Depletion forces induce visco-elasto-capillary thinning of non-Brownian suspensions

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Abstract – Droplet pinch-off, which occurs when a drop of liquid detaches from a capillary, can be strongly modified in the presence of complex fluids such as polymer solutions and suspensions giving rise to long and slender filaments that thin slowly in time. While for polymers, the molecular conformations of the molecules in the filament are responsible for such a behavior, in suspensions the mechanisms at play remain to be deciphered. Here we show, experimentally, that while liquid bridges of non-Brownian suspensions of moderate concentrations have a thinning behavior very close to that of the solvent, the addition of short-chain polymers inducing depletion attractions between the particles in the suspension changes the thinning dynamics and gives rise to exponential thinning in time. The characteristic time of this dynamics increases with polymer concentration and therefore the intensity of the depletion forces at play. The tunability of this dynamics may be important for inkjet and 3D printing applications where short rupture times are sought for or in other situations where drop formation has to be minimized or inhibited.

Complex fluids exhibit an array of properties that set them apart from Newtonian fluids like water [1,2]. A major difference between these types of liquids is the presence of mesoscopic constituents, such as polymers, surfactant aggregates, colloidal or non-Brownian particles which render the interaction of the complex fluid with any perturbation complicated due to the multiplicity of length and time scales that may come into play [1,2]. The understanding of the complicated interactions between the constituents in a complex fluid as well as their interactions with an external perturbation such as a flow field is essential for the taming of such fluids which are relevant to a variety of applications. Particle suspensions are an important class of complex fluids, they are familiar to us in our daily lives and extremely important for industrial applications in the food industry, in paint production and for building materials. They are mixtures of soft or solid particles in a liquid with the particle volume fraction playing an important role in determining their behavior: at low volume fraction they behave like a Newtonian fluid with a constant viscosity but at high enough volume fractions, these systems have other rheological responses and notably shear thickening [3–5]. In general model suspensions are constituted of non-Brownian particles with no particular interactions apart from hard sphere repulsion. Real suspensions on the other hand are made of particles and other entities and interactions between the constituents may be important.

In a model suspension of particles the interactions can be tuned by different methods such as the addition of polymers, the addition of salts, or by designing particles with embedded properties for example. These additives or modifications give rise to (or inhibit) different particle-particle interactions such as depletion forces, hydrophilic/hydrophobic interactions, electrostatic interactions, or magnetic interactions among others. Understanding and controlling the role of interparticle interactions in the behavior of suspensions is essential in numerous areas of technology, ranging from inkjet printing to the behavior of concentrated bacterial solutions for biotechnology [6,7]. Different studies have focused on the role of interactions in setting the shear rheology of suspensions and important results on the role of interactions in setting the yield stress or the shear thickening behavior of.
these suspensions have been obtained [8]. Much less work concerns their extensional behavior and its modification by particle interactions.

A powerful way to study the extensional behavior of complex fluids is the thinning and the ensuing rupture of liquid columns [2,9–22]. The rupture of Newtonian liquid cylinders can be modeled using self-similar solutions for the neck profile and power laws for the thinning of the neck [23]. Some complex fluids, however, exhibit an inhibition of such singular dynamics which is replaced, in a sudden fashion, by single time dynamics represented by exponential thinning of the neck [15–18]. Different classes of complex fluids have shown such a phenomenology: polymer solutions, corn starch solutions [24], and micellar phases of surfactant [25]. Even more recently, concentrated colloidal suspensions and non-Brownian suspensions of particles have been shown to exhibit such a behavior [24,26]. This exponential thinning has become a powerful tool to characterize complex fluids [2,16,18–20,27]. Despite the generality of such a thinning law, known as the visco-elasto-capillary regime, the exact reasons behind its existence or the tailoring of fluid properties to obtain such a law has been lacking [2]. Only few experiments make a link between such a behavior and the interaction between the flow and the dynamics of the constituents of the complex fluid. Such work has been carried out for polymer solutions [22] but for other classes of complex fluids such as suspensions much less is known.

