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Simulations of drop formation in complex rheological fluids - can rheology improve jetting performance?

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Abstract

The processes of jetting and drop formation is strongly affected by fluid rheology, which may be complex, particularly under the extreme conditions of high shear and extensions rates that occur during jetting. Fluids containing a particulate phase are normally shear-thinning and so may have different characteristic viscosities during different key stages of the inkjet flow. Moreover, even trace amounts of long chain polymers can cause substantially different breakup dynamics compared to that of an ordinary (Newtonian) fluid.

In this work we investigate the dependency of jet breakup behaviour upon viscoelastic and shear-thinning effects in the context of drop-on-demand inkjet drop formation. In drop-on-demand printing, each ejected drop remains connected temporarily to the printhead by a trailing ligament of fluid which undergoes capillary thinning while the drop is in flight. Upon pinch-off the severed ligament may recoil downstream towards the leading drop, or alternatively it may fragment into multiple satellite droplets. Whilst complex rheology is often seen as a problem, particularly given the lack of instrumentation able to measure and characterize fluid properties at the appropriate deformation rates and timescales, it also offers a potential solution to controlling satellite drops at higher printing speeds.

We show the results of numerical simulations of drop-on demand inkjet printing with fluids that exhibit different types of non-Newtonian behaviour (shear-thinning and viscoelasticity) and compare with experiments on model inks. Our aim is to establish the parameter values controlling the break-up length and character of jet break-up. In particular, we examine whether for appropriate choices of rheological parameters it is possible to prevent or impede the creation of satellite drops without compromising on printing speed.

Introduction

Inkjet printing relies upon accurate and reliable delivery of drops generated in the jetting process. Although the droplet speed is determined by the momentum imparted during the drive phase, the subsequent formation of the ejected fluid into drops is controlled by the surface tension driven Rayleigh-Plateau instability. Consequently the formation of well controlled drops requires an appropriate balance of surface tension, fluid inertia and viscosity, expressed through the Ohnesorge number, $Oh = \mu/\sqrt{\rho\Gamma R}$, where Γ is the coefficient of surface tension, ρ the fluid density, μ viscosity and R drop radius. Roughly, for successful drop-on-demand printing the fluid Ohnesorge number must lie in the range $0.1 < Oh < 1$ [1]. At higher Ohnesorge numbers the high viscosity of the fluid delays the initial break-off of the ejected fluid from the nozzle, producing a long trailing ligament behind the drop. At lower Ohnesorge numbers the initial break-off is controlled by inertia, but the trailing ligament is more unstable to the Rayleigh-Plateau instability and disintegrates into satellite drops. This limits the range of fluids that can be successfully jetted. One of the key challenges for the inkjet research is to increase the diversity of the materials that can be successfully printing process in order to broaden the range of industrial and commercial applications. Moreover even within this range there is a limit on the speed at which drops can be formed without satellite drops.

As inkjet develops as a fabrication technology there is a need to be able to jet complex fluids, such as those that contain concentrated particle dispersions or polymers [1]. However, this requires a detailed understanding of how the complex rheological properties of these fluids affect jetting behaviour and drop formation. The forces between particles that stabilise colloidal suspensions typically mean that they exhibit some degree of shear-thinning behaviour [2]. The local variation of viscosity in such a fluid can modify the breakup dynamics of a compared to those of Newtonian fluids. Whilst this may determine whether the fluid is suitable for a particular jetting application, the capacity to impose explicit control upon the breakup behaviour by making appropriate modifications to the rheological properties of the ink is potentially a means to improve the jetting performance of an ink. Even at very low concentrations high molecular weight polymers can profoundly affect jetting behaviour [3]. Under the high extension strains that occur in the thinning liquid bridges connecting drops, the conformation of polymer molecules can become highly extended away from their equilibrium "coiled" state. As a consequence of this "coil-stretch" transition the polymers exert an elastic stress that acts to stabilise these liquid bridges resulting in a "beads on a string" structure [3]. In previous work [4] we showed that whilst this can delay and even prevent break-off from the nozzle in drop-on-demand printing, by stablising the ligament it can reduce satellite formation.

