Suspensions of cornstarch in water exhibit strong dynamic shear thickening. We show that partly replacing water with ethanol strongly alters the suspension rheology. We perform steady and nonsteady rheology measurements combined with atomic force microscopy to investigate the role of fluid chemistry on the macroscopic rheology of the suspensions and its link with the interactions between cornstarch grains. Upon increasing the ethanol content, the suspension goes through a yield-stress fluid state and ultimately becomes a shear-thinning fluid. On the cornstarch grain scale, atomic force microscopy measurements reveal the presence of polymers on the cornstarch surface, which exhibit a cosolvency effect. At intermediate ethanol content, a maximum of polymer solubility induces high microscopic adhesion which we relate to the macroscopic yield stress.

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Non-steady-state rheology. The experimental setup, shown in Fig. 1(a), consists of a cylindrical container (diameter $D = 19.5$ cm, height $H = 25$ cm) filled with the suspension into which we drop a sphere (mass $m_s = 248$ g, radius $R_s = 1.54$ cm). The release height $H_{fall}$ varies between $−2R_s$ (sphere starting immersed) and 30 cm. In order to follow the settling dynamics, a thin and rigid metal wire with tracers is attached to the top of the sphere. The mass of the wire ($\sim 1$ g) and its resulting buoyancy force can be neglected compared to the sphere. We follow the tracers at a frame rate between 500 and 5000 Hz using a high speed camera (SA7, Photron). Correlating successive images, we determine the sphere vertical position $z$, velocity $\dot{z}$, and acceleration $\ddot{z}$ of the sphere for $\Phi_{EtOH}^m = 10\%$ and $H_{fall} = 15$ cm. The insets in (c) and (d) show two zoomed-in oscillations with their respective mean velocities ($\bar{v}_1, \bar{v}_2$) and mean accelerations ($\bar{a}_1, \bar{a}_2$).

![Diagram of experimental setup](image)

FIG. 1. (a) Experimental setup schematic. (b)–(d) Typical time evolution of vertical position $z$, velocity $\dot{z}$, and acceleration $\ddot{z}$ of the sphere for $\Phi_{EtOH}^m = 10\%$ and $H_{fall} = 15$ cm. The insets in (c) and (d) show two zoomed-in oscillations with their respective mean velocities ($\bar{v}_1, \bar{v}_2$) and mean accelerations ($\bar{a}_1, \bar{a}_2$).

The flow curves obtained from steady-state classical rheology and from our dynamic system present a convincing qualitative agreement, although the numerical values are different, probably due to approximations (Stokes’ law) or geometrical factors. For $\Phi_{EtOH}^m$ above $\sim 20\%−25\%$ these suspensions all
FIG. 3. Non-steady-state and classical rheology as a function of \( \Phi_{\text{EtOH}} \): (a)–(c) Sphere velocity \( \dot{z} \) as a function of time for various \( H_{\text{rel}} \). (d)–(f) Drag force \( F_D \) encountered by the sphere as a function of its velocity for the same and additional experiments. The gray squares in (d) show the mean drag force as a function of mean velocity \( \bar{v} \) during oscillations. (g)–(i) Flow curves from classical rheological measurements (blue circles) and apparent flow curves obtained from settling experiments (orange diamonds). The dashed lines in (g)–(i) are the best fits of the data with the Bingham model and the orange line in (g) corresponds to the bulk oscillations’ mean behavior.

present a yield stress and can be described by a simple Bingham equation, \( \eta_B = \eta_{pl} + \sigma_Y / \gamma \), in which \( \eta_{pl} \) is the plastic viscosity and \( \sigma_Y \) the yield stress. This is consistent with earlier observations in CS suspensions with \( \{\text{water-polypropylene glycol}\} \) solutions [17]. For lower \( \Phi_{\text{EtOH}} \), a Bingham equation can also approximate the flow curves for low shear rates. The values of \( \sigma_Y \) as a function of \( \Phi_{\text{EtOH}} \) from both rheological measurements are shown in Fig. 4(e). For both methods, \( \sigma_Y \) reaches a maximum value for intermediate \( \Phi_{\text{EtOH}} \) (between \( \sim 25\% \) and \( \sim 70\% \)). Finally, for low \( \Phi_{\text{EtOH}} \) and high shear rates the steady-state rheology exhibits a strong shear thickening which corresponds to the conditions in which bulk oscillations are observed during the settling experiments.

Particle-particle interactions. We probe the interactions between CS particles using atomic force microscopy (AFM) by attaching single CS grains to tipless cantilevers (see the Appendix for experimental details). We measure the force curves [Fig. 4(a)] while approaching and retracting this CS grain to other CS grains glued on the surface of a stainless steel disk in different water-EtOH solutions. From the force curves, we measure the adhesion force \( F_{\text{adh}} \) between individual CS grains and their apparent Young’s modulus \( E^* \). We also estimate an interaction length \( L_{\text{int}} \) corresponding to the separation at which grains start to feel each other. Details on the analysis procedure can be found in the Appendix.

