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Suspensions of attractive microcapsules: a non-colloidal fragile gel?

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(Dated: 22 October 2024)

We investigated the rheological properties of suspensions of attractive microcapsules, which formed a weak gel at volume fractions ϕ as low as 0.1. These microcapsules, measuring 100 μm in diameter, were constructed with a droplet of positively charged chitosan solution protected by a membrane formed through the complexation of chitosan with a negatively charged surfactant. Iso-density matched suspensions were achieved by dispersing these microcapsules in silicone oils. Plate-plate rheometry revealed that these suspensions displayed a yield stress ranging from about 0.1 to 3 Pa for ϕ increasing from 0.1 to 0.5. At much higher stresses, the suspension viscosity was almost shear independent. Furthermore, these suspensions exhibited a frequency sweep signature akin to attractive colloidal suspensions, with a shear elastic modulus plateauing at low frequencies, indicative of an elastic microstructure within the suspensions. Remarkably, a degree of microstructural anisotropy, reminiscent of fragile matter, was evidenced by the transient fluidization of the suspension when the direction of applied stress, which remained below the yield stress, was reversed. Beyond the yield stress, both symmetric and asymmetric stress reversal experiments demonstrated that the suspension structure was influenced by the applied stress. It changed from an anisotropic and fragile network at low stress levels to a dispersion of isolated particles at high stress levels. We concluded that suspensions of attractive microcapsules could be classified as a fragile particulate gel, whose microstructure depends on the stress and its direction.

I. INTRODUCTION

Suspensions of non-Brownian particles are ubiquitous in nature and industry, presenting rheological features that are challenging to describe, as small changes in composition or driving forces can tune their flow properties from liquid to solid.^{1,2}

At low volume fractions, the viscosity of suspensions of hard and non-Brownian particles increases with the solid volume fraction ϕ until it diverges at a jamming volume fraction ϕ_m ranging from 0.50 to 0.63, depending on the system. Numerical simulations, considering both lubricated and contact friction, show that the contact friction controls ϕ_m .^{3,4} Rheological investigation of soft and adhesive suspensions of micro-particles show that the presence of adhesive forces induces shear-thinning.⁵ A way to demonstrate that the liquid-to-solid transition depends on the driving forces is to plot ϕ_m as a function of the applied shear stress σ at a fixed ϕ . In this framework, at the same applied stress, Gilbert *et al.* show that ϕ_m increases with the particle elasticity. For stresses much higher than the characteristic adhesion stress, such suspensions behave like usual frictional suspensions with a viscosity controlled by both ϕ and the contact friction.

Considering now the transient response to stress/strain of non-Brownian suspensions, one important feature is the fact that the flow and the interactions lead to the emergence of an anisotropic microstructure. Key features of the microstructure was revealed by shear reversal experiments, where a suspension initially sheared in steady state is suddenly sheared with a rate of opposite

direction.^{6,7} Usually, the viscosity displays a sudden decrease upon reversal, reaching a minimum value before gradually returning to its steady-state level over a few strain units. This phenomenon is attributed to the presence of an anisotropic microstructure, which is developed under finite strain conditions and can bears stress at high concentrations only in the shear direction.^{3,6,8} The drop in viscosity occurs because the anisotropic microstructure cannot sustain the new shear direction. Moreover, shear reversal experiments demonstrated the decreasing relative contribution of hydrodynamic stresses versus contact stresses as the particle volume fraction ϕ increased.⁸

When the size scale is changed, this description undergoes significant alterations owing to colloidal interactions between Brownian particles. Suspensions of attractive colloidal particles form elastic gels at very low volume fractions, and their rheological properties depend on the strength of the attraction potential and the volume fraction ϕ .^{9,10}

Strikingly, non-Brownian suspensions, resembling colloidal systems, have been reported very recently by Dhand *et al.*¹¹ Their system consisted of water and polyelectrolyte droplets protected by a composite membrane of cellulose nanofibrils dispersed in an organic solution. These suspensions of microcapsules exhibited a yield stress for a volume fraction as low as 0.2. Such behavior cannot be explained by classic factors influencing non-Brownian suspensions, like friction, adhesion, or deformability; instead, their results suggest attractive interactions between the objects, leading to the formation of a network, such as in attractive colloidal suspensions.

In this article, using another system, we describe the rheology of this new class of non-Brownian suspensions consisting of attractive microcapsules, connecting the spontaneous formation of aggregates and the anisotropy of the structure in shear flow by both steady-state shear

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86 rheology and shear reversal experiments. 140
87 The microcapsules studied were composed of a droplet¹⁴¹
88 of a positively charged biopolymer, chitosan, protected¹⁴²
89 by a thin membrane obtained through the complexation¹⁴³
90 at the oil-water interface of chitosan with a short-chain¹⁴⁴
91 fatty acid dissolved in the oil phase^{12,13}. The membrane¹⁴⁵
92 is on the order of few micrometers in thickness,¹⁴ and its¹⁴⁶
93 elasticity is characterized by a surface shear elastic modu-¹⁴⁷
94 lus G_s ¹⁵. G_s can be controlled and varied, by varying the¹⁴⁸
95 complexation time and the fatty acid concentration^{13,15},¹⁴⁹
96 enabling to discriminate the role of the particle deforma-¹⁵⁰
97 bility on the rheological behavior. 151

98 Firstly, we provided qualitative evidence of the aggre-¹⁵²
99 gation of these microcapsules when immersed in silicone¹⁵³
100 oil. Secondly, small amplitude oscillatory tests demon-
101 strated that these suspensions form gels. Thirdly, we
102 investigated the steady rheological properties for differ-¹⁵⁴
103 ent formulations of microcapsules. Finally, shear reversal
104 experiments were carried out, not only to evaluate the
105 relative contribution of contact and hydrodynamic forces¹⁵⁵
106 on the shear stress, but also to probe the structure of¹⁵⁶
107 the suspensions, thanks to an original asymmetric shear¹⁵⁷
108 reversal protocol. The latter revealed its sensitivity to¹⁵⁸
109 the shear history. We concluded that this system can be¹⁵⁹
110 classified as a fragile gel, whose microstructure depends¹⁶⁰
111 on the applied stress. 161

112 II. MATERIALS AND METHODS

113 A. Chemicals and Solutions

114 The assembly of microcapsules was achieved¹⁶⁹
115 by interfacial complexation of oppositely-charged¹⁷⁰
116 polyelectrolytes.^{12,15,16} Chitosan, a water soluble¹⁷¹
117 cationic polymer, forms a complex with oil soluble¹⁷²
118 anionic phosphatidic fatty acids (PFacid) at a water/oil¹⁷³
119 interface. 174

120 PFacid was used in a form of a commercial lecithin¹⁷⁵
121 known as lecithin YN (Palsgaard 4455, food-grade, E442)¹⁷⁶
122 which was kindly provided by Palsgaard. PFacid was¹⁷⁷
123 dissolved in food-grade rapeseed oil (Géant Casino) at a¹⁷⁸
124 concentration of 20% w/w at 35 °C during the night to¹⁷⁹
125 create a stock solution. Then PFacid solution was cen-¹⁸⁰
126 trifuged at 3500 g to remove the insoluble residuals. The¹⁸¹
127 stock solution was further diluted with rapeseed oil at re-¹⁸²
128 quired concentrations (0.1 % w/w for droplet generation¹⁸³
129 and 3 % w/w for interfacial complexation of the shell). 184