Rheological Constitutive Equations

For an incompressible fluid, the governing equations are conservation of momentum and mass given by

$$\rho\frac{D\mathbf{u}}{Dt} = -\nabla p + \nabla\cdot\sigma, \qquad \nabla\cdot\mathbf{u} = 0, \tag{1}$$

where p and $\mathbf{u}$ are the fluid pressure and velocity respectively and σ is the extra stress. In the case of a Newtonian fluid the extra stress σ, is proportional to the local rate of strain tensor $\mathbf{E} = \frac{1}{2}\left(\nabla\mathbf{u} + (\nabla\mathbf{u})^T\right)$, as

$$\sigma = 2\mu\mathbf{E}, \tag{2}$$

where μ is the fluid viscosity. When substituted into equation (1) this gives the Navier-Stokes equations.

For the case of colloidal fluids where the shear viscosity is not constant, but depends upon the local shear-rate, equation (2) may be generalised to

$$\sigma = 2\mu(\dot\gamma)\mathbf{E}, \tag{3}$$

where μ is now a function of the local shear-rate $\dot\gamma = \sqrt{2\mathbf{E}:\mathbf{E}}$. Here we use the Carreau fluid model [5], in which the fluid viscosity thins from a zero-shear-rate viscosity μ_0, in which colloidal forces are active to a lower high-shear-rate viscosity μ_∞

where hydrodynamic forces are dominant, via a power-law region of index n,

$$\mu(\dot{\gamma}) = \mu_\infty + (\mu_0 - \mu_\infty)\left(1 + (\dot{\gamma}/\dot{\gamma}_0)^2\right)^{(n-1)/2}. \quad (4)$$

Here $\dot{\gamma}_0$ is a representative value of the shear rate associated with the onset of shear-thinning. Figure 1 shows the form of this viscosity function for $\mu_0 = 50$m Pa s, $\mu_\infty = 3$m Pa s, $\dot{\gamma}_0 = 10^5 \mathrm{s}^{-1}$ and $n = 0.3$.

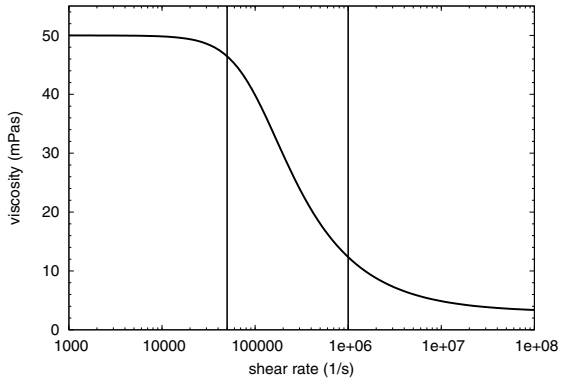

Figure 1. *The viscosity function $\mu(\dot{\gamma})$ for $\mu_0 = 50m$ Pa s, $\mu_\infty = 3m$ Pa s, $\dot{\gamma}_0 = 10^5 s^{-1}$ and $n = 0.3$.*

It should be emphasized that for this generalized Newtonian fluid (GNF) the term "shear-thinning" really means "strain-rate thinning", in the sense that the viscosity is assumed to decrease as a function of the inner product of the strain-rate tensor. Thus this fluid exhibits a reduced viscosity both in pure shearing flow and in purely extensional flow. Whilst this is representative of the behaviour of colloidal fluids, polymeric fluids behave qualitatively differently in shear and extensional flows and so their rheology cannot be captured by this model.