Figure 4(a) shows a typical force curve obtained in water, representing the force between the CS particle on the cantilever and one on the surface when approaching (blue) and retracting (red). On the retracting curve we observe sharp steps called pulling events. These events are signatures of high density dangling polymers disentangling in mediocre solvents [20]. This is a plausible explanation as CS is made of alternating semicrystalline and amorphous layers of the biopolymers amylose and amylopectin [27], being respectively slightly and mostly soluble in cold water [28] but less and less soluble as ethanol is added to the solvent (see, e.g., Refs. [29,30]) until being insoluble in ethanol [31]. Figure 4(b) shows the percentage of measurements with pulling events as a function of \( \Phi_{\text{EtOH}} \). We observe them for all ethanol concentrations with a minimum for ethanol, logical with amylose and amylopectin solubilities, and a maximum for intermediate concentrations, which indicates a cosolvency effect which is a solubility maximum at intermediate \( \Phi_{\text{EtOH}} \) [20–22].

Figure 4(c) shows the apparent elastic modulus \( E^* \) of one grain (blue) and the interaction length \( L_{\text{int}} \) between two grains (orange). As the grains are not spherical and have sizes ranging from 5 to 20 \( \mu \)m, contact areas and curvature radii are difficult to assess, which are responsible for the large error bars. Therefore, we should not attach too much significance to the absolute values, but information from the data comparison for the different values of \( \Phi_{\text{EtOH}} \) is to be trusted. Thus we...
observe that the apparent particle softness and the interaction length vary with \( \Phi_{\text{EtOH}} \) which we interpret as a result of the cosolvency effect: \( \Phi_{\text{EtOH}}^{\text{app}} \approx 25\% \) appears to be the best solvent, which is consistent with more pulling events being observed for this concentration. Indeed, a better solvent allows for deeper interdigitation of the polymers in opposing grains. Although \( L_{\text{int}} \) varies inversely to \( E^* \), from our data it is not possible to determine the origin of the repulsive force before elastic contact: It could be either interdigitation of the polymers or some form of noncontact repulsion, such as static charges.

After the approach, it is possible to keep two CS grains in contact for a given contact time \( t_c \) before retracting. By doing so, we can investigate the effect of the contact time on the adherence force \( F_{\text{adh}} \). Figure 4(d) shows the evolution of \( F_{\text{adh}} \) as a function of \( \Phi_{\text{EtOH}}^{\text{app}} \) for zero contact time \( F_{\text{adh}}^{0} \) (blue) and in the limit of infinite contact time \( F_{\text{adh}}^{\infty} \) (orange). For all \( \Phi_{\text{EtOH}}^{\text{app}} \), \( F_{\text{adh}} \) increases with \( t_c \), following an exponential decay characterized by a decay time \( \tau \) (see the Appendix for details), which is again consistent with our interpretation of free dangling polymers interpenetrating with time. We observe that \( F_{\text{adh}}^{\infty} \) is maximal in pure water whereas \( F_{\text{adh}}^{\infty} \) exhibits a maximum for \( \Phi_{\text{EtOH}}^{\text{app}} = 25\% \). We attribute the latter to the larger effective interaction area due to particle softness and polymer interpenetration.

These results are consistent with the macroscopic rheology. Indeed, \( F_{\text{adh}}^{\infty} \) must be related to the suspension behavior at small shear rate, i.e., the yield stress \( \sigma_Y \), which we obtain from the Bingham fits to the flow curves of Fig. 3. Although slightly shifted, \( F_{\text{adh}}^{\infty} \) shows similar variations as the yield stress extracted from rheology experiments [Fig. 4(e)]. Moreover, the shear-thinning part of the flow curves observed for all \( \Phi_{\text{EtOH}}^{\text{app}} \) is also consistent with an increase of \( F_{\text{adh}}^{\infty} \) with \( t_c \). On the other hand, one could expect that the suspension behavior at high shear rates could be related to \( F_{\text{adh}}^{\infty} \) and \( \tau \). But the present measurements do not show any quantitative indication of that, although \( \tau \) does vary with \( \Phi_{\text{EtOH}}^{\text{app}} \). Namely, \( \tau \) is minimal for pure water (\( \tau_{\text{min}} = 0.5 \pm 0.1 \) s) and maximal for intermediate concentrations (\( \tau_{\text{min}} = 2.0 \pm 0.7 \) s) (see the Appendix). Therefore, friction measurements as described in Ref. [32] could provide additional insights [13,33], although with interpretation difficulties due to CS particle irregularity and roughness.