130 Chitosan (CAS n° 9012-76-4, Sigma-Aldrich) with¹⁸⁵
131 medium molecular weight and 75-85% deacetylation was¹⁸⁶
132 dissolved in Millipore water (Resistivity > 18.2 mΩ.cm)¹⁸⁷
133 at a concentration of 1 % w/w by adjusting the pH with¹⁸⁸
134 hydrochloric acid (1 mol/L) at 3.0. The chitosan solution¹⁸⁹
135 was then filtered to remove undissolved particles through¹⁹⁰
136 Minisart syringe filters (pore size 5.0 μm). The solution¹⁹¹
137 was diluted at 0.25 % w/w with water and glycerol (99.5¹⁹²
138 % purity, VWR) mixture. The water to glycerol ratio was¹⁹³
139 adjusted when needed in order to control the density of¹⁹⁴

the microcapsules.

Two silicone oils were used: AK1000
($C_3H_9Si(OSiC_2H_6)_xSiC_3H_9$, $M_w = 15.000$ M,
viscosity 0.855 Pa.s, CAS 63148-62-9) and AP1000
($C_3H_9Si(OSiC_8H_8)_x(OSiC_2H_6)_ySiC_3H_9$, unkown
molecular weight, viscosity 1.03 Pa.s, CAS 63148-58-
3) purchased from Wacker Chemie GMBH. AK are
dimethylpolysiloxanes whose unbranched chains are
made up of alternate silicone and oxygen atoms, the
free valancies of the silicone being saturated by methyl
groups. AP are polydimethylsiloxanes with a high
proportion of phenyl groups. The presence of phenyl
groups increases the relative permittivity from 3.1 for
AK to 3.35 for AP.¹⁷

162 B. Production and Preparation of suspensions

163 Suspensions of microcapsules were prepared with a
164 lab-scale membrane emulsification system marketed by
165 Micropore Technologies Ltd (UK) under the commer-
166 cial name Micropore LDC-1, as detailed in our pre-
167 vious publication.¹⁶ Briefly, it included a hydrophobic
168 micro-engineered emulsification membrane with 20 μm
diameter pores under a paddle-blade stirrer.¹⁸ 500 mL
of PFacid dissolved in commercial rapeseed oil (0.1 %
w/w) were stirred by the paddle at a rotational speed
of 600 rpm. 50 mL of chitosan solution was injected
by a syringe pump (neMESYS, CETONI) with a flow
rate of 2 mL/min through the membrane. The droplets
were sucked up from the dispersion cell with a tube and
collected in a beaker. Once the injection was finished,
a large volume of rapeseed oil highly concentrated in
PFacid was added to the suspension, bringing the over-
all PFacid concentration to 3%. Then the microcapsules
were kept under gentle stirring in the PFacid solution
until the membrane reached the desired stiffness. The
duration of chitosan / PFacid complexation process de-
termines the structure and elasticity of the membrane of
microcapsules.^{13,15} Thus, two suspensions with complex-
ation times of 4 and 8 minutes were produced to create
two populations of capsules with distinct shell elasticity.

The complexation of the PFacid with chitosan was
stopped by washing the rapeseed oil phase with large
volumes of cyclohexane. The washing procedure was
repeated ten times to ensure the removal of all PFacid
traces. Then the microcapsules were resuspended in sili-
cone oil AP1000 or AK 1000. The residual cyclohexane
in the suspending fluid was removed through dilution with
a large amount of silicone oil, then centrifuging the sus-
pension and removing the silicone oil. At each step of
dilution and centrifugation, the size distribution, shape,
and the presence of shell fragments were compared to the
control population to ensure that microcapsules were not
damaged. This procedure was continued until the differ-
ence in the viscosity between the extracted and pure oils
was less than 1 %. This precaution was taken to ensure
that there was no evaporation of residual of cyclohexane

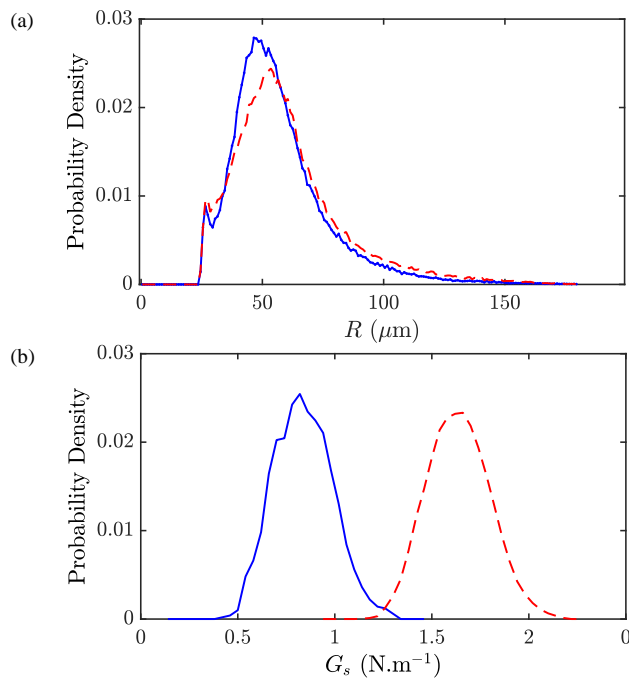


FIG. 1. Properties of two populations of microcapsules : (a) Size distribution and (b) surface elastic modulus G_s . Plain line: complexation time of 4 minutes. Dashed line: complexation time of 8 minutes.

195 during rheometric experiments, and thus the viscosity of
196 the continuous phase was a constant throughout the ex-
197 periments.

198 The densities of AP1000 and AK1000 were respec-
199 tively 1085.78 and 968.57 kg/m^3 at 25 $^\circ\text{C}$ which were
200 measured by a precise densimeter (DMA 4500M, Anton
201 Paar). Glycerol was added to the chitosan solution in
202 order to tune the density of the microcapsules. The den-
203 sity of the capsules suspended in AP1000 was adjusted
204 at 1065.52 kg/m^3 by adding 28 % w/w of glycerol in the
205 chitosan solution. For capsules suspended in AK1000, it
206 was not required to add glycerol in the chitosan solution.
207 The difference in density between the silicone oil and the
208 chitosan solution was of 1.86 % and 2.93 % for AK1000
209 and AP1000 respectively. This small density contrast fa-
210 cilitated the washing procedure in the suspension prepa-
211 ration.

212 C. Characterization of physical properties

213 Volume fraction and size distribution of microcapsule
214 suspensions were measured by bright field microscopy.
215 Firstly, 40 mL of the produced dense suspension of mi-
216 crocapsules was well mixed to be homogenized. Then at
217 least three samples of 0.4 mL were diluted with 10 mL
218 of silicone oil. Microcapsules were placed on large mi-
219 croscope slides and scanned entirely by an inverted mi-

220 croscope Olympus IX-73 equipped with a 4, 10, or 20 \times
221 objective, a Marzhauser motorized stage, and a camera
222 Hamamatsu ORCA-Flash 4.0. The size and total vol-
223 ume of the microcapsules were measured with a custom
224 written software based on the Matlab image processing
225 toolbox (Mathworks). The volume fraction of the pro-
226 duced dense suspension of microcapsules was then calcu-
227 lated by determining the total volume of microcapsules
228 in the three samples. Then the dense suspension was
229 diluted with silicone oil to produce suspensions with vol-
230 ume fraction ranging from $\phi = 0.1$ to 0.52.

