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From elastocapillarity to phase separation

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Capillary thinning of elastic and viscoelastic threads: From elastocapillarity to phase separation

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The formation and destabilization of viscoelastic filaments are of importance in many industrial and biological processes. Filament instabilities have been observed for viscoelastic fluids but recently also for soft elastic solids. In this work, we address the central question of how to connect the dynamical behavior of viscoelastic liquids to that of soft elastic solids. We take advantage of a biopolymer material whose viscoelastic properties can be tuned over a very large range by its pH, and study the destabilization and ensuing instabilities in uniaxial extensional deformation. In agreement with very recent theory, we find that the interface shapes dictated by the instabilities converge to an identical similarity solution for low-viscosity viscoelastic fluids and highly elastic gels. We thereby bridge the gap between very fluid and strongly elastic materials. In addition, we provide direct evidence that at late times an additional filament instability occurs due to a dynamical phase separation.

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Introduction. Viscoelastic fluids exhibit an array of properties that differentiate them from Newtonian fluids like water [1–3]. Striking differences in flow behavior are observed due to the presence of mesoscopic constituents such as polymers that introduce an elasticity into an otherwise viscous system. In particular, the formation of viscoelastic filaments has attracted much attention. The obvious importance of viscoelastic filaments for fiber spinning [4,5] has become a benchmark problem for testing viscoelastic fluid mechanics [6–12]. When pushing a polymeric liquid out of a syringe, instead of breaking off at the orifice by a Rayleigh-Plateau instability to form a drop as a Newtonian fluid does [13,14], long and slender filaments form that are very long lived. These subsequently undergo spectacular beads-on-a-string (BOAS) [15–20] and blistering [21–23] instabilities while undergoing capillary thinning. Such BOAS instabilities can be viewed as the viscoelastic equivalent of the Rayleigh instability. However, due to the elasticity of the filaments these do not break up until very late times. Recently, instabilities strikingly similar to the BOAS structure have been observed on filaments made of very soft elastic gels [24] that do not break up at all. This poses the question of how to connect the dynamical behavior of viscoelastic liquids to that of soft elastic solids.

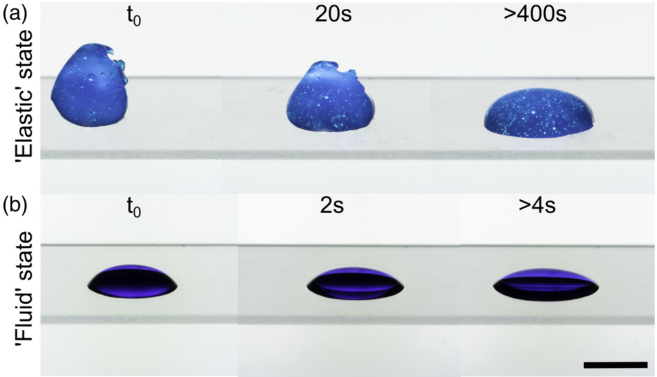

FIG. 1. Time-lapse photographs of blue-colored droplets of HA (3 mL volume), on a glass substrate, prepared at pH 2.5 representing the elastic state (a, upper panel) and at pH 7 representing the fluid state (b, lower panel). The fluid solution spreads like a liquid, while the elastic sample only flows on a timescale of minutes. The scale represents 15 mm.

Very recent theory by Snoeijer *et al.* [25] and Eggers *et al.* [26] investigates this question in detail. In the generic models for the flow of viscoelastic polymeric liquids, one has to adopt a Lagrangian reference frame: The polymers that are being stretched move with the fluid and are stretched by velocity gradients in the moving fluid. For elasticity theory, on the other hand, the reference frame is Eulerian, and all the deformations are calculated in the laboratory frame of reference. These recent theories show that the two reference frames can be mapped onto each other (at least for some explicit models for polymeric fluids) by considering the relaxation timescale λ of the polymer. When this relaxation time goes to infinity, the deformations calculated in the moving reference frame for polymeric fluids simplify to purely elastic (but nonlinear) deformations in the elastic models. The most striking conclusion is that in practice the instability is identical between purely elastic and viscoelastic materials. For instance, for the pertinent example of the BOAS structure the prediction is that the interface shapes connecting the filament (the string) to the drops (the beads) has an identical shape [25–27]. To test these proposals and investigate how the crossover between elastic and viscoelastic filaments happens, we here investigate the capillary thinning of filaments of a biopolymer with a tunable elasticity, varying from an almost Newtonian liquid to a gel.

