‘Beads on a String’ Structures and Extensional Rheometry using Jet Break-up

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1. Introduction:

Surface tension driven break-up of cylindrical fluid elements into droplets plays a crucial role in the use or processing of many multicomponent complex fluids like paints, inks, insecticides, cosmetics, food, etc [1, 2]. These industrial fluids are typically formulated using dilute polymer solutions, and are exposed to a wide range of shear and extension rates. Since the polymer solutions and the resulting dispersions have low viscosity and short relaxation times, their non-Newtonian behavior is not apparent in the conventional rheometric measurements. However, the presence of even a dilute amount of polymer alters the character of capillary break-up during dripping, jetting and thinning of a stretched liquid bridge [2]. In all three scenarios (sketched in figure 1), the presence of polymers leads to a delayed pinch-off.

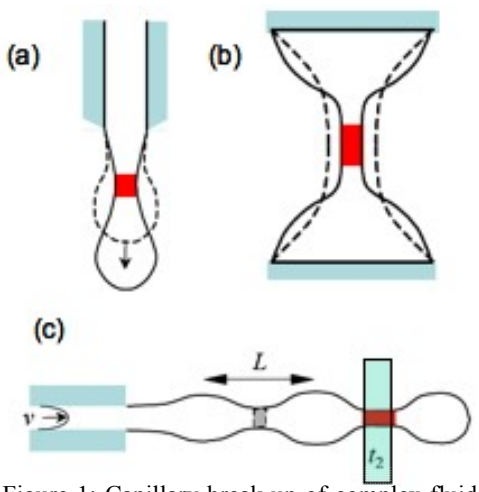

Figure 1: Capillary break-up of complex fluids (a) Dripping (b) Liquid bridge (c) Jetting.

The interplay of capillary, inertial, elastic and viscous effects on small length and time scales typically leads to complex dynamics in a necking fluid thread and in some cases, the extensional stresses generated in the neck lead to formation of very thin and stable filaments between drops, or to ‘beads-on-a-string’ structure [2, 3]. In a capillary-thinning extensional rheometry experiment (or CABER test), the self-thinning of liquid bridge of a viscoelastic fluid follows the elasto-capillary scaling $R/R_0 \sim \exp\left(-t/3\lambda\right)$, where R_0 is the initial radius. In this case, the relaxation time, λ, of the fluid can be measured directly, but practically the use of this method is restricted to fluids with relaxation times of 1 ms or higher (or extension rates of 10^3 s^{-1} or lower) [4].

In this paper, we explore the influence of transient extensional rheology in the breakup of thin fluid threads at time scales of 1 ms and below. We study the influence of both elasticity and extensibility on the growth of instability and capillary break-up of the viscoelastic fluids. Using experiments and simulations, we show that by carefully controlling the excitation frequency at which a fluid jet is excited, it is possible to drive the break-up in a particularly simple and symmetric mode, which can be used to extract extensional viscosity information using familiar capillary thinning analysis. While bead formation and extension rates are self-determined in a CABER experiment, we infer that it is possible to influence the dynamics of the bead formation in the capillary break-up during jet process by controlling the amplitude and frequency of the imposed disturbances.

2. Theory and simulation

The temporal evolution of the jet depends on the relative magnitude of the viscous, inertial, and elastic stresses and the capillary pressure within the liquid jet [1, 2]. In order to study