231 The surface shear elasticity G_s of the microcapsule
232 shell, i.e. its interfacial linear elastic modulus, was mea-
233 sured in an extensional flow chamber¹⁹ that has been
234 automatized to study a large number of microcapsules
235 according to the methodology shown in our previous pub-
236 lication, see Ref.¹⁶ for details. Briefly, the character-
237 ization involves injecting a sample of microcapsules into
238 a millifluidic cross-slot chamber and observing their de-
239 formation under a range of hydrodynamic extensional
240 stresses, σ_h , by bright field microscopy and high speed
241 imaging. In such flow, the capsules deform into ellipses.
242 In the small deformation regime, the Taylor parameter
243 ($= (L - S)/(L + S)$, with L and S the large and small
244 length of the ellipse, respectively of the ellipse) evolves
245 linearly with the Capillary number, $Ca = \sigma_h R/G_s$, al-
246 lowing us to determine G_s for each microcapsule. Since
247 the suspension of microcapsules is not homogeneous, we
248 plotted the probability distribution function of G_s and
249 computed the mean value for the sample, Figure 1.

Finally, size and G_s distribution are shown in Figure
1 for both populations of microcapsule suspensions. As
expected, the average G_s increased from 0.8 to 1.7 N/m
when the time of complexation increased from 4 to 8 min,
standard deviation of 18% and 8% respectively. Both
populations had a mean radius of 57 μm with a standard
deviation of 36%. These values were independent of the
kind of silicone oil in which the capsules were dispersed.
From previous studies,^{13,14} we expect that the thickness
of the membrane was about 1 μm .

D. Rheometry

261 Rheological measurements were carried out with a
262 stress-controlled rheometer (DHR3, TA) with a rotating
263 parallel plate disk geometry. The gap and the diameter
264 of the geometry were 1.5 mm and 60 mm respectively.
265 This gap value was chosen to accommodate 10 to 15 mi-
266 crocapsules in the gap. Moreover, we observed that the
apparent viscosity of the suspension was independent of
the gap, if the latter was larger than 1 mm. Smooth and
rough surfaces were used, without any incidences on the
results, meaning that there was no evidence of wall slip
effects. Since in a parallel plate geometry the shear rate
is not constant and varies from the center to the rim,
we corrected the measured viscosity with the Mooney-

274 Rabinovitch correction,²⁰

$$\eta_s = \eta_{app} \left[1 + \frac{1}{4} \frac{d}{d} \frac{\ln(\eta_{app})}{\ln(\dot{\gamma})} \right] \quad (1)$$

275 where η_{app} is the apparent viscosity measured by the
276 rheometer, d the diameter of the geometry and $\dot{\gamma}$ the
277 shear rate at the rim. The temperature was controlled
278 with a Peltier system at 25°C.

279 The shear viscosities of the suspending silicone oils
280 AP1000 and AK1000 were measured. Both oils were a
281 Newtonian fluid at least up to 200 s⁻¹ with a viscosity of
282 $\eta_c = 1.03 \pm 0.01$ Pa.s for AP1000 and 0.855 ± 0.01 Pa.s
283 for AK1000 at 25°C. Additionally, it was verified that³²⁷
284 silicone oils did not have a viscoelastic behavior.

285 Shear-reversal experiments were carried out to study³²⁸
286 the microstructure of the suspension under a given shear
287 stress, as proposed by Gadala-Maria *et al.*⁶ The suspen-
288 sions were pre-sheared with a shear stress σ of 10 Pa for³²⁹
289 30 s. Then, a constant shear stress (from 1 to 100 Pa)³³⁰
290 was imposed on the suspension until the measured vis-³³¹
291 cosity achieved a steady state. Then, the imposed stress³³²
292 was set to zero for 20 seconds. The last step consisted in³³³
293 shearing the suspension with the same stress but in the³³⁴
294 opposite direction.³³⁵

295 Carrying out shear reversal experiments required care-³³⁶
296 ful consideration of inertia issues.²¹ To confirm that the³³⁷
297 rheometer measures an accurate shear rate after rever-³³⁸
298 sal, we performed shear reversal on newtonian silicone³³⁹
299 oil AP1000 without microcapsules, testing waiting times³⁴⁰
300 of 1, 2, and 10 s for torques ranging from 8 to 2,048 $\mu\text{N}\cdot\text{m}$.³⁴¹
301 When the stress was reversed after the waiting time, it³⁴²
302 took 0.1 seconds to reach a steady viscosity value, re-³⁴³
303 gardless of the waiting time or torque. This indicates³⁴⁴
304 that the reliable time over which we can assess shear re-³⁴⁵
305 versal was 0.1 s for waiting times longer than 1 s. We³⁴⁶
306 also hypothesized that the suspension of microcapsules³⁴⁷
307 could rearrange during the waiting period. To rule out³⁴⁸
308 this hypothesis, we tested waiting times of 1, 10, and³⁴⁹
309 100 s at a stress of 10 Pa for a suspension of microcap-³⁵⁰
310 sules ($\phi = 0.23\%$) in AP1000, and observed no significant³⁵¹
311 impact on the viscosity dynamics with respect to strain
312 rate.³⁵²

313 The transient evolution of the viscosity after stress re-³⁵³
314 versal was analyzed within the same framework as for³⁵⁴
315 non-Brownian suspensions,^{6,7,21} by decoupling the steady³⁵⁵
316 viscosity of the suspension η_s into hydrodynamic viscos-³⁵⁶
317 ity η_h and contact viscosity η_c , i.e., $\eta_s = \eta_c + \eta_h$. Just³⁵⁷
318 before shear reversal, the suspension is in a steady state.³⁵⁸
319 Upon reversal, in hard-sphere systems, contact forces will³⁵⁹
320 drop to zero immediately after reversal. It takes a few³⁶⁰
321 units of strain for the contact forces to rebuild, mak-³⁶¹
322 ing the viscosity temporarily dominated by the hydrody-³⁶²
323 namic contribution. Consequently, the minimum viscos-³⁶³
324 ity observed is interpreted as the hydrodynamic viscosity,³⁶⁴
325 and the contact viscosity is deduced by the relationships³⁶⁵
326 $\eta_c = \eta_s - \eta_h$.³⁶⁶

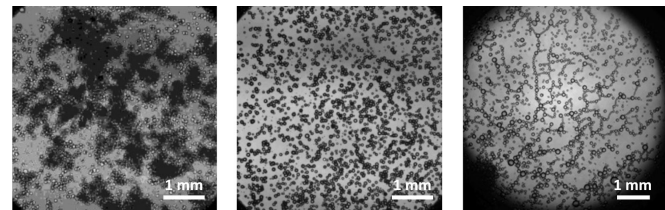


FIG. 2. Aggregates of microcapsules in AK 1000 (left), AP 1000 (middle) and chains formation under an electric field for AK 1000 (right).