For polymer solutions a simple constitutive model that incorporates the essential physics of the coil-stretch transition in extensional flow is the finitely extensible non-linear elastic dumbbell model with the Chilcott-Rallison closure approximation [6], also known as the FENE-CR model. In this model the extra stress is given by

$$\sigma = 2\mu_s \mathbf{E} + Gf(\mathbf{A} - \mathbf{I}),$$

where μ_s is the solvent viscosity, $\mathbf{E}$ is the strain rate tensor and the polymer stress consists of the elastic modulus G, the conformation tensor $\mathbf{A}$ and the FENE factor

$$f = \frac{L^2}{L^2 + 3 - \mathrm{tr}(\mathbf{A})}, \quad (5)$$

that accounts for the finite extensibility L of the polymer chain. The conformation tensor $\mathbf{A}$ satisfies the evolution equation

$$\frac{D\mathbf{A}}{Dt} = (\nabla \mathbf{u})^T \cdot \mathbf{A} + \mathbf{A} \cdot \nabla \mathbf{u} - \frac{f}{\tau}(\mathbf{A} - \mathbf{I}), \quad (6)$$

where τ is the relaxation time of the polymer. In this model the viscosity in steady shear-flow is constant and given by $\mu_s + G\tau$, whereas the extensional viscosity increases from three times the shear viscosity to $3\mu_s + 2G\tau L^2$ at large extension rates. Thus for high large values of the extensibility, L there is a much greater resistance to extension than shear.

For a dilute, monodisperse polymer solution the parameters in the FENE-CR model, namely elastic modulus G, relaxation time τ and finite extensibility L, can be determined as functions of the molecular weight M_w, weight fraction concentration ϕ and solvent quality factor ν using Zimm theory [7], and are given by:

$$G \sim \phi M_w^{-1} \quad ; \quad \tau \sim M_w^{3\nu} \quad ; \quad L \sim M_w^{(1-\nu)}. \quad (7)$$

Numerical Method and Flow Geometry

The governing equations are solved using an axisymmetric Lagrangian finite element method. Although originally developed for the study of creeping flow of dilute polymer solutions [8], this method has been extended to inertial flows and applied to inkjet drop formation of Newtonian and complex fluids [4]. Further details of the computational methods may be found in these references.

The nozzle and drive waveform used in the simulations are identical to that used in reference [4] and are based on a Xaar XJ126-200 printhead with nozzle radius $R = 25$m. For a particular fluid the amplitude of the waveform is amplified to obtain the desired drop speed. Because of this amplification, the total volume of ejected ink is not necessarily constant. The boundary condition is the pressure jump due to surface curvature,

$$[-p\mathbf{n} + \sigma \cdot \mathbf{n}]_{\mathrm{air}}^{\mathrm{jet}} = -\Gamma \nabla_s \cdot \mathbf{n}\mathbf{n}, \quad (8)$$

where $\mathbf{n}$ is the normal to the fluid surface. In our Lagrangian finite element method the node points are material points that move with the fluid, so that the position of the interface is represented by the boundary of the mesh. This ensures a more accurate representation of the position of the free surface than is possible using interface capturing methods. The accuracy of the simulations for Newtonian fluids have been verified by comparison with experimental measurements of drop-on-demand jet formation [9].

Satellite-free Inkjet Printing for Shear-thinning Fluids

In inkjet printing applications a fluid element ejected at a speed of order 6 m/s through a nozzle of diameter 50 μm will experience shear-rates of around $10^6 \mathrm{s}^{-1}$, before being subjected to significant extension during the capillary thinning of the ejected ligament. However these extension rates are typically an order of magnitude lower than nozzle shear-rates. As a consequence a shear-thinning fluid is likely to undergo a substantial fluctuation in its viscosity during the printing process. In order to probe the effects of these flucuations we have chosen parameter values for the Carreau model (see figure 1) for which there is a significant change in the viscosity for shear-rates in the range 10^5 to $10^6 \mathrm{s}^{-1}$ by choosing $\dot{\gamma}_0 = 10^5 \mathrm{s}^{-1}$. We have then varied the high and low shear-rate viscosities μ_∞ and μ_0.

For the particular nozzle and drive waveform used in this study satellite-free drop formation with Newtonian fluids is only possible for jet speeds below 5.4 m/s, with the optimal viscosity being $\mu = 20$mPas corresponding to an Ohnesorge number, $Oh = 0.6$. However, by increasing the low shear-rate viscosity μ_0 it is possible to increase the jet speed without forming satellites. By increasing μ_0 we increase the ligament viscosity suppressing the growth-rate of the Rayleigh-Plateau instability to allow a longer ligament to remain intact while it absorbed into the main drop.

