Regimes of Polymer Behaviour in Drop-on-Demand Ink-Jetting

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Abstract

A recent model for the drop-on-demand (DoD) jetting of mono-disperse linear polymer solutions has identified three regimes of behaviour: with the polymer chains fully relaxed; with significant viscoelastic effects; and with the chains fully extended. These regimes have now been confirmed by experimental observations in several different systems. The model predicts the maximum jettable concentration of polymer as a function of molecular weight. The highly extensional flows in high-speed jetting with viscous solvents can fully stretch linear polymer chains outside the nozzle, permitting jetting of solutions with higher polymer contents than for purely elastic behaviour. These results are significant for DoD printing at high jet speeds and will be relevant to jet formation from linear polymer solutions for any DoD printhead.

Introduction

Drop-on-demand (DoD) ink-jet printing of dilute polymer solutions, with a fixed drive waveform to achieve a main drop tip speed of ~ 6 m/s at ~ 1 mm standoff had been studied by high-resolution spark flash imaging [1]. Dilute solutions of polystyrene (PS) with near mono-disperse molecular weights (M_w) from 24,000 to 488,000 g/mol were prepared in a good but viscous solvent, diethyl phthalate (DEP). The dependence on polymer molecular length (L) of the maximum PS concentration for DoD jetting was determined. Zimm-Rouse theory for polymers in dilute solution provides a quantitative relation between L and M_w as described elsewhere [2].

These polymer solutions with low M_w and dilutions were expected to show jetting behaviour either controlled by linear viscosity tending towards the Newtonian solvent viscosity at the lowest polymer concentrations, or "elastic" behaviour, with the maximum jettable concentration falling rapidly (at least as an inverse square law) with M_w. However results from both our experiments [3, 4] and our numerical simulations [5] appeared to show the variation of this limiting concentration to be close to $1/M_w$, which was unexplained by polymer theory. Earlier results, from de Gans *et al* [6], for slower (~ 2 m/s) jets of mono-disperse polystyrene solutions in another "good" solvent from a different print head type appeared to show "elastic" behaviour at high M_w. We have sought to understand these apparent discrepancies.

Numerical simulations & models

Numerical code developed by Morrison and Harlen has been validated separately for DoD and CIJ jetting conditions, using a large-scale drop generator system [7] as well as by various results on the scale of industrial inkjet printing [8]. This axi-symmetric code for fluid flow incorporates polymer Zimm models [5] and at high shear rate predicted a relationship between the required print head drive and M_w which was unexpected but which was consistent with the jetting data for PS in DEP obtained in earlier work.

Recently [9], another possible regime for polymer behaviour was considered: if polymer chains become fully stretched, i.e. beyond the viscoelastic region, how does this affect the fluid jetting? Once the polymer chains are fully stretched they behave like rigid rods of length L in solution, with very high viscosity >100 times the viscosity at low extension rate. (The viscosity ratio between fully stretched chains and the Newtonian viscosity in this model [9] is given by $\frac{2}{3}L^2$, and for a linear polymer with $M_w >$ 100,000 g/mol the value of $L >$ ~15.) This higher viscosity suggests a power-law dependence on polymer concentration that still does not conform directly to all ink-jet measurements, since it neglects key aspects of high speed ink-jets.

A previous approach to understanding polymer solution ink-jets [10] was based on a simple model of an extending ligament combined with the polymer theory. This approach gave very good descriptions of viscoelastic behaviour and predicted the conditions under which fluid is initially ejected from the nozzle but never separates, and retracts back inside ("bungee jumpers"). However, this approach was applied only to relatively low extension rates (jet speeds) compared with those reported here.

Figure 1 shows the model for the rapidly extending ink-jet.