Here we show that the introduction of attractive forces between otherwise non-interacting particles can induce this exponential thinning behavior. In order to do so we use suspensions of non-Brownian particles suspended in short-chain polymer solutions at different concentrations. Our main observation is that while the solvent (water), the polymer solution, or the suspension in water at volume fractions up to 40% all behave as inviscid liquids for the pinch-off behavior, the suspension with addition of polymers shows a much slower thinning dynamics which is well approximated by visco-elasto-capillary pinch-off. This transition occurs for relatively low polymer concentrations for which the polymer solution shows a power law thinning behavior. The characteristic time of the observed exponential thinning increases with increasing polymer concentration and increasing particle volume fraction. The change in polymer concentration allows to tune the depletion potential between the particles and the characteristic time is found to increase linearly with the depth of this potential. We suggest that the formation of aggregates and their eventual breakup by the extensional flow in the liquid bridge is at the origin of this behavior.

Fig. 1: (Colour online) Pictures showing droplet breakup for (a) water at 2.47, 0.82, 0.082 and 0 ms before rupture, (b) polymer solution at 4.77, 1.48, 0.66 and 0.083 ms before rupture, (c) particle suspension at 2.16, 1.08, 0.54 and 0.027 ms before rupture, (d) polymer-particle suspension at 16.75, 8.42, 3.42 and 1.75 ms before rupture. The width of the images is 1.65 mm except for (b) for which it is 2.25 mm. Thinning curves $D_{\text{min}}^{3/2}$ as a function of $t_c - t$ for particle suspensions at different volume fractions (e) and polymer solutions at different concentrations (f). The dashed lines show the expected inertial-capillary thinning law before neck breakup with a surface tension of 70 mN/m.

Our solutions were prepared using PMMA particles with a diameter of 6 μm, a short-chain polymer PEG of molecular weight 35000 in water. Glycerol (at 20% by weight) was added to the water to minimize the sedimentation of particles. The PMMA particles, obtained as a powder, were washed several times and centrifuged in water to obtain a concentrated paste. The polymer was used as received and dissolved in water at different concentrations. Solutions of different concentrations of polymer in water and for different particle volume fractions were then prepared. The solutions were made to drip from a capillary of 4 mm diameter connected to a syringe. A syringe pump was used to inject the solution (at rates of 0.5 ml/h) and induce droplet detachment. Images were recorded using a fast camera (Phantom V641) working at rates up to 50000 frames/s and equipped with different lenses allowing to reach a spatial resolution near 10 μm per pixel.

Our main observation is reported in the images of fig. 1. Here a sequence of images at different times before rupture
is displayed for the pure solvent (water), for the polymer solution, and for the suspension. All three cases show similar pinch-off behavior and dynamics. The behavior obtained is that of rupture controlled by inertia and capillarity at the late instants before neck breakup. The minimum neck diameter in this case varies in time \( t \) as
\[
D_{\text{min}} = 0.7(\gamma/\rho)^{1/3}(t_{\text{c}} - t)^{2/3},
\]
where \( \gamma \) is the surface tension, \( \rho \) is the density and \( t_{\text{c}} \) is the breakup time. The data for the three samples (water, suspensions of different volume fractions (c) and different-concentration polymer solutions (f)) agrees with this expression as shown in fig. 1(f) albeit for the constant 0.7; the dashed lines use 0.8 which seems to give a better agreement for a surface tension of 70 mN/m. Variations in slope between the different samples may be due to small variations in this surface tension. The polymer solutions and the suspensions behave as inviscid fluids as found previously [26] for volume fractions less than 45%. When the polymer is added to the suspension, the behavior changes. The rupture time increases drastically and the neck elongates to form a long filament reminiscent of visco-elasto-capillary thinning often observed with polymer solutions [2]. While the neck shapes at breakup are similar for the three control samples as expected for the inertial capillary regime (fig. 1(e)), the suspension with added polymer has a neck shape that is drastically different, symmetric, and cylindrical. This large change in behavior is obtained with other combinations of polymer concentration and particle volume fraction.