III. RESULTS AND DISCUSSION

A. Aggregation in suspensions of microcapsules

The microcapsules used to create the various suspen-
sions were produced through interfacial complexation of
a positively charged biopolymer, chitosan, with a nega-
tively charged surfactant, PFacid. Three different sys-
tems were examined. Two density-matched suspensions
were prepared in AP1000 silicone oil with capsules ex-
hibiting a twofold increase in shear elasticity, as shown in
Fig. 1. The stiffer capsules were also studied in AK1000
silicone oil. The rheological properties were studied for
 ϕ varying between 0.1 and 0.52.

When dispersed in silicone oil, microcapsules tended
to spontaneously form aggregates at rest. Figure 2-a, b
shows a suspension of microcapsules with a volume frac-
tion ϕ of about 0.3 suspended in AK1000 and AP1000.
Initially, the microcapsules were well dispersed in the
petri dish. After few hours at rest, the capsules were
assembled. Millimetre flocs were observed for both oils
with AP1000 having smaller aggregates than AK1000,
whereas the microcapsules tended to form chains in
AP1000. These structures were easily broken by touch-
ing them with a needle. When subjected to an electric
field, the microcapsules created a network-like structure,
Fig. 2, c.

What arouses our curiosity in these preliminary qual-
itative observations is that this system of non-brownian
particles exhibits a reversible aggregation phenomenon
that is ubiquitous in colloidal suspensions.⁹ The fact that
such behaviour is not common in suspensions of parti-
cles, where interactions are mainly controlled by hydro-
dynamic and friction, motivated us to study the rheologi-
cal properties of such suspensions. The physical origin of
these interactions is an open question outside the scope
of this paper. However, it is highly unlikely that the at-
traction is due to depletion phenomena, as the continuous
phase (silicone oil) was washed several times to remove
any excess surfactant (PFacid). The formation of chains
led us to speculate that these capsules could exhibit a
dipole moment when subjected to an electric field.

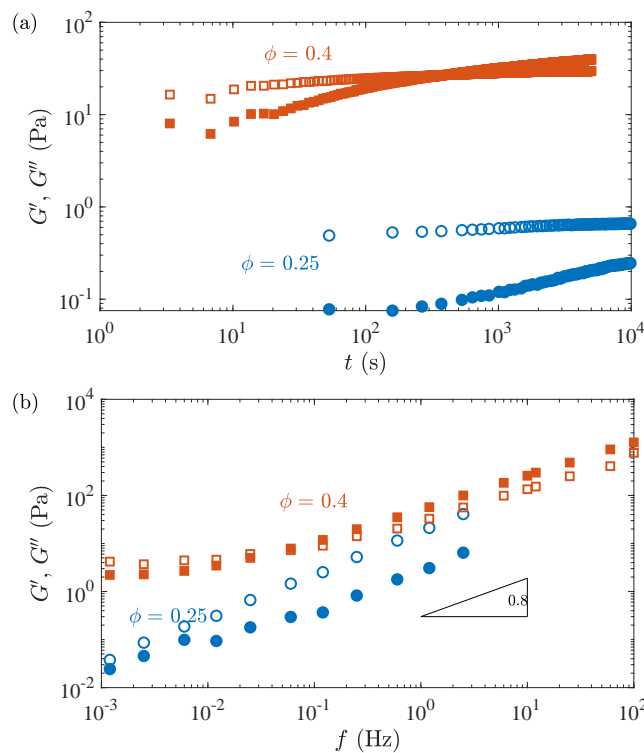


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367 B. Viscoelastic properties

368 The kinetics of gelation was characterized with a time
369 sweep oscillation at constant amplitude γ and frequency
370 f for the microcapsules suspended in AK1000, which had
371 shown the strongest aggregation, Fig. 2-left. For each
372 sample, the choices of γ and f were justified by a com-
373 promise between signal sensibility and minimizing the
374 disturbance of the gelation by the applied stress, see cap-
375 tion of Fig. 3 for details. For the largest volume fraction
376 ($\phi = 0.4$), G' increased slowly, whereas G'' gained almost
377 one order of magnitude in one hour, Fig. 3-a. The elastic
378 contribution was larger than the viscous one after 100 s,
379 which corresponded to the critical onset of a solid net-
380 work. This rheological behaviour is typical of colloidal
381 systems in the process of forming a network.²² At low
382 volume fraction ($\phi = 0.25$), G' also increased with time
383 but never exceeded G'' on the time scale investigated.

384 The linear viscoelastic properties of the suspensions
385 when the network was formed were probed by frequency



386 FIG. 3. Gelation and viscoelastic properties of suspensions of
387 microcapsules. (a) G' (closed symbols) and G'' (open sym-
388 bols) as a function of time t for suspensions of microcapsules
389 at volume fraction $\phi = 0.4$ in AK1000 (red squares, $\gamma = 0.2\%$,
390 $f = 0.3$ Hz) and 0.25 (blue circles, $\gamma = 1\%$, $f = 0.02$ Hz).
391 (b) Frequency sweep experiments for the same suspensions
392 after a pre-shear to break up the network of microcapsules.
393 Pre-shear of 100 Pa during 10 s and waiting time of 400 s for
394 $\phi = 0.4$. Pre-shear of 30 Pa during 10 s and waiting time of
395 3000 s for $\phi = 0.25$. $G_s = 1.7$ N/m.

386 step tests at constant γ , Figure 3-b. Before each fre-
387 quency step, the suspension was pre-sheared to rejuve-
388 nate the sample and break the network formed during
389 the previous step. The pre-shear was set to 100 and 30
390 Pa for 10 seconds for $\phi = 0.4$ and 0.25, respectively, at
391 which point continuous shear rheometry showed that the
392 network was broken (see details below). Then, the sus-
393 pension left to rest for a given time in order to let it form
394 a new microstructure. Waiting times were set to 400 and
395 3000 s for $\phi = 0.4$ and 0.25, respectively, the time at
396 which G' roughly stabilized, Fig. 3-a.