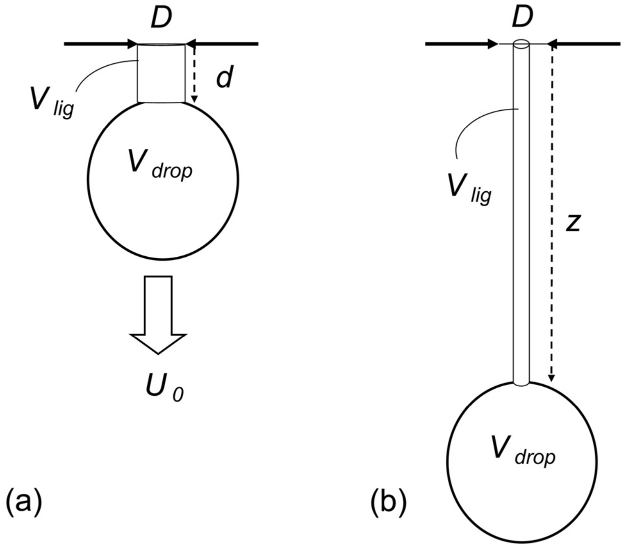

***Figure 1**: Basic model of extending ink-jet [9], following earlier approach [10].*

Using the previous model approach [10] and the multi-mode Zimm model, it was found [9] that at high extension rates in fast jetting conditions a combination of fully stretched polymer chains and thinning of the ligament during fluid extension reduced the predicted overall power-law dependence on concentration close to that observed for ink-jets of PS in the (viscous) solvent diethyl phthalate (DEP), also providing some explanations for the scaling law that was found in the earlier simulation results [5].

Model results

Three regimes of ink-jet jetting behaviour are predicted [9]: two are well-known but the third had not previously been clearly identified in the literature or experimental data. Transitions between these regimes depend on the initial Weissenberg number (Wi) given by the product of initial extension rate ($\dot{e}$) and polymer relaxation time (τ), where we approximate the extension rate from the initial jet speed (U_0) and length scale (d) for the jet neck (see Figure 1):

$$\mathrm{Wi} = \dot{e} \times \tau \tag{1}$$

$$\dot{e} = U_0/d \tag{2}$$

Newtonian, viscoelastic and fully stretched chains are associated with the extensional flow conditions $0 < \mathrm{Wi} < ½$, $½ < \mathrm{Wi} < L$, and $L < \mathrm{Wi}$ respectively, and correspond to particular scaling laws in L (or M_w). The power law exponents for the M_w dependence of the maximum jettable concentration (in g/cc, wt%, etc.) in the three regimes are ($1-3\nu$), ($1-6\nu$) and (-2ν) respectively, where ν is the solvent quality factor which generally lies between 0.5 (poor) and 0.6 (very good). For PS in the "good" solvent DEP (diethyl phthalate), ν=0.567 and the scaling law exponents are -0.70, -2.40 and -1.12 respectively. Figure 2 shows the three regimes, for PS in DEP, indicating the scaling laws and the transition points at $\mathrm{Wi} \approx ½$ and $\mathrm{Wi} \approx L$; the solid curve is based on numerical simulations with a more exact model for deceleration. The model fails for $L < 5$. Higher extensional rates and solvent viscosities increase Wi linearly: both transitions move towards lower M_w values and shrink the viscoelastic region, such that jetting is then limited for most M_w by extensional behaviour of fully stretched polymer chains.

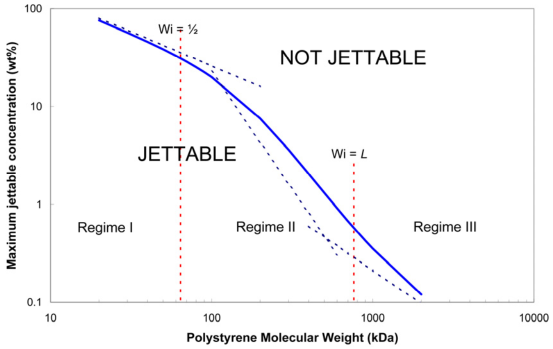

***Figure 2**. Predictions (see Appendix) for maximum jettable concentrations for PS solutions in the "good" solvent DEP, indicating power law slopes in the 3 regimes and Weissenberg number Wi values at transitions between them.*

Experimental results

Experimental techniques for imaging and analysis have been presented previously: for high speed flash by Hutchings *et al.* [1] and for high speed video imaging by Hsiao *et al.* [11]. Methods for rheological characterization [4] and related experiments on polystyrene solutions in DEP filament stretching and thinning [8, 12, 13, 14], as well as full details of the materials and solution preparation, are described elsewhere [9]. Experimental values for the maximum jettable concentration for solutions of PS in DEP, corresponding to ~6 m/s tip speeds, were evaluated at a nominal "standoff" distance of ~1 mm, for a Xaar XJ126-200 (non-wetting nozzle) print head. Concentration limits were extrapolated to a drive voltage setting of EFF=1.3±0.2 in the print head control software, which is responsible for the error bars plotted in Figure 3.

Figure 3 compares the results for jetting of PS in DEP at ~6 m/s (■) [9] and of PS in acetophenone (ATP) at ~ 2 m/s (□) from de Gans *et al* (2004) [6], together with appropriate scaling law slopes adjusted to the data. For PS in DEP the data are consistent with fully stretched chains at $\mathrm{M_w}$ > 100 kDa (probably with a Newtonian regime I, shown as a dashed line, but almost no viscoelastic regime II), whereas PS in ATP is consistent with scaling in the regimes I and II (and the highest M_w point may possibly lie in regime III as shown by the dotted line) [9].