this inertio-elasto-capillary balance in detail, we introduce two dimensionless parameters: the intrinsic Deborah number *De* defined as the ratio of the time scale for elastic stress relaxation, λ, to the "Rayleigh time scale" for inertio-capillary breakup of an inviscid jet, $t_R = \left(\rho R_0^3/\sigma\right)^{0.5}$ and the Ohnesorge number $Oh = \eta_0 \Big/ \sqrt{\rho\sigma R_0}$ which is the ratio of viscous to inertio-capillary time scale. Here ρ is the fluid density, η_0 is the zero shear viscosity, η_s is the solvent viscosity, and σ is the surface tension. In this study, we particularly focus on jetting behavior at a small Ohnesorge number and a Deborah number of order unity where it is challenging to perform the CABER test. The concatenated image of a jet of dilute solution of 0.01% PEO (Mw = 300,000 Daltons) in glycerol-water mixture in figure 2 illustrates the typical behavior of a weakly viscoelastic jet. The thinning dynamics of the jet at different distances downstream reveals information about either the initial growth rate of instability on a harmonically perturbed jet as predicted by linear stability analysis or about relaxation time, as computed from the elastocapillary regime, exactly like in CABER. The schematic shows both these regimes, along with two other regimes that can be observed in certain cases: 1) inertio-capillary regime with scaling law $R^{(ic)}/R_0 \sim \left([t_{ic}-t]/t_R\right)^{2/3}$ and 2) finite extensibility regime with $R/R_0 \sim \left([t_{ec}-t]/t_R\right)^n$. The inertio-capillary regime with asymmetric pinch-off is always observed in capillary break-up during dripping of a low viscosity fluid, but in a jetting experiment, the scaling observed depends upon frequency and the elasto-capillary regime can kick in directly, and as chains get stretched, the finite extensibility will dictate the thinning dynamics in the last stage.

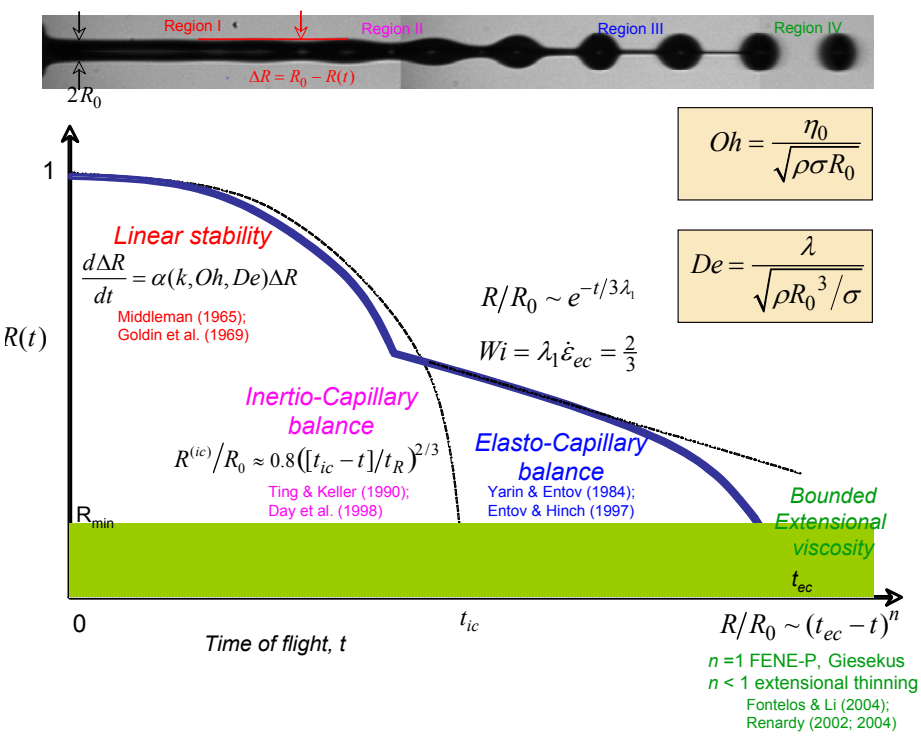

Figure 2: Life and Death of a Viscoelastic Jet. The concatenated image of a jet of 0.01% PEO in glycerol /water issuing out of 175 μm nozzle showing instability growth and pinch-off as observed in experiment. The schematic illustrates the multiple scaling regimes observed during thinning in a viscoelastic jet undergoing break-up. Shaded region shows that minimum observable size is limited by experimental spatial resolution.