Figure 2 shows the profile of the jet shortly after break-off at the maximum speed for which satellite free jetting is obtained. It can be seen that increasing μ_0 allows a longer ligament to remain intact after break-off. Furthermore by decreasing the high-shear-rate viscosity to reduce the effective viscosity in the nozzle and

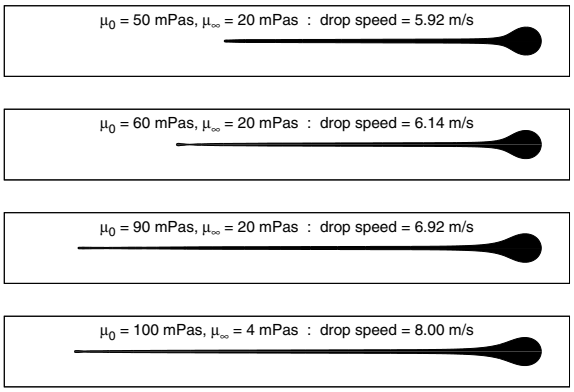

Figure 2. *Snapshots of ligament shapes (shortly after breakoff) for the fastest satellite-free jet for various shear-thinning cases.*

at the point of break-off we can increase jet speed further without increasing the length of the ligament.

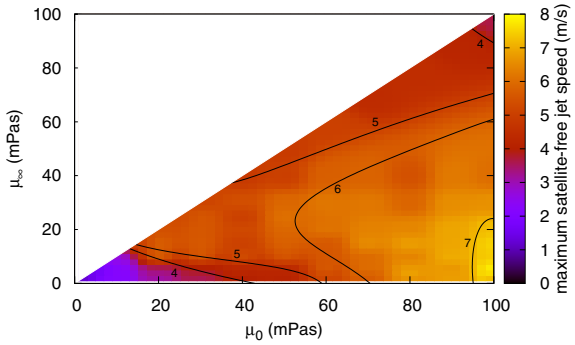

Figure 3. *Contour plot of maximum satellite-free jet speed plotted against the zero-shear-rate, μ_0, and high-shear-rate, $\mu\infty$, viscosities. The diagonal line $\mu_\infty = \mu_0$ corresponds to Newtonian fluids*

The effects of varying the two viscosities on the maximum satellite-free jetting speed are summarised in figure 3 where we plot contours of maximum satellite-free jet speed in the space of zero-shear-rate, μ_0, and high-shear-rate, μ_∞, viscosities, with the line $\mu_\infty = \mu_0$ representing the range of Newtonian fluids. By choosing the fluid properties such that viscosity in the nozzle is low compared to the viscosity in the ligament it is possible to achieve satellite-free drops with a jet speed of 8 m/s. This is supported qualitatively by experiments performed by Hoath *et. al.* [10], who concluded that ability of PE-DOT:PSS solutions to produce satellite-free inkjets is at least in part due to shear-thinning.

Effect of Polymeric Additives on Inkjet Drop Formation

We now consider the effects of polymeric additives using the FENE-CR constitutive model. We have shown previously [4] that this model is able to reproduce the range of different break-up phenomena observed experimentally in reference [11], for appropriate values of model parameters, G, τ and L. In order for the polymer molecules to undergo the "coil-stretch" transition the extension-rates in the ligament must exceed the rate of relaxation of the polymer molecules, $1/\tau$. The ligament extension-rates can be estimated from the growth rate of the Rayleigh-Plateau instability as $\sqrt{\Gamma/\rho R^3}$ from which we can define the Deborah number, De as