Experimental section. We take advantage of the fact that the viscoelastic properties of the biopolymer hyaluronic acid (HA) can be tuned by means of its pH [28], and study the effect of elasticity on filament instabilities. HA solutions were prepared following a frequently used protocol [28,29]: 1 wt% HA solutions were prepared using hyaluronic acid sodium salt powder from *Streptococcus equi* bacteria (1.5–1.8 MDa, Sigma Aldrich) in distilled water, together with a fixed NaCl concentration (0.15 M) and HCl concentrations ranging from 0 to 50 mM to obtain pH values from 1.6 to 7. Samples were vortexed for a few seconds to ensure mixing of the ingredients and homogenized under modest rotation during a period of 5 days. As illustrated in Fig. 1, the viscoelastic behavior of HA solutions strongly depends on the pH. Samples prepared at pH values 1.6–1.9 and 3–7 form a fluid state and spread like a liquid, while an elastic state forms at pH 2.5 retains its shape and only deforms significantly on a timescale of minutes. Oscillatory shear rheology at 0.5 Hz and a strain amplitude of 0.5%, well within the linear regime of HA (see the Supplemental Fig. 1 [30]), also show that at pH 2.5 an increase of the storage modulus of more than two orders of magnitude occurs (see Fig. 2(c) and Supplemental Fig. 2 for experimental details [30]). For pH values both lower and higher than 2.5, the viscoelastic gel becomes a viscoelastic liquid. In the remainder, we use the term “elastic” state for the solution state at pH 2.5 and “fluid” state for the other pH. Such responsiveness of biopolymers is of relevance biologically and consequently observed in various biological systems such as curvature-driven instabilities of lipid

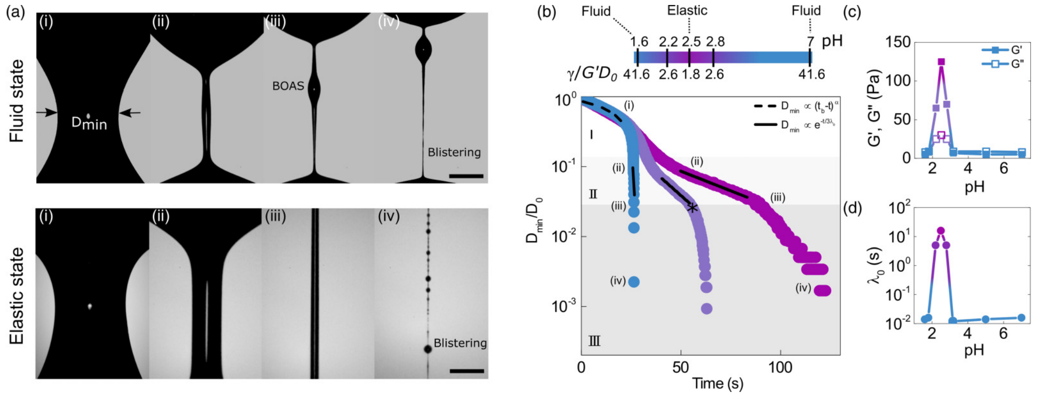

FIG. 2. (a) Photographs of the neck breakup dynamics of HA in the fluid state (upper panel, pH 7) and in the elastic state (lower panel, pH 2.5). The scale represents 75 μm in the upper panel and 400 μm in the lower panel. (b) Minimum filament diameter normalized by the initial bridge size as a function of time for three different solutions at different elastocapillary numbers $\gamma/G'D_0$ given in the upper colored bar: blue for pH 1.6 and 7, violet for 2.2 and 2.8, and purple for 2.5. The numbers correspond to the photographs in panel (a). (c) The viscoelastic moduli from oscillatory shear measurements. (d) Relaxation times obtained from panel (b).

bilayer membranes [31] and crawling cells [32] and plays a role in the fabrication of scaffolds in tissue engineering [33,34], 3D cell cultures [35,36], electrospun nanofibers [4,37], and 3D printing [38]. In a number of these examples, one observes the formation of filaments which are prone to the capillary instabilities that we investigate here.

To study the extensional thinning and destabilization of HA filaments for different pH values, we use a custom built filament stretching rheometer (see Supplemental Fig. 3 for sketch of setup and experimental details [30]), similar to the one described in Refs. [12,39]. A small sample of 40-μL fluid is initially placed between two circular end plates ($D_0 = 5$ mm and $L_0 = 2.5$ mm) which are moved apart at a slow and constant velocity of 0.1 mm/s until the bridge breaks due to surface tension (the low velocity does not introduce any additional velocity in the problem). The evolution of the liquid bridge is recorded with a fast camera (Phantom V7) allowing frame rates up to 10 000 frames per second. The camera is equipped with a microscope tube lens, with an objective up to 12× magnification (Navitar) and a spatial resolution of 3 μm per pixel. The setup is placed in a closed chamber (80% RH) to prevent evaporation during the measurements.