To quantify this behavior, we plot, in fig. 2(a), the thinning dynamics of the different solutions. This dynamics is fast for the first three solutions (water, polymer solution, and the suspension), follows the 2/3 power law characteristic of inertial capillary thinning, but becomes slower and slower as the concentration of polymer in the suspension increases. This slowing-down is much more important compared to the polymer solution behavior as illustrated in this figure where a polymer solution ruptures much faster than a suspension with much less polymer. Figure 2(b) shows the slowing-down caused by the increase in the volume fraction of the particles while the polymer concentration varies over a small range. Even if the polymer slows down the dynamics, the slowing-down caused by the presence of the particles is much more important and increases in importance (with respect to the suspension without added polymer or to the polymer solution itself) as the suspension volume fraction increases. Note here that the last instants before breakup seem to follow an inertial capillary thinning dynamics as observed before for suspensions. For these last instants, the decrease of the suspension volume fraction is generally observed giving rise to dynamics dominated by the solvent properties [11, 28, 29]. Figure 2(c) shows the thinning dynamics of 2 suspensions at a volume fraction of 35% with 60 and 120 mg/mL of added polymer. Different thinning laws are used to model the full thinning dynamics; the latest instants are fit to a power law dynamics with an exponent of 2/3 characteristic of the inertial-capillary regime while an exponential thinning law is used to approximate the dynamics at intermediate times. The straight lines in this figure are the expected visco-capillary breakup dynamics with a linear thinning law \( D_{\min} = 0.14(2c - t) \), with the viscosity \( \eta \) determined using rheology measurements to be shown below. Note that the solutions used have dynamics which is difficult to reconcile with the visco-capillary thinning expected for the Newtonian suspensions studied here. The indicated exponential thinning works better.

Two important features characterize the thinning curves in the presence of particles and polymers shown in fig. 2(a) and (b). While at the late times before rupture, the dynamics seems similar and fast for all volume fractions, the intermediate time region shows a roughly exponential behavior. The dynamics for this part can be reasonably approximated by \( D_{\min} = A \exp(-t/\tau) \).
This regime appears linear in the semi-log representation of fig. 2. The characteristic time $\tau$ of this exponential regime increases with polymer concentration and with particle volume fraction as seen in fig. 2. The variation of this characteristic time is displayed in fig. 3 vs. polymer concentration and for different volume fractions of particles. Note that for each volume fraction this time increases roughly linearly with polymer concentration. Also, and for the smallest volume fraction (15%), the characteristic time is relatively close to that measured in the bare polymer solution for high enough concentrations; the exponential regime is not observed for polymer concentrations below a certain value (vertical dashed line) for the low suspension volume fractions or for polymer solutions without added particles. Otherwise and for higher volume fractions (> 15%), the exponential regime is present even for polymer concentrations not exhibiting the exponential regime. The appearance of this exponential regime seems to occur above a threshold polymer concentration which increases as the volume fraction decreases. For the 15% suspensions, this transition occurs very close to the concentration for which the bare polymer solution also shows a transition to an exponential regime. This indicates that the effect at 15% is difficult to attribute to the mixture instead of the polymer alone; even if the characteristic times seem to be very close. For the higher volume fractions the exponential regime is present even for polymer concentrations not exhibiting the exponential regime. The question then is why the mixture (polymer and added particles) gives rise to such a slowing-down of its thinning behavior which is characteristic of viscoelastic fluids such as polymer solutions? Observations of similar exponential thinning in colloidal as well as non-Brownian suspensions have been made but at concentrations sufficiently high that normal stresses are important. The emergence of this behavior, at least for non-Brownian suspensions, has been shown to be directly related to the appearance of positive normal stresses in the system [24,26]. The characteristic time of the exponential dynamics in such systems has been found to correlate very well with the inverse shear rate, $\dot{\gamma}_N$, for the onset of positive normal stresses ($3/\dot{\gamma}_N = \tau$) pointing to their role in setting the characteristic time of viscoelastic pinch-off [24,26]. A priori, and for the volume fractions used here ($\leq 40\%$), the viscosity of the solutions is constant and independent of shear rate and the onset of positive normal stresses does not occur (or if it occurs it does so at much higher shear rates) according to our rheological measurements shown in fig. 4. Since at onset of positive normal stresses, concentrated solutions usually show a shear thickening behavior, our solutions which remain Newtonian at shear rates higher than $3/\tau$ as shown in figs. 3 and 4(a) do not obey this simple criterion. The viscosity of the polymer laden suspensions is roughly constant for shear rates in the range 1 to 1000 s$^{-1}$, fig. 4(a), and simply increase as the polymer concentration increases as found in other measurements [30]. The bare polymer solutions (without added particles) are also Newtonian in this range of shear rates, fig. 4(b). Some shear thinning is observed for the polymer laden suspensions but only for high polymer concentrations. Our own measurements of normal stresses in these solutions do not show positive normal stresses and when they are present seem to
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solvent. Nonetheless our simple argument gives the correct qualitative scaling of the thinning time.