397 For both volume fractions, G' and G'' increased nearly
398 linearly with the frequency f ($G \sim f^{0.8}$) at high f . For
399 the largest volume fraction ($\phi = 0.4$), a plateau for both
400 moduli at low frequency was found and G'' was lower
401 than G' . These rheological characteristics were reminis-
402 cent of those of suspensions of attractive colloids forming
403 a percolated network. Trappe and Weitz⁹ established
404 that the frequency-dependent linear viscoelastic moduli
405 of suspensions of attractive colloidal suspensions can be
406 scaled onto a universal master curve characterized by a
407 plateau at low frequency and a power law at high fre-
408 quency. The suspensions of microcapsules behaved re-
409 markably similar to their Brownian counterpart. Behind
410 this scaling, the physical picture is that the microcapsules
411 form a solid network with a frequency-independent elastic
412 modulus G'_0 , obtained at low frequency. G'_0 increases
413 with ϕ , meaning that the network becomes more robust
414 when ϕ increases. At large frequencies, the viscosity of
415 the suspending phase inside the network dominates the
416 viscoelastic response.⁹

417 C. Steady state rheology

418 Steady state viscosities η_s of the suspensions of mi-
419 crocapsules were measured in a stress-controlled plate-
420 plate geometry. Figure 4-a shows the steady-state flow
421 curve σ vs. $\dot{\gamma}$. The flow curves were obtained in stress-
422 imposed experiments, following a pre-shear of 10 Pa for
423 each stress. In this example, the suspensions behaved like
424 a yield stress fluids even for ϕ of 0.1. Flow curves were
425 well-fitted by the Herschel-Bulkley constitutive equa-
426 tions $\sigma = \sigma_y + K\dot{\gamma}^n$ where σ_y is the yield stress, K is the
427 consistency factor and n the shear-thinning exponent. σ_y
428 was deduced from the transient response of the suspen-
429 sion, η as a function of the deformation γ , as shown in
430 Figure 4-b. At high stress, η reached a steady state for
431 γ of about 10. At low stress, η diverged for $\gamma = 2$, which
432 allowed us to identify σ_y . σ_y was so indicated arbitrarily
433 at a shear rate of 10^{-3} s^{-1} in Figure 4-a.

434 Figure 5 shows σ_y and n as a function of ϕ for AK1000
435 and AP1000 and microcapsule complexation time of 4
436 and 8 min. For AK1000, the suspensions showed a yield
437 stress σ_y of 0.2 Pa as soon as ϕ was larger than 0.1 and
438 increased exponentially with ϕ up to 4 Pa for $\phi = 0.4$.
439 The behaviour was slightly different for AP1000. Be-
440 low a critical volume fraction of 0.25, the suspensions

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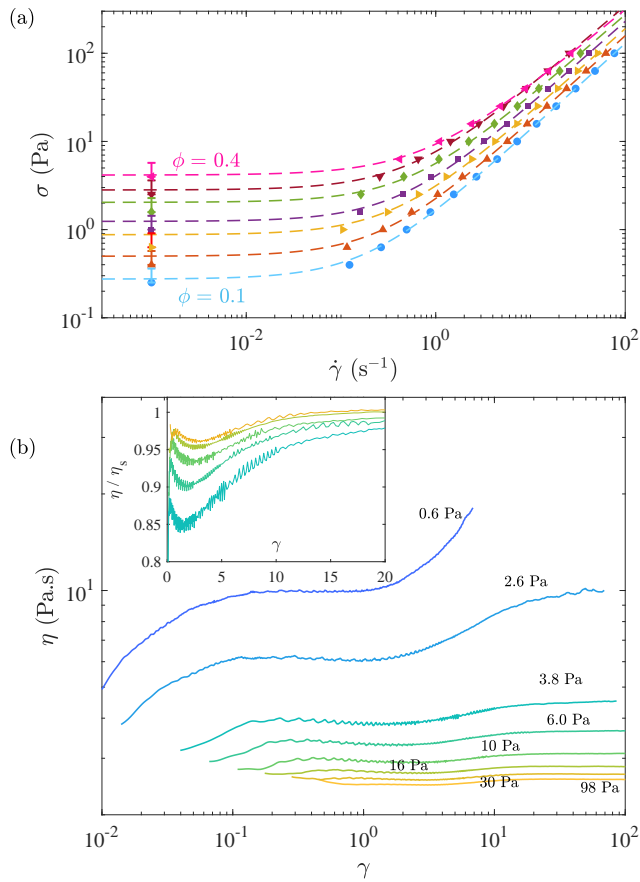


FIG. 4. Flow curves of suspensions of microcapsules in stress-imposed experiments, following a pre-shear of 10 Pa. (a) Steady-state flow curves $\sigma(\dot{\gamma})$ for different ϕ . From bottom to top, ϕ increases from 0.1 to 0.4 by steps of 0.05. The value of σ_y are arbitrarily indicated at $\dot{\gamma} = 10^{-3} \text{ s}^{-1}$. The dashed lines are the Herschel-Bulkley fits for each flow curve. (b) Apparent shear viscosity η at $\phi = 0.25$ as a function of the deformation γ after symmetric reversal of the stress σ (see text). Decreasing values of σ from yellow to blue. The yield stress σ_y is determined when η diverges with γ . The sub-caption shows the same set of data in a linear-linear plot, where the y-axis represents η/η_s , and the x-axis represents γ . The local minimum at $\gamma = 2 - 3$ is interpreted as corresponding to the hydrodynamic viscosity η_h . $G_s = 1.7 \text{ N/m}$, AK1000.

441 were Newtonian. Above this value, σ_y was well-fitted
442 by critical-like functional form introduced by Trappe *et*
443 *al.*¹⁰ for attractive colloidal suspensions $\sigma_y = \sigma_0(\phi - \phi_c)^\alpha$
444 where $\phi_c = 0.2$ is the critical volume fraction, $\alpha = 2.2$
445 is a power law exponent and $\sigma_0 = 15 \text{ Pa}$, solid line in
446 Fig. 5-a. Regardless of the suspending fluid, n decreased
447 slightly up to 0.8 for $\phi = 0.52$.

448 While it is expected to obtain yield stress fluids at
449 low volume fraction for attractive colloids, suspensions of
450 athermal solid particles jam when ϕ approaches the max-
451 imal volume fraction ϕ_m which ranges between 0.55 and
452 0.63 due to contacts.²³ Our system of microcapsules ex-
453 hibited an astonishing rheological behavior, which closely

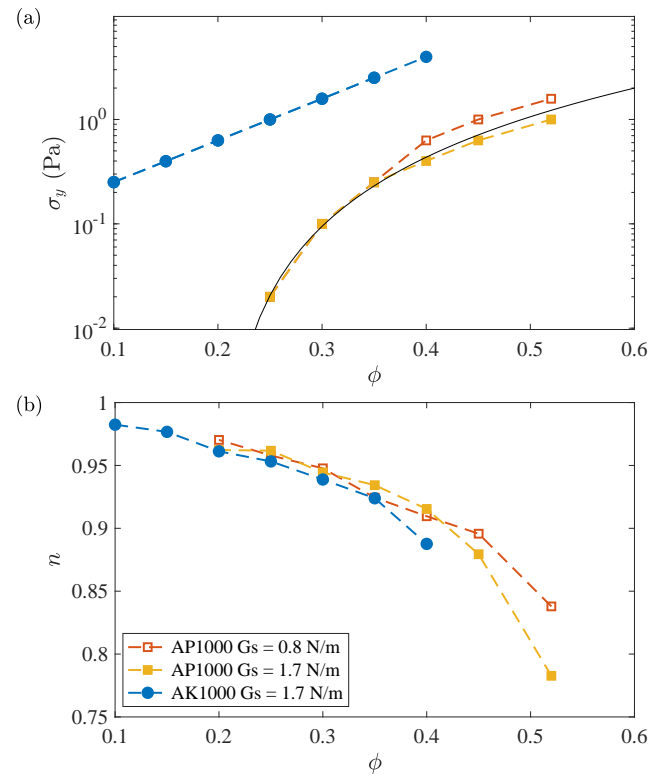


FIG. 5. Constitutive parameters of the suspensions of microcapsules. (a) Yield stress σ_y as a function of the volume fraction ϕ . Dashed line is the fit $\sigma_y = \sigma_0(\phi - \phi_c)^\alpha$ with $\sigma_0 = 15$, $\phi_c = 0.2$ and $\alpha = 2.2$. (b) Shear-thinning exponent n as a function of ϕ .