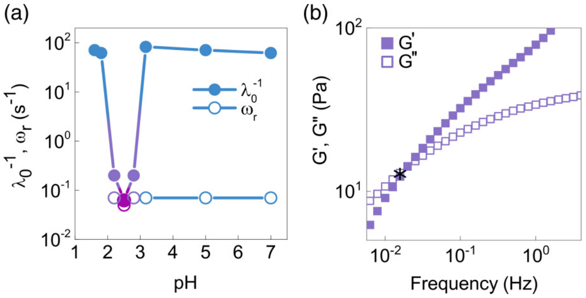

FIG. 3. (a) BOAS instabilities are observed when the growth rate of the Plateau-Rayleigh instability is smaller than the inverse characteristic time of the polymer ($\lambda_0^{-1} > \omega_R$); for pH 2.5, no bead is formed (the color gradient is the same as in Fig. 2). (b) Viscoelastic moduli at pH 2.8 as function of frequency. The crossover point at very low frequencies (marked with an asterisk) indicates the timescale at which the BOAS instability appears, corresponding to the transition between regimes II and III in Fig. 2(b).

Results and discussion. Figure 2(a) shows typical photographs of the breakup dynamics for the fluid state (blue, at pH 7) and the elastic state (purple, at pH 2.5) and the corresponding thread radius as a function of time in a semilogarithmic plot [Fig. 2(b)], where also an intermediate state is added at pH 2.8 and 2.2 (violet) to emphasize the tunability of HA (see Supplemental Fig. 4 [30] for the thread radius as function of time for all pH and see Supplemental Fig. 5 [30] for the corresponding breakup pictures). The observed filament thinning of the HA solutions with different pH can be separated into three regimes. We first observe a power-law regime (I) where the neck thinning is similar to that of a power law fluid following a viscocapillary balance [9,12,40–42]. The breakup pictures in Fig. 2(a) designated by (i) correspond to this regime. This regime follows $D_{\min} = (t_b - t)^{\alpha}$ [43], indicated by the black dashed fit in Fig. 2(b), where t_b refers to the breakup time of the filament and α depends on the rheology of the fluid. The α values corresponding to the fluid and elastic state are respectively 0.3 and 0.9, which also correspond to the power-law exponents from the shear thinning rheology of the polymers (see Supplemental Fig. 6 and Supplemental Note 1 for experimental details [30]).

The extensional rate is directly obtained from the evolution of the filament diameter as $\dot{\varepsilon} = \frac{-2}{D_{\min}} \frac{dD_{\min}}{dt}$, which are shown in the Supplemental Fig. 7 [30] for the fluid and elastic states. The extensional rate shows that in the power-law regime (I) the extension rate increases as the neck diameter decreases. This regime has been observed previously for strongly shear thinning but weakly elastic samples and reflects the modification of the Newtonian thinning regime by the shear thinning [7,39]. Subsequently, an exponential regime is reached where a long and slender cylindrical filament is formed [breakup photographs indicated by (ii)]: This is the classical elastocapillary regime (II) defined by the exponential thinning of the filament, $D_{\min} \propto e^{-t/3\lambda_0}$, with λ_0 being the longest relaxation time of the polymer solution [6]. The black straight lines in Fig. 2(b) indicate the exponential fit from which the relaxation times of the solutions are determined. For the low-elasticity sample called the fluid state, there is also a short elastocapillary regime, as shown in the Supplemental Fig. 3 [30]. After the exponential regime II, we observe an even steeper than exponential decay (regime III), eventually leading to the breakup. Within regime III, instabilities occur: The BOAS structure is observed in the fluid state [photographs indicated by (iii)]. For the elastic state, the cylinder remains symmetric and does not show BOAS instabilities. In addition, for all pH, just before the breakup, a blistering pattern is observed [photographs indicated by (iv)] that is clearly very different from the BOAS.

In Fig. 2(c) the storage G' and loss G'' shear moduli are plotted as a function of pH, and in Fig. 2(d) the corresponding relaxation times from the extensional rheology measurements on a logarithmic scale, as they cover several orders of magnitude. The longest relaxation time is observed for the elastic state at pH 2.5 and we find that the moduli follow the same trend as the relaxation times.

