-controlled tests. The maximum of structural heterogeneity and the recovery of homogeneity occur near two characteristic shear rates (as obtained from a TC model fit to the flow curves), namely, the shear rate $\dot{\gamma}_p$ for the crossover from dynamic yield stress plateau to shear thinning, and the shear rate $\dot{\gamma}_v$ associated with the emergence of a relevant viscous contribution and with the incipient Newtonian-like behavior. Focusing on the coordination number Z , we have also shown that $\dot{\gamma}_p$ corresponds to a maximum in the relative fluctuations, whereas $\dot{\gamma}_v$ is associated with the saturation of the average value to a low plateau. Numerical creep tests reveal a rich phenomenology, including Andrade-like deformations for stress below the creep yield stress σ_c , as well as delayed yielding above σ_c . Yielding under creep is followed by an asymptotic viscous regime at high stress. At lower stress, instead, we observe resolidification into structurally distinct states whose long-term fate remains elusive. At variance with standard depletion gels, a kind of weak resolidification is observed even for stresses exceeding the dynamic yield stress.

The persistence of resolidification even for stresses exceeding the dynamic yield stress, together with the markedly ductile character of both yielding and resolidification

observed in our system, may be attributed to the stabilizing role of long-range repulsive interactions. These repulsions can hinder catastrophic coarsening and irreversible collapse after bond rupture, thereby favoring the rebuilding of a percolated network even under relatively large stresses. In this sense, charged vesicle gels with competing attractive and repulsive interactions may be viewed as exhibiting an intermediate behavior between purely repulsive suspensions, yielding quite homogeneously, and purely attractive gels, which tend to yield heterogeneously, i.e., along localized interfaces, as highlighted by a recent work on colloidal suspensions with tunable interactions [43].

As for future perspectives, it would be interesting to explore in depth how the interplay between attractive and repulsive forces affects the properties of vesicle gels, for instance, by systematically varying the relative energy scales and ranges of the two interactions. Such a study will also allow assessing the robustness of the rheological features reported here with respect to these variations. A thorough structural analysis of the network would be called for, also in view of preliminary tests suggesting that the underlying percolation is strongly correlated and resembles models associated with glassy dynamics [53]. Future challenges include performing longer-lasting simulations that may help clarify the long-time nature of stress-controlled steady states (if any) following resolidification. Another interesting question is whether weak resolidification differs from the strong one merely in quantitative terms, or whether it involves qualitatively distinct processes. From a broader perspective, a deeper understanding of resolidification—especially its long-time fate and its location with respect to the flow curves—remains an interesting open issue.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

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