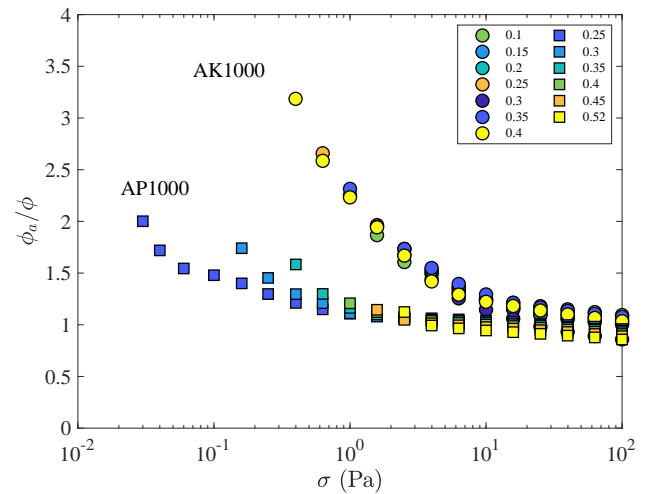


FIG. 6. Re-scaled apparent volume fraction ϕ_a/ϕ as a function of the shear stress σ for ϕ ranging from 0.1 to 0.4 in AK1000 (circles) and from 0.2 to 0.52 in AP1000 (squares). $G_s = 1.7 \text{ N/m}$.

matched the Bingham fluid with the emergence of a yield stress at very low ϕ (0.1). It is unlikely that this be-

456 haviour could be attributed to the deformability of the
457 particles, as numerical simulations have shown that def-
458 formability tends to increase the maximal volume frac-
459 tion ϕ_m .^{24,25} Moreover, the maximal capillary number
460 $Ca = \sigma R/G_s$, that represents the ratio of viscous stress
461 over the elastic shell response, was of the order of 10^{-3} for
462 $\sigma = 20$ Pa. Moreover, the low degree of shear-thinning
463 contrasts with suspensions of soft particle glasses near
464 jamming, which interact via soft elastic interactions and
465 exhibit a n coefficient of 0.5 ²⁶⁻²⁸ due to elasto-hydro-
466 dynamic interactions.²⁹ For microcapsules suspended in
467 AP1000, we compared a twofold increase in surface shear
468 elasticity G_s . For ϕ below 0.4, there were no effects of
469 G_s on σ_y . For ϕ values exceeding 0.4, σ_y was slightly
470 larger for the softest capsules but remained within the
471 uncertainty of the yield stress measurement, Fig. 5. If
472 the yielding of these suspensions of microcapsules were
473 controlled by soft lubrication interactions, we would ex-
474 pect σ_y to scale with G_s .²⁹ However, post-yielding, the
475 fact that n decreases with ϕ could be attributed to soft
476 lubrication between the microcapsules at high stress, a
477 hypothesis further supported by shear reversal experi-
478 ments.

479 To the best of our knowledge, only one similar system
480 has been presented recently by Dhand *et al.*¹¹ in which
481 the interactions between microcapsules of few hundreds
482 micrometers were induced, equally, by the presence of a
483 charged polymer in the capsule. Similarly to our system,⁵¹⁰
484 yield stresses of the order of 10^{-2} Pa were reported for ϕ ⁵¹¹
485 of 0.2. 512

486 It is also instructive to compute the apparent volume⁵¹³
487 fraction ϕ_a as a function of the applied stress σ of the⁵¹⁴
488 suspensions by using correlations established for repul-⁵¹⁵
489 sive suspensions of solid particles. Chevremont *et al.*^{4,516}
490 introduced the following correlations 517

$$\eta_s = \frac{\mu_1}{(\phi_m/\phi_a - 1)^2} + \frac{\mu_2 - \mu_1}{(\phi_m/\phi_a - 1)^2 + I_0} + (1 - \phi_a)^{-5/2} \quad (2)$$
518
519
520
521
522

491 where $\mu_1 = 0.36$, $\mu_2 = 0.7$, $I_0 = 0.0133$ are coefficients⁵²³
492 obtained by fitting this relation to a minimal model based
493 on lubrication and contact forces between hard particles.⁴
494 This expression is asymptotically equivalent to Einstein
495 relation³⁰ at low ϕ and also asymptotically equivalent to⁵²⁴
496 the Krieger-Dougherty form when ϕ is approaching ϕ_m .³¹
497 ϕ_m can range from 0.63 to 0.55 depending on the friction⁵²⁵
498 coefficient between the particles.⁴ 526

499 Figure 6 shows the ratio ϕ_a/ϕ as a function of σ for⁵²⁷
500 AK1000 (circles) and AP1000 (squares) for different ϕ ⁵²⁸
501 (color code). At low stress, ϕ_a was 2 to 3 times larger⁵²⁹
502 than ϕ . This is consistent with the existence of aggre-⁵³⁰
503 gates at low stress, since the effective volume of an ag-⁵³¹
504 gregate is larger than the volume of capsules constituting⁵³²
505 it. Thus, the apparent volume fraction of a suspension of⁵³³
506 aggregates of particles is higher than that of a suspension⁵³⁴
507 of isolated particles. At high stress, ϕ_a/ϕ tends to 1,⁵³⁵
508 meaning that the stress was enough to overcome the at-⁵³⁶
509 tractive interactions and broke the aggregates. Moreover,⁵³⁷

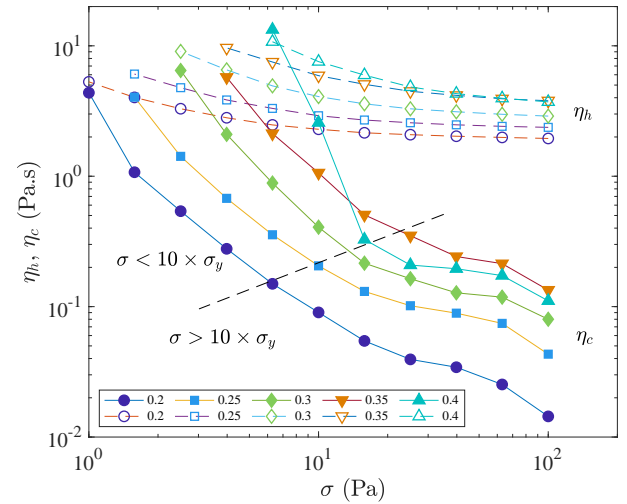


FIG. 7. Symmetric shear reversal. Hydrodynamic and contact viscosities, η_h (open symbols) and η_c (closed symbols) respectively, as a function of the stress σ for suspensions of microcapsules; ϕ ranged from 0.2 to 0.35. The applied stress was always larger than the yield stress of the suspension. The dashed line corresponds to the point where the stress is equal to 10 times the yield stress. $G_s = 1.7$ N/m, AK1000.

the viscosity of the suspension was controlled by conventional hydrodynamic and contact interactions. The value of ϕ_m to calculate ϕ_a from the experimental data did not provide any meaningful interpretation regarding the frictional nature of the contact. Comparing the two oils revealed a tenfold difference in the critical stress separating the two regimes. This set of results suggested strongly that the aggregated state of the suspension under flow was dependent on the applied stress. If the stress was low enough, a percolated network of aggregates was formed in the suspension leading to an apparent gelation of the fluid. At high stress, these aggregates were broken and the system behaved as a classic suspension of solid particles.