Figure 4 shows c/c* vs M_w from A-Alamry *et al*. [15], where c* is the concentration limit for dilute solutions (e.g. [2]).

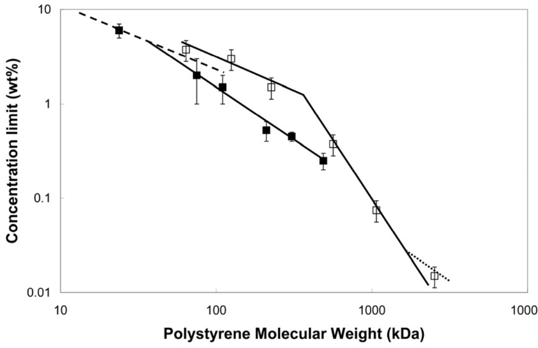

***Figure 3**. Jetting limit data for PS in "good" solvents DEP (■) [9] and ATP (□) [6] overlaid with model predictions from the 3 regimes. Solutions in DEP (■) appear consistent with fully stretched chains at most M_w, but solutions in acetophenone (□) are consistent with regimes I & II (& III?)[9]. See Appendix.*

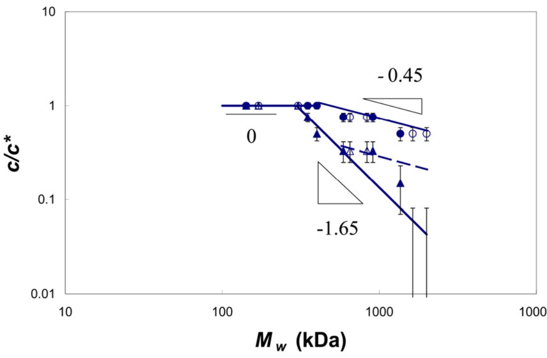

***Figure 4**. Jetting limit data, from A-Alamry et al [15], for PS and PMMA in a "good" solvent, overlaid by the scaling predictions for the slope of the c/c* vs. M_w plot from the new model [9] for solvent quality factor ν=0.55. Jetting data for a 50 µm MicroFab print head, at drives of 30V (▲) and 50V (●), are shown for each polymer solution, with PMMA as solid symbols and PS as open symbols. The slopes (0, -1.65 and -0.45) depicted on the c/c* vs. M_w plot are close to the regime slopes for PS in DEP (Fig 2) after subtracting the M_w dependence of c*. The uncertainties are estimated as ± 0.08 in c/c*.*

Jetting of solutions of PMMA (polymethylmethacrylate, another linear polymer) and PS in the "good" solvent γ-butyrolactone

(GBL) has been reported recently by A-Alamry *et al.* [15]. Dividing the scaling predictions (i.e. subtracting the slopes) for maximum concentration c *vs.* M_w (in three regimes equivalent to Figure 2) by the scaling for c^* *vs.* M_w (as given in the first regime), the predicted scaling for c/c^* data *vs.* M_w is readily found. The data in Figure 4 [16] show trends that reflect the power law scaling in all three regimes from Figure 2. The possible change of slope, and hence regime, between jetting at 30V and 50V drive is linked to a higher initial jet speed U_0 associated with higher drive, and hence higher Weissenberg number through increased extension rate $\dot{e}$, as shown by equation (2). Observation of three regimes in data for jetting in quite different systems strongly supports the model [9].

Table 1 lists the M_w scaling laws from the model predictions, and the values of the exponents for solvent quality factor $0.5 < \nu < 0.6$, for the maximum jettable concentration c (and c/c^*) for the three regimes of behaviour.

Table 1: M_w scaling laws in three regimes of polymer behaviour

Regime: Law:	Viscous: I	Viscoelastic: II	Fully stretched: III
c	1-3ν	1-6ν	-2ν
c/c*	0	-3ν	ν-1
c	-0.65±0.15	-2.30±0.30	-1.10±0.10
c/c*	0	-1.65±0.15	-0.45±0.05