We find that when the elastic modulus is the highest (at pH 2.5), the elastic stresses resist the formation of a bead. Comparing to the results of Mora *et al.* [24], their soft solids show instabilities when the ratio of the elastocapillary length to the cylinder diameter is larger than 6 ($\gamma/G'D_0 > 6$). In our system, when we calculate the elastocapillary length for the elastic state at pH 2.5 at a finite frequency (taken at 0.5 Hz, roughly the inverse of the typical timescale of the experiment), the ratio is 1.8 using a surface tension γ, initial cylinder radius D_0, and elastic modulus G' of respectively 67 mN/m [44,45], 300 μm, and 125 Pa; hence, no purely elastic instability can occur. Although the elastic sample at pH 2.5 does not exhibit BOAS, the still rather elastic state at pH 2.8 [breakup dynamics shown in Fig. 2(b)] does show this instability. At pH 2.8, somewhat smaller relaxation time and storage modulus are found, but the calculated ratio of length scales is 2.6, which is still smaller than the limiting value of 6 reported by Mora *et al.* [24]. It is worthwhile noting that the shear modulus in the system of Mora *et al.* is the zero-frequency shear modulus. In our system, since the elastic state flows at a long timescale, one would not anticipate a purely elastic instability in any case. The origin of this BOAS instability must then still be controlled by viscous rather than elastic forces and induced by local symmetry breaking in the fluid neck [18,46], as for low-viscosity polymer solutions. In the experiments, BOAS indeed always start by symmetry breaking in the filament

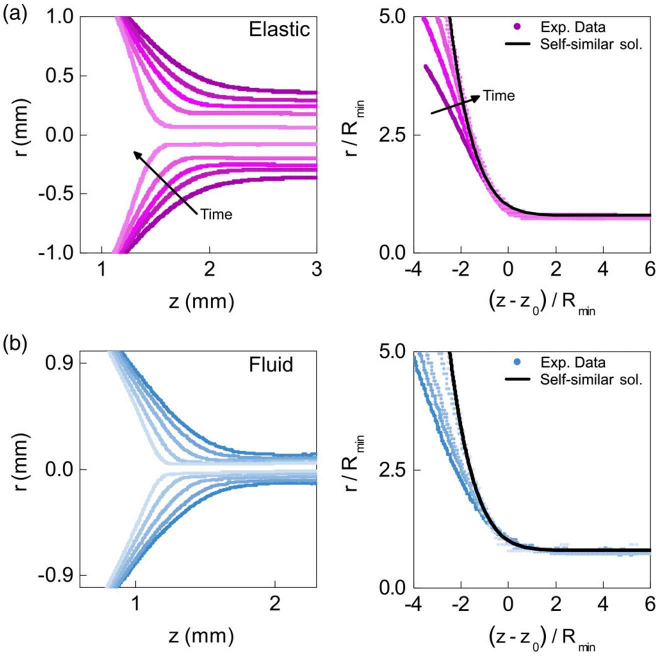

FIG. 4. Time evolution of the filament shapes in (a) the elastic (pH 2.5, $\gamma/G'D_0 = 1.8$), 12.5 s between each profile, and (b) the fluid states (pH 7, $\gamma/G'D_0 = 40.2$), 10 ms between each profile. (Right) The same profiles rescaled by the minimum neck radius, $R_{\min}$, and with the location for which the experimental profiles are collapsing, z_0. The universal self-similar solution is the black line.

from which a bead forms together with the elastic string. In Fig. 3, we compare the experimentally observed growth rate of the Rayleigh-Plateau instability ω_R with the inverse relaxation time λ_0^{-1}, which is a quantitative criterion for the occurrence of a *fluid* BOAS instability [18,46]: A bead is formed until $\omega_R > \lambda_0^{-1}$. The growth rate is determined from the initial perturbation in the very beginning of regime I [18,46], and further details for the determination of the growth rate can be found in Supplemtnal Fig. 8 [30]. While for most of the HA solutions a similar growth rate is observed, the relaxation time λ_0 strongly increases when the pH approaches 2.5 (elastic state). This causes $\omega_R \sim \lambda_0^{-1}$, preventing a BOAS structure from occurring.