To better understand the complex evolution of thinning filament during jetting, we numerically investigate the growth and evolution of surface-tension-driven instabilities on an axisymmetric viscoelastic jet using a nonlinear 1D theory for a range of different constitutive equations. The linear instability analysis for small perturbations shows that a viscoelastic jet is initially more unstable when compared to a Newtonian fluid of the same viscosity and inertia as shown in figure 3. As the radius of local constrictions in the jet thins under the action of surface tension, elastic stresses grow and become comparable to the capillary pressure, leading to formation

of a uniform thread connecting two primary drops. This 'beads-on-a-string' structure can be captured by the Oldroyd-B model, and the radius of the thin cylindrical ligament connecting the beads necks down exponentially in time. The finite time breakup of the jet observed experimentally can be captured using the nonlinear Giesekus model. The spatial frequency of small imposed disturbances, which is proportional to the perturbation wave number, can be used to control the self-thinning dynamics of fluid jet breakup as shown in the space-time diagrams of figure 4. The contour plots of $\log_{10}(R)$ in the *z-t* plane shows that for a wave number smaller than the one corresponding to the maximum growth rate (kR_0=0.67) a satellite droplet forms. Both the satellite and main drops oscillate due to coupling with capillary forces (at the Lamb's frequency) as clearly illustrated in the space time-diagram.

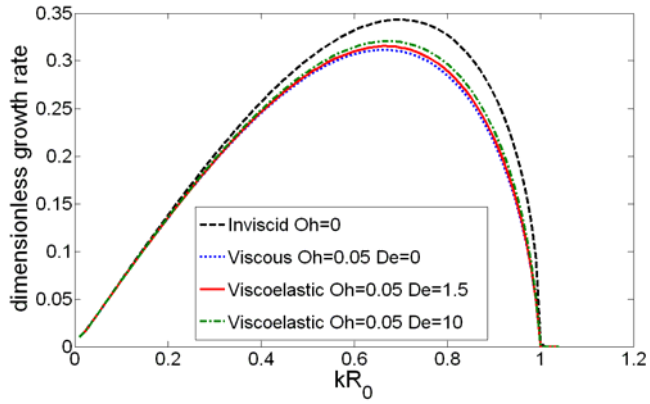

Figure 3: Dispersion curve predicted by linear stability analysis of a viscoelastic jet compared to viscous and inviscid jet.

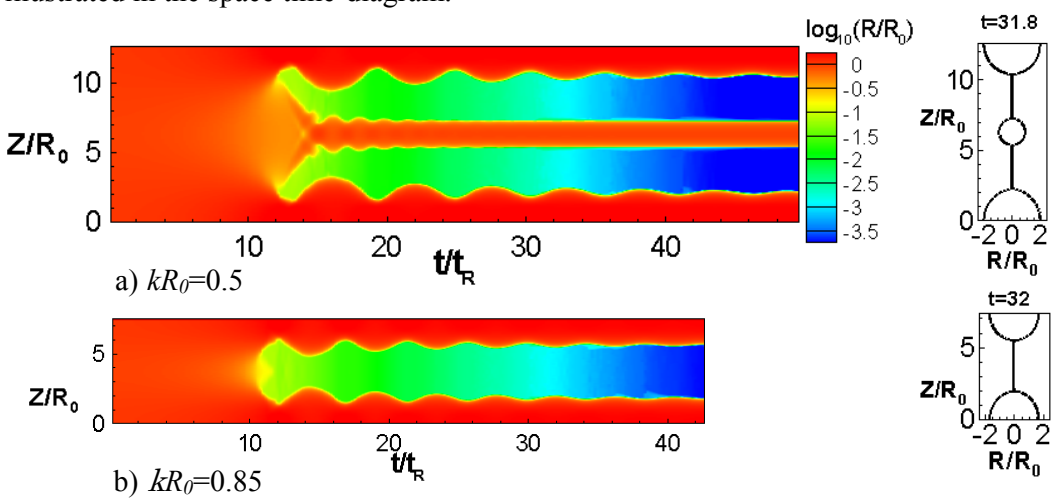

Figure 4 Space-time diagrams for thinning and breakup of an Oldroyd-B liquid jet at different disturbance wave numbers, Oh = 0.05, De = 1.5, $\beta = \eta_s/\eta_0$ = 0.6. Simulations are continued till a minimum dimensionless radius of R/R_0=0.0003 is obtained. Dimensionless axial position, z, varies

In these simulations we find that an exponential thinning can be observed in the thread connecting the main and the satellite drops, demonstrating elasto-capillary scaling applies for this system. For a wave number larger than the one corresponding to the maximum growth rate, the formation of the satellite droplet is strongly suppressed which is desirable in an extensional rheometer.