D. Hydrodynamic & contact viscosities

Transient rheometrical tests were carried out in order to probe the relationships between the applied stress and the structure of suspensions of microcapsules. We tested two protocols of shear reversal experiments: symmetric and asymmetric.

In symmetric shear reversal experiments, a specific shear stress magnitude (σ^-) is initially applied in one direction. The direction of this shear stress is then reversed when the shear rate reaches a steady state, maintaining the same magnitude in the reversed direction, i.e. $\sigma^+ = \sigma^-$.

Figure 4-b and its sub-caption shows the apparent viscosity η as a function of γ after reversal of the stress direc-

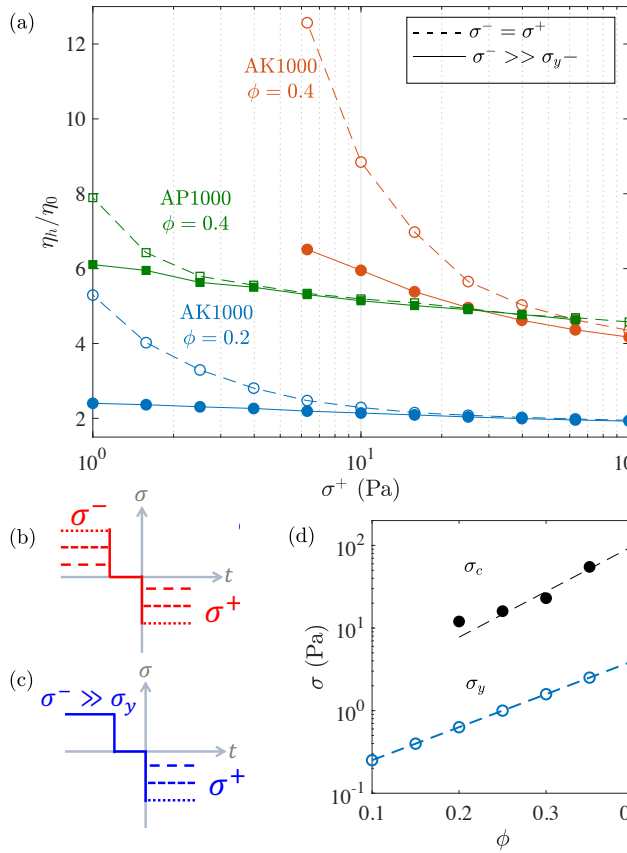


FIG. 8. Symmetric and asymmetric shear reversal. (a) Normalised hydrodynamic viscosity η_h/η_0 as a function of the reversal stress σ^+ in symmetric (dashed lines, $\sigma^- = \sigma^+$) and asymmetric (plain lines, $\sigma^- \gg \sigma_y$) shear reversal experiments for three suspensions. η_0 is the viscosity of the suspending silicone oil. (b) In symmetric shear reversal experiments, only the direction of the stress was reversed, while its magnitude remained constant, i.e. $\sigma^- = \sigma^+$. (c) In asymmetric shear reversal experiments, the pre-stress σ^- was always larger than the yield stress, i.e. $\sigma^- \gg \sigma_y$ in order to break the aggregates of microcapsules, before the reversal of the stress. (d) σ_c as a function of ϕ for AK1000. σ_c is defined such that η_h equals $\pm 5\%$ in both symmetric and asymmetric reversal experiments. The plot also shows the evolution of σ_y with ϕ . Dashed lines represent exponential fits. $G_s = 1.7$ N/m.

tion. One initial observation is that when the stress was below the yield stress (blue curve, $\sigma < \sigma_y$), the viscosity η experienced a sudden drop to a minimum, followed by a continuous increase until it reached an apparent plateau within the range of γ values between 0.1 and 1. Beyond $\gamma = 2$, η diverged: the reversal of the stress induced a transient fluidization of the suspension. This feature is characteristic of an anisotropic structure of the suspension, that has to rearrange when the stress is reversed.⁸

When the stress was greater than σ_y , the apparent viscosity decreased to reach a minimum for a deformation of about 2-3 decreased (interpreted as η_h) and then con-

tinuously increased to reach the steady state value η_s . This qualitative behaviour is in line with the case of solid particles. When the shear is reversed, it triggers a rapid relaxation of contact forces.⁶ This relaxation occurs over a deformation typically on the order of unity and results in a notable decrease in viscosity, the viscosity reaching a minimum value. Subsequently, the long-term evolution of the system is influenced by the development of shear-induced microstructure. In the case of solid particles, numerical simulations^{32,33} enabled to interpret the minimum viscosity at $\gamma = 2-3$ as the hydrodynamic viscosity η_h , obtained when the contact forces are vanished. The difference between the steady viscosity η_s and η_h is shown to be proportional to the contact contribution to the steady viscosity.^{32,33} Due to the similarity of the transient evolution of the viscosity after reversal with the case of solid particles, we adopted the same interpretation of $\eta(t)$ when $\sigma > \sigma_y$.

Fig. 7 shows η_h (open symbol) and η_c (closed symbols) as a function of σ and different ϕ for AK1000. σ is always larger than σ_y . At low stress, η_c and η_h are of the same order of magnitude, whereas η_c drops of several orders of magnitude and η_h stabilize when $\sigma > 10 \times \sigma_y$. For a given σ , η_c and η_h increases with ϕ . It is worth highlighting that η_c was strongly shear-thinning, with n being approximately 0.5. This is potentially a signature of hydrodynamic interactions controlled by the deformability of the microcapsules.²⁹

In our asymmetrical shear reversal experiments, we ensured that σ^- exceeded the critical threshold necessary to break the clusters of microcapsules, i.e. $\sigma^- \gg \sigma_y$. Following this step, we systematically varied σ^+ within the range of σ_y to $100 \times \sigma_y$. Fig. 8 illustrates the behavior of η_h as a function σ^+/σ_y for different ϕ , employing both symmetric (open symbols) and asymmetric (closed symbols) protocols. At low stress, η_h exhibited a marked increase in the asymmetric protocol compared to the symmetric one. This is consistent with the picture that, in the asymmetric protocol, we reversed the shear with a suspension of individual particles, whereas in the symmetric one, aggregates of microcapsules were initially formed. Conversely, at high stress, the values of η_h were consistent, regardless of the employed protocol. The stress σ_c above which both protocols lead to the same values of η_h was much larger for suspension in AK1000 than in AP1000. Since this characteristic stress could be interpreted as the typical stress to overcome attractions between capsules, this difference between the two suspensions is consistent with the interpretation of the fact that the yield stress originated from attractive interactions, the latter being stronger for capsules dispersed in AK1000 than in AP1000. As shown in Figure 8-d, the stress σ_c increased when the volume fraction was increased, and is typically 10 times higher than the yield stress. Above this characteristic stress, the suspension could be viewed as a suspension of weakly interacting isolated spheres, in contrast with weaker stresses where the suspension is made of dispersed aggregates, whose size



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608 increased up to percolation when the stress is decreased⁶⁶³
609 down to the yield stress. We reported this transition⁶⁶⁴
610 from aggregated to isolated spheres in Fig. 7. Clearly,⁶⁶⁵
611 even above this stress, the contribution of contact forces⁶⁶⁶
612 to the viscosity is shear-thinning.