Discussion

The data for PS in acetophenone at the higher M_w in Figure 3 lie in regime II (and possibly III) but the behaviour was not interpreted as completely elastic by de Gans *et al.* (2004) [6], perhaps because the slope is slightly too shallow if regime III is missed [9]. With the identification of a fully stretched regime in jetting, the data from de Gans *et al.* (2004) [6] can be considered good evidence for both the critical concentration c^*-limited regime I and viscoelastic-limited regime II, with the transition between these taking place at $M_w \approx 360$ kDa for 2 m/s jetting from a 70 µm diameter MicroDrop print head. The scaling law prediction for the fully stretched chain is $M_w \approx 1650$ kDa under these conditions. The data for PS in DEP are for ~6 m/s jetting from a 50 µm diameter XJ126-200 printhead, and equation (2) suggests that $\dot{e}$ was ~4 times that for PS in ATP. However, theory suggests that the polymer relaxation time is proportional to the solvent viscosity [2], so equation (1) implies that Wi_{DEP} is $\sim 7\text{Wi}_{\text{ATP}}$ under the same jetting conditions. This becomes ~28 times greater than under the de Gans *et al* [6] conditions. This large factor moves the points for both the transitions for PS in DEP to much lower values of M_w that produce relaxation times 28 times shorter than the equivalent values for PS in ATP. This effectively reduces the gap between regime I and regime III, almost (but not quite) enough to eliminate regime II for PS in DEP [9]. Chain relaxation times from the Zimm model also underestimate the effective relaxation time for PS in DEP at lower M_w [14], which most probably prevents access to viscoelastic regime II in our data [9].

Many previous authors have claimed fully stretched ligaments in their jetting experiments without proof, but rather based on expectations. In the present work, the experimental power law scaling dependence was tested by matching polymer theory to the model of jet thinning, and backed up by numerical simulations, with good agreement that also excludes other interpretations such as viscoelastic behaviour for the highest molecular weights. The implications for ink-jetting of polymer solutions are several: it proves far easier to jet fully stretched chains of high molecular weight polymer than in the viscoelastic mode, since in the latter the limiting concentration has a M_w exponent of $(1\text{-}6v)$ not $(-2v)$; the use of low viscosity solvent can suppress (through the polymer relaxation time) the onset of full stretching for high M_w polymer (as seen but perhaps not fully identified by de Gans *et al.* [6]).

Depending on the choice of solvent viscosity, DoD print head nozzle diameter and jetting speed, there is a rather narrow range of molecular weight which can give viscoelastic $(1\text{-}6v)$ behaviour, because the separation in Wi value between regimes I and III is only $\sim\frac{2}{3}L$; applications with higher jet speeds (and narrower nozzles) can reach $\text{Wi} > L$ at lower M_w, as seen in the data for PS in DEP in Figure 3.

The precise value of the solvent quality factor v does not significantly affect the implications of the three different scaling laws for inkjet printing of polymer solutions, because a "poor" solvent has $v = 0.5$ and a "good" solvent has $v = 0.6$. Thus the exact value of v for the polymer/solvent combination might be unknown, but can reasonably be represented by the value $v = 0.55$ without much error. Thus the slopes for c/c^* *vs.* M_w in Figure 4 (0, -1.65, -0.45), or their equivalent slopes in dimensional concentration as in Figure 2 but evaluated with v=0.55 (-0.65, -2.30, -1.10), should provide reasonable limits for the jetting of linear polymer solutions from all DoD print heads. This simplification of the more exact results may assist in practical application of the theory to other solvents, as the three regimes will exist for all solvents.

Extension of this approach to commonly jetted polymer molecules is clearly of interest for industrial DoD applications: branched, star and flexible polymers often behave differently in jetting from linear polymers, as has been reported elsewhere [16, 17]. The influence of a high poly-dispersity index (a measure of the range of molecular weight in a sample) in bulk commercial polymers has been investigated in detail for DoD jetting of aqueous solutions of polyethylene oxide (PEO) [17].

Knowledge of the polymer relaxation time is important in this approach, although this parameter has only recently become measurable experimentally at extension rates approaching those in inkjet printing, e.g. as shown by Vadillo *et al* [13, 14]. New methods for measurements of the rheology of inkjet fluids have also been introduced by Jung *et al* [18]. Further presentations on the numerical simulations of polymer jetting were also given elsewhere, e.g. Morrison et al (2011), Harlen et al (2012) [19, 20].

Conclusions

Extensional strain and fully stretched polymer chains are relevant to fast drop-on-demand ink-jetting. Evidence from experiments, models and numerical simulations, for high jet speeds and viscous solvents, strongly supports this. Other results for jetting of linear polymer solutions, at lower speed in far lower viscosity solvents and with different printhead technology, are also explained, allowing the formulation of general scaling rules that should for useful guidelines for the jetting of solutions of any linear polymer from any drop-on-demand printhead.

Appendix