3. Jetting experiments

The growth of instability and the thinning of neck before pinch-off for a low viscosity (η_0=4.1 mPas) and short relaxation time (theoretical value for Zimm time, λ_{Zimm}~ 0.05 ms) were visualized using a special set-up developed in the group. The jet is perturbed using a piezoelectric transducer and visualized using a CCD camera and strobe system, where we achieve a temporal resolution of a microsecond by changing the phase difference between the strobe and perturbation frequency, and spatial resolution of 2.5 microns. As the frequency of perturbation or kR_0 is

increased, we find that the growth rate of the instability goes through a maximum around $kR_0 = 0.65$, and the shape of the neck tends to become increasingly symmetric as we go to higher wave-numbers, as shown in figure 5. The concentrations examined and the range of parameters used here are too low for observing stable "beads on a string" morphology, which is discussed in detail elsewhere [1-3, 5]. At lower excitation frequencies, longer wavenumbers (hence shorter wavelength) instability has faster growth rate, and hence it competes with the applied frequency. At higher frequencies, the more unstable wavelengths are larger, therefore the faster growing modes cannot be accommodated and hence do not influence the shape of the jet. Thus at high wavenumbers, we are closest to the highly desirable case of fluid with a constant stretch history. In the two montages, we show the change in neck diameter as a function of time, and as wavenumber is increased from $kR_0 = 0.55$ to $kR_0 = 0.85$, the number of necks visible increases, showing that the wavelength is becoming shorter. By following radius as a function of time, growth rate is computed from the slope of log ($\Delta R/R_0$) vs time. The relaxation time obtained from the elastocapillary regime, (as discussed before), turns out to be 0.16 ms, which is a factor of three larger than the estimated Zimm relaxation time. Using the radius of the neck, we can determine the extension rate, $\dot{\varepsilon} = (-2/R)(dR/dt)$, and the apparent extensional viscosity in the elastocapillary region is then given by $\eta_E = (\sigma/R)/\dot{\varepsilon}$. The initial extension rates are a function of excitation frequency or wavenumber as well as the perturbation amplitude and in these experiments on PEO system, extension rates $\dot{\varepsilon} \sim 10^4\ s^{-1}$ were achieved.

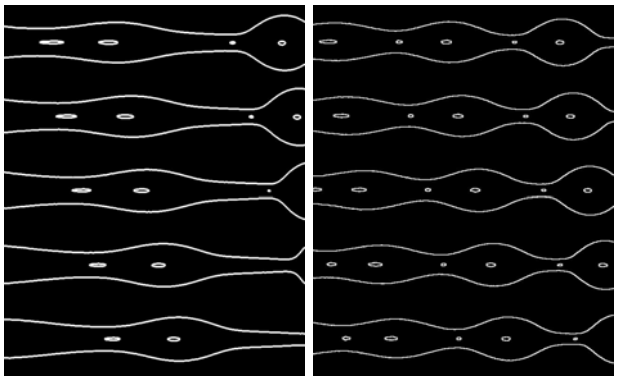

Figure 5: Digitized edge profiles of 0.01% PEO solution (M_w = 300,000 Daltons) in Glycerol/Water; Oh = 0.05, t_R =0.11 ms, We = 20 (a) $kR_0 = 0.55$ (b) kR_0=0.85.

4. Conclusions:

In this study, we describe how the instability growth and capillary break-up in a weakly viscoelastic jet contain information about elasticity and extensibility at time scales and length scales that are not apparent in conventional extensional or shear rheometry measurements. The filament thinning before pinch-off allows us to determine the relaxation time and apparent extensional viscosity for highly dilute polymer solutions. We show an example of 0.01% PEO solution in Glycerol/Water mixture where the relaxation time of 0.16 ms was measured for a solution with c/c^*=0.03, or in other words for a concentration that is 3% of overlap concentration.

5. References:

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[4] L. E. Rodd *et al.*, Applied Rheology **15**, 12 (2005).

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