In conclusion, we show that the addition of attractive depletion interactions in non-Brownian suspensions gives rise to an elastic regime in the extensional flow of such suspensions which are nonetheless Newtonian under shear. The large difference between the extensional measurements carried out here and the shear measurements of these suspensions brings forth fundamental questions about the nature of the rheological response of particle laden fluids.

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REFERENCES

[1] Larson R. G., The Structure and Rheology of Complex Fluids (Oxford University, New York) 1999.
[2] McKinley G. H., Rheol. Rev. (2005) 1.
[3] Lin N. Y. C. et al., Phys. Rev. Lett., 115 (2015) 228304.
[4] Fall A. et al., Phys. Rev. Lett., 100 (2008) 018301.
[5] Seto R. et al., Phys. Rev. Lett., 100 (2013) 018301.
[6] Kulkarni A. M. et al., Phys. Rev. Lett., 83 (1999) 4554.
[7] Tanaka S. and Ataka M., J. Chem. Phys., 117 (2002) 3504.
[8] Brown E. et al., Nat. Mater., 9 (2010) 220.
[9] Miskin M. Z. and Jaeger H. M., Proc. Natl. Acad. Sci. U.S.A., 109 (2012) 4389.
[10] Furbank R. J. and Morris J. F., Phys. Fluids, 16 (2004) 1777.
[11] Bertrand T. et al., Granular Matter, 14 (2012) 169.
[12] Smith M. I. et al., Nat. Commun., 1 (2010) 114.
[13] Doshi P. et al., J. Non-Newtonian Fluid Mech., 113 (2003) 1; Doshi P. and Basaran O. A., Phys. Fluids, 16 (2004) 585; Suryo R. and Basaran O. A., J. Non-Newtonian Fluid Mech., 138 (2006) 134.
[14] Huisman F. M., Friedman S. R. and Taborek P., Soft Matter, 8 (2012) 6767.
[15] Amarouchene Y. et al., Phys. Rev. Lett., 86 (2001) 3558.
[16] Anna S. L. and McKinley G., J. Rheol., 45 (2001) 115.
[17] Sattler R., Kityk A. and Wagner C., Phys. Rev. E, 75 (2007) 1.
[18] McKinley G. H. and Sridhar T., Annu. Rev. Fluid Mech., 34 (2002) 375.
[19] Stelter M. et al., J. Rheol., 46 (2002) 507.
[20] Entov V. M. and Hinch E. J., J. Non-Newtonian Fluid Mech., 72 (1997) 31.
[21] Louvet N., Bonn D. and Kellay H., Phys. Rev. Lett., 113 (2014) 218302.
[22] Ingremeau F. and Kellay H., Phys. Rev. X, 3 (2013) 041002.
[23] Eggers J., Rev. Mod. Phys., 69 (1997) 1833; Eggers J. and Villermaux E., Rep. Prog. Phys., 71 (2008) 036601.
[24] Roché M., Kellay H. and Stone H. A., Phys. Rev. Lett., 107 (2011) 134503.
[25] Rothstein J. P., J. Rheol., 47 (2003) 1227.
[26] Pan Z. et al., Phys. Rev. E, 92 (2015) 052203.
[27] Thiriaatmadja V. T. and Sridhar T., J. Rheol., 37 (1993) 1081.
[28] Mathues W. et al., Phys. Fluids, 27 (2015) 093301; McIlroy C. and Harlen O. G., Phys. Fluids, 26 (2014) 033301.
[29] Zhao H. et al., Phys. Fluids, 27 (2015) 063303.
[30] Abdul Haleem B. and Nott Prabhu R., J. Rheol., 53 (2009) 383.
[31] Lekkerkerker H. N. W. and Tuinier R., Colloids and the depletion interaction, in Lect. Notes Phys., Vol. 833 (Springer) 2011.
[32] Bergenholtz J., Poon W. C. K. and Fuchs M., Langmuir, 19 (2003) 4493.
[33] Kroes-Nijboer A. et al., Langmuir, 26 (2010) 13097.
[34] Verma R. et al., Phys. Rev. Lett., 81 (1998) 4004.
[35] Li J. et al., Polymer, 80 (2015) 205.