$$De = \tau\sqrt{\frac{\Gamma}{\rho R^3}}. \tag{9}$$

Defined in this way, the Deborah number represents the ratio of the fluid relaxation time to the reciprocal of the ligament extension rate, so that the condition for the "coil-stretch" transition to occur is that $De > 1/2$. For the particular geometry being simulated here this condition requires that $\tau > 15\mu$s. Whilst this is a necessary condition for the polymers to become extended, their concentration must be sufficient for this to affect the flow. Furthermore, provided this condition is met the value of relaxation time has little effect on the dynamics. A polymer solution is considered to be dilute if the polymer contribution to the zero-shear-rate viscosity is less than that of the solvent. In terms of the FENE-CR model the solution is dilute if $G\tau < \mu_s$. However, as noted above, at high Deborah numbers transition to the stretch state means the contribution of the polymers to the extensional viscosity is magnified by a factor of L^2, where L is the extensibility. Since L is large for a high molecular weight polymer, this means that there is a range of concentrations where the polymer has a negligible effect on the shear viscosity and hence on the flow within the nozzle, but where the extensional stresses can profoundly affect the subsequent dynamics of the drop and ligament.

The increased resistance to extension introduced by the addition polymer has two detrimental effects on inkjetting. First, the time taken for the ejected drop to break-off from the nozzle is increased, leading to a lengthening of the ligament. Second, the increased resistance of the ligament to stretching, while it remains attached to the nozzle reduces the drop speed [12]. As a consequence even trace amounts of a high molecular weight polymer can render an ink unjettable. However, we also find that a small amount of moderate molecular weight polymers, for which L is around 10, can reduce or even eliminate satellite drops by stabilising the ligament [4].

We can also go further and make a direct comparison with jetting experiments on weakly elastic polymer solutions consisting of mono-disperse polystyrene in diethyl-phthalate. These fluids have been used in a number of previous studies of jetting of low viscosity viscoelastic fluids [13, 14] and have been shown to follow the predictions of the Zimm model, equation(7), with a solvent quality factor $\nu = 0.567$ [15]. In Reference [14] the effects of varying molecular weight on jetting from a MicroFab (MF) ink-jet nozzle was studied. Here we compare the jet evolution in the Xaar XJ126-200 printhead with our simulations using the FENE-CR model. The printhead was set up such that every third nozzle fired simultaneously, so that a single image provides a snapshots of the jet evolution at 3 different time points, as shown in the example in Figure 4. In this figure the solution being jetted is a 1000ppm solution of polystyrene of molecular weight 210 KDa. This is predicted to have a relaxation time of $\tau = 20\mu$s so that the Deborah number is greater 0.5 and an extensibility, $L = 21$. At this concentration $G\tau/\mu_s = 0.023$ meaning that the solution is dilute, but $G\tau L^2 >> \mu_s$, so that polymer stresses can be significant if the polymers are highly stretched. As shown in Figure 4, this is sufficient to delay break-up so that long ligaments are formed behind the main drop, but although satellite drops are formed, these remain connected to the main drop by liquid bridges stabilised by the polymer stress. The insert in this figure shows the result of the simulations using the parameter values listed above, which are in very good agreement

with the experiments.

Conclusions

In this paper we have shown that provided it is properly controlled complex fluid rheology can improve the performance of inkjet printing above that of Newtonian fluids. In particular, by designing a fluid that has a lower shear-viscosity at the high-shear-rates experienced in the nozzle compared with its viscosity in the ligament provides a means to jet without satellites at higher speeds. For polymeric fluids the picture is more mixed, but whilst very high molecular additives are to be avoided, a small quantity of moderate molecular weight polymer has the potential to reduce satellite formation. Moreover the two mechanism are quite separate and so can be used in combination.

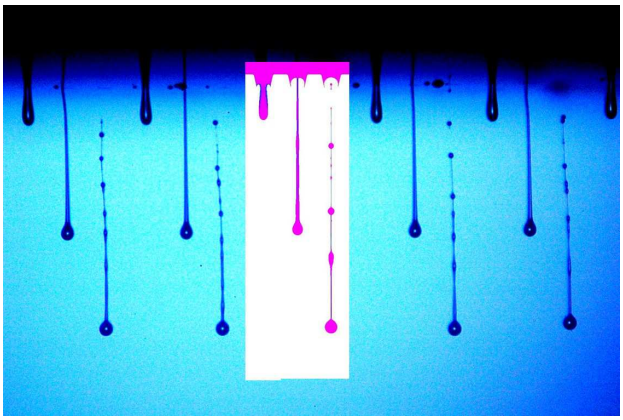

Figure 4. *Image showing the jetting of a 1000ppm solution of monodisperse polystrene ($M_w = 210$ KDa in diethyl-diethyl-phthalate in a Xaar XJ126-200 printhead. Insert shows the simulations at the corresponding times.*

Acknowledgments

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References

[1] B. Derby, Inkjet printing of functional and structural materials: fluid property requirements, feature stability, and resolution, Annu. Rev. Mater. Res., 40, 395 (2010).