**Summary.** In this Rapid Communication we show that by gradually replacing the suspending fluid of the well-known suspension of cornstarch and water with ethanol, the familiar shear-thickening behavior completely disappears. Going from pure water to pure ethanol, the suspension behavior changes continuously with ethanol concentration from dynamic shear thickening for pure water to low viscosity shear thinning for pure ethanol, passing through a yield-stress-fluid phase for intermediate mixtures. A comparison of classical (steady-state) and non-steady-state settling rheology shows qualitative agreement. More specifically, it shows that flow conditions for which shear thickening is observed in classical rheology measurements correspond to the conditions for which bulk oscillations are observed in non-steady-state experiments.

These behaviors are related to the interactions between CS grains in the different suspending fluids measured using atomic force microscopy. We first present evidence that CS grains are covered by free dangling polymers behaving as polymer brushes. Then, the variation of the adherence force with the suspending fluid is shown to be consistent with the yield stress observed in macroscopic rheology. This indicates that the macroscopic behavior is closely linked to the details of the particle-particle interactions. It appears that the presence of dangling polymers may not only be at the origin of the strikingly different behaviors observed while changing the suspending fluid, but also of the peculiar dynamic behavior of suspensions of CS in water. In order to validate this hypothesis, it is essential to perform additional research on better controlled systems such as suspensions of spherical particles functionalized with known polymer brushes.

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**APPENDIX: ATOMIC FORCE MICROSCOPY (AFM)**

1. **Experimental details**

We use a Bruker AFM (Multimode 8 with a Nanoscope V controller) using a JV vertical engage scanner and a Bruker glass liquid cell. Using a micromanipulator and UV curing...
fluids. The maximum force reached is 60–80 nN. Interpretation but can be compared for different suspending apparent modulus. Thus, absolute values have no concrete round and their radius not well defined, we only obtain an as the contact point. As the cornstarch grains are not perfectly the contact starts to become elastic. This point is considered Refs. [34,35] to obtain Hertzian contact model following the procedure presented in (and from these surfaces in different water-EtOH solutions while approaching and retracting the cornstarch grain to covered with cornstarch particles, attached using an epoxy and resonance frequencies of 85, 75, and 79 kHz, respectively [Fig. 5(a)]. The tested surfaces consist of stainless steel disks covered with cornstarch particles, attached using an epoxy two-component glue [Fig. 5(b)]. Force curves are measured while approaching and retracting the cornstarch grain to and from these surfaces in different water-EtOH solutions (EtOH = 0%, 10%, 25%, 50%, 75%, and 100%) with a velocity of 0.77, 1.44–2.88 μm s−1, for which the analysis shows no influence of the approaching and retracting velocity.

With the different cantilevers, we probe three positions on two different samples and compared them to reference force curve measurements on bare glue to ensure that we truly probe the CS-CS interactions. For each position, force curves are averaged over at least 50 measurements. Figure 4 shows averaged results for one cantilever and sample set. Other cantilevers and samples show similar trends.

2. Force curve analysis

The force measured upon close approach was fitted with the Hertzian contact model following the procedure presented in Refs. [34,35] to obtain E* [Fig. 4(c)] and the position at which the contact starts to become elastic. This point is considered as the contact point. As the cornstarch grains are not perfectly round and their radius not well defined, we only obtain an apparent modulus. Thus, absolute values have no concrete interpretation but can be compared for different suspending fluids. The maximum force reached is 60–80 nN.

3. Effect of contact duration on the adhesion

As the rheology of cornstarch suspensions is observed to strongly depend on the shear rate, we study the evolution of the adhesion force as a function of the contact duration between two grains. To do so, we approach the grain to the surface, keep the grains in contact during a waiting time Δt ranging from 0 to 20 s, and then retract. These measurements are performed in different water-EtOH solutions with a velocity of 1.44 μm s−1.

As the geometry of the contact may vary from one probing position to another, for each position we normalize the adhesion force by the one corresponding to zero waiting time:

\[ \tilde{F}_{\text{adh}}(\Delta t) = \frac{F_{\text{adh}}(\Delta t)}{F_{\text{adh}}(\Delta t = 0 \text{ s})} . \]  

(A1)

Figure 6(a) shows the variation of the normalized adhesion force \( \tilde{F}_{\text{adh}} \) as a function of the waiting time for \( \Phi_{\text{EtOH}}^\text{m} = 0 \% \) and for each different probing position. The normalized adhesion force can be fitted by an exponential

\[ \tilde{F}_{\text{adh}}(\Delta t) = \tilde{F}_{\text{adh}}^\infty - (\tilde{F}_{\text{adh}}^\infty - 1) \exp \left( -\frac{\Delta t}{\tau} \right) . \]  

(A2)

\( \tilde{F}_{\text{adh}}^\infty \) and \( \tau \) are measured for each position and for each \( \Phi_{\text{EtOH}}^\text{m} \). The values shown in Figs. 4(d) and 6(b) correspond to the average over all positions for each \( \Phi_{\text{EtOH}}^\text{m} \).