613 E. Key Findings

614 The different key rheological elements of these suspen-⁶⁷²
615 sions of attractive microcapsules, which show rheological⁶⁷³
616 features akin to colloidal attractive systems, are summa-⁶⁷⁴
617 rized.⁶⁷⁵

618 Time and frequency sweep oscillations demonstrate the⁶⁷⁶
619 spontaneous aggregation of these microcapsules, lead-⁶⁷⁷
620 ing to the formation of a gel depending on the vol-⁶⁷⁸
621 ume fraction, Fig. 3. Analogous to attractive colloidal⁶⁷⁹
622 systems^{9,10}, G' tending to a constant at low frequency⁶⁸⁰
623 was interpreted as the signature of a percolated network⁶⁸¹
624 of aggregates.⁶⁸²

625 In consistency with these oscillatory experiments,⁶⁸³
626 steady-state rheology shows the emergence of yield stress⁶⁸⁴
627 for volume fractions as low as 0.1, Fig. 4, 5. Moreover,⁶⁸⁵
628 over the range of volume fractions studied (up to 0.5),⁶⁸⁶
629 the shear thinning is very moderate, making these sus-⁶⁸⁷
630 pensions a rare example of a Bingham fluid. All these⁶⁸⁸
631 elements support the idea that at low stress, microcap-⁶⁸⁹
632 sules form a percolated network of aggregates, and at⁶⁹⁰
633 high stress, the suspension of microcapsules resembles⁶⁹¹
634 that of a suspension of non-Brownian hard spheres, Fig.⁶⁹²
635 6.⁶⁹³

636 Unsteady rheology was also tested by symmetric shear⁶⁹⁴
637 reversal experiments, Fig. 7. The apparent viscosity⁶⁹⁵
638 showed a decay when the stress was reversed at low⁶⁹⁶
639 stress, demonstrating that the microstructure of the per-⁶⁹⁷
640 colated network of aggregates is anisotropic, depends on⁶⁹⁸
641 the shear direction, and is unable to sustain changes in⁶⁹⁹
642 stress direction. This makes these suspensions a kind⁷⁰⁰
643 of "fragile gel" based on non-colloidal particles.^{34,35} A⁷⁰¹
644 "fragile" gel has a self-organized internal structure com-⁷⁰²
645 posed of force chains, whose mechanical properties have⁷⁰³
646 evolved to support the load itself. However, the material⁷⁰⁴
647 is not an elastic body; if one attempts to shear the sample⁷⁰⁵
648 in a slightly different direction, static equilibrium cannot⁷⁰⁶
649 be maintained without altering the existing force chains⁷⁰⁷
650 and creating new ones with a slightly different orienta-
651 tion. Consequently, when the force direction is changed,
652 the suspension flows again and stops only once a certain⁷⁰⁸
653 strain is accumulated to recreate the force chains.

654 Shear reversal also revealed that the interaction be-⁷⁰⁹
655 tween the microcapsules is controlled by elasto-hydrody-⁷¹⁰
656 namic interactions at high stress, similar to soft glassy⁷¹¹
657 particles,²⁹ as the contact viscosity was strongly shear-⁷¹²
658 thinning. This allowed us to interpret the moderate de-⁷¹³
659 cay of n at high volume fractions as a sign of soft lubri-⁷¹⁴
660 cation. Moreover, it is interesting to note that transient⁷¹⁵
661 rheological experiments, such as shear reversal, appear⁷¹⁶
662 to be much more sensitive to elasto-hydrodynamic inter-⁷¹⁷

actions than classic steady-state rheometry. This could
be further analyzed through numerical simulations.

We also introduced asymmetric shear reversal proto-
cols, which provide physical insights for this kind of frag-
ile suspension: the hydrodynamic viscosity was larger at
low stress when the pre-stress (σ^-) was high enough to
break the aggregates compared to when the prestress was
equal to the stress ($\sigma^- = \sigma^+$). At high stress, there was
no influence of the protocol on the hydrodynamic stress,
and the hydrodynamic contribution to the viscosity tends
to be rate independent. These results confirm our inter-
pretation of the steady-state rheology.

All these observations differ significantly from those
of a soft adhesive suspension, as recently reported by
Gilbert *et al.*⁵. The systems are rather different since
homogeneous PDMS particles were considered instead of
microcapsules. Gilbert *et al.* demonstrated that this sys-
tem is deformable (with an elastic modulus of 1.8 MPa)
and adhesive (with a characteristic adhesive stress of a
few Pa). The main rheological signature of this system is
the presence of shear-thinning behavior at low shear rates
and high volume fractions (greater than 0.3). No yield
stress was directly evidenced. This behavior is thus very
different to the present observations of a Bingham fluid
down to very low volume fraction. It indicates that adhe-
sion plays a minor role. The fact that the surface modu-
lus has no influence on the rheological properties, and the
presence of a reduced viscosity after reversal also confirm
that adhesion is negligible. Indeed, adhesion forces are
very sensitive to contact area and thus to particle stiff-
ness, and, if contacts were adhesive, they would mostly
remain just after shear reversal.

To sum up, the rheology of these suspensions of at-
tractive microcapsules is controlled by long-range inter-
actions at low stress, making them a kind of fragile gel.
However, at high stress and high volume fraction, soft
lubrication also plays a role in shear-thinning.

We also identified that the type of silicone oil changes
the constitutive parameters of these suspensions and the
stress at which the aggregates are broken. Preliminary
experiments (Fig. 2) lead us to speculate that this is
due to dipolar or coulombic interactions between the ob-
jects, whose range depends on the relative permittivity
of the oil. The detailed physical characterization of these
interactions however require dedicated investigations.

IV. CONCLUSION

In conclusion, this article shows that these suspensions
of droplets of a positively charged biopolymer, chitosan,
encapsulated by complexation with an anionic fatty acid,
constitute a novel class of non-Brownian suspensions,
exhibiting similarities with their Brownian counterparts
due to the presence of long-range interactions between
particles. At low stress and low volume fraction, these
attractive microcapsules form an anisotropic percolated
network. Due to this anisotropy, these gels cannot sus-



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- tain changes in shear direction, categorizing these sus-
pensions as an example of a fragile suspension.^{34,35}
- The exact physical origin of the attractive interaction
remains an open question, and deserve further investiga-
tions. We showed in this paper that it is possible to tune
this interaction - and thus to tune the gel elasticity and
yield stress - by changing the suspending liquid dielectric
properties, which we believe to be a promising outcome
in terms of potential applications.
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