[2] D. C. Vadillo, A. C. Mulji, and M. R. Mackley, The rheological characterization of linear viscoelasticity for ink jet fluids using piezo axial vibrator and torsion resonator rheometers, J. Rheol., 54, 781, (2010).

[3] Y. Christanti and L.M. Walker, Effect of fluid relaxation time of dilute polymer solutions on jet breakup due to a forced disturbance, J. Rheol., 46, 733 (2002).

[4] N. F. Morrison and O. G. Harlen, Viscoelasticity in inkjet printing, Rheol. Acta, 49, 619 (2010).

[5] P.J. Carreau, D. De Kee and M. Daroux, An analysis of the viscous behaviour of polymeric solutions, Can. J. Chem. Eng., 57, 135, (1979).

[6] M. D. Chilcott and J. M. Rallison, Creeping flow of dilute polymer solutions past cylinders and spheres, J. Non-Newt. Fluid Mech., 29, 381 (1988).

[7] C. Clasen, J.P. Plog, W.M. Kulicke, M. Owens, C. Macosko, L.E. Scriven, M. Verani and G.H. McKinley, How dilute are dilute solutions in extensional flows?, J. Rheol., 50,849, (2006).

[8] O. G. Harlen, J. M. Rallison, and P. Szabo, A split Langrangian-Eulerian method for simulating transient viscoelastic flows, J. Non-Newt. Fluid Mech., 60, 81 (1995).

[9] J. R. Castrejon-Pita, N. F. Morrison, O. G. Harlen, G. D. Martin, and I. M. Hutchings, Experiments and Lagrangian simulations on the formation of droplets in drop on-demand Mode, Phys. Rev. E, 83, 036306 (2011).

[10] S.D. Hoath, S. Jung, W.-K. Hsiao and I.M. Hutchings, How PEDOT:PSS solutions produce satellite-free inkjets, Org. Electron., 13,3259, (2012).

[11] A. D. Basilevskii, J. D. Meyer, and A. N. Rohzkov, Dynamics and breakup of pulse microjets of polymeric fluids, Fluid Dyn., 29, 381 (2005).

[12] C. McIlroy, O. G. Harlen, and N. F. Morrison, Modelling the jetting of dilute polymer solutions in drop-on-demand inkjet printing, J. Non-Newt. Fluid Mech. 201, 17, (2013).

[13] S. D. Hoath, O. G. Harlen, and I. M. Hutchings, Jetting behaviour of polymer solutions in drop-on-demand inkjet printing, J. Rheol. 56, 1109-1127 (2012).

[14] S. D. Hoath, D. C. Vadillo, O. G. Harlen, C. McIlroy, N. F. Morrison, W. K. Hsiao, T. R. Tuladhar, S. Jung, G. D. Martin, and I. M. Hutchings, Inkjet printing weakly elastic polymer solutions, J. Non-Newt. Fluid Mech., 205, 1 (2014).

[15] D. C. Vadillo, W. Mathues, and C. Clasen, Microsecond relaxation processes in shear and extensional flows of weakly elastic polymer solutions, Rheol. Acta 52, 755-769 (2012).

Author Biography

Oliver Harlen received his BA in mathematics (1987) and PhD in applied mathematics from the University of Cambridge (1991). Following research fellowships at Cornell University and Jesus College, Cambridge he joined the School of Mathematics at the University of Leeds, where he is currently a Reader (Associate Professor). His research has focused on modelling the flow of complex rheological fluids, particularly of polymeric fluids and on simulations of free surface flows. This has led him to examine the effects of rheology on jet break-up and droplet generation in inkjet printing.