We now focus on the detailed comparison with the elastic and viscoelastic theories [26,27] for the shape of the interface. Figure 4 shows the interface profiles during the filament thinning and near the main drop attached to the plate that forms due to capillary instability. As time progresses, the neck region connecting the thread with the drop becomes steeper and converges to a universal shape. Comparing these interface shapes to the recent elastic and viscoelastic calculations using the Oldroyd-B model for viscoelastic fluids and neo-Hookean calculations for elastic solids, we find an excellent agreement: All converge to the same universal self-similar solution profile (black line), showing that indeed the elastic and viscoelastic instabilities have the exact same signature.

Finally, we focus on the last stages of the breakup, where yet another instability is observed. Figure 2(a) shows that in the last photos before the breakup, indicated by (iv), blistering patterns are observed at all pH values. These may superficially look somewhat similar to the BOAS instabilities, but it has been argued recently that the origin is very different, namely a partial phase separation between the polymer and the solvent that is induced by the stretching [46,47]. For dilute polymer solutions, this has been observed to happen [46] below a critical filament diameter $D_c = \sqrt{\Delta/\dot{\epsilon}} = \sqrt{3\Delta\lambda_0}$, with $\dot{\epsilon}$ being the stretching rate defined as $\dot{\epsilon} = 1/3\lambda_0$, and $\Delta = k_bT/6\pi\eta_s a$

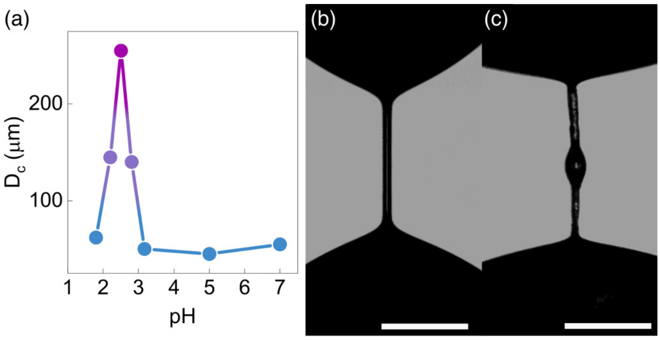

FIG. 5. (a) Critical neck diameter measured at the occurrence of the blistering pattern as a function of pH. Blistering is observed for a larger neck diameter when the pH approaches 2.5. Photographs of the breakup dynamics of two samples of 5 mm length at pH 1.9 extended at 100 μm/s (b) and 1000 μm/s (c). In panel (c), a pearl instability is observed (see Supplemental Video 1). The apparent roughness of the thread is consistent with polymer material, while the smoothness of the pearl indicates it contains the solvent. Scale bar is 2.5 mm.

[47], with a being the polymer radius and η_s the viscosity of the solvent. This calculation compares the timescale of advection of concentration heterogeneities to their homogenization by diffusion. We considered that in our much more concentrated system, the flow-concentration coupling must be substantially more complicated than assumed by the above calculation. When we put the numbers of our system in this calculation, we find for pH 2.5 that the critical radius should be on the order of 10 nm, whereas the data show the emergence of blistering at a radius that is approximately three orders of magnitude larger [see Fig. 5(a)]. This therefore necessitates further theoretical study. The fact that the idea of flow-induced phase separation is nevertheless the correct one follows from the qualitative observation that the pearling instability appears sooner when stretching the filament faster, i.e., at higher $\dot{\epsilon}$. One typical example is shown in Figs. 5(b) and 5(c) where we show that, provided the stretching is fast enough, the phase separation is even directly visible in our experiments. The blisters remain smooth and contain mostly solvent, whereas the filament itself becomes rough because it is highly concentrated in polymer. The roughness of the filament is not an evaporation effect: The emergence of the blisters on a solid string is reversible (see Supplemental Video 1).

Conclusion. In conclusion, we have used a material with tunable viscoelasticity to bridge the gap between very fluid, viscoelastic, and elastic polymeric materials. We have studied the process of filament formation and its ensuing instabilities and have developed a quantitative understanding of the rich dynamics of the different processes that occur. Perhaps surprisingly, viscoelastic fluid mechanics and solid mechanics lead to a unified description of the dynamics that is borne out in notably the interface profiles of the BOAS structure. These are first observed to have a shape given by both elastic and viscoelastic theory, that at later times converges to the universal interface profile and agrees excellently with the theoretical prediction for this profile. These results open the way to a better understanding of the correspondence between fluid-mechanical theories that operate in a Lagrangian frame of reference and elasticity theory that uses the Eulerian reference frame. In addition, the understanding and control of the surface instabilities can have important repercussions for both fiber spinning of regular polymers [4,5] and a wealth of instabilities observed for biopolymer systems similar to the one studied here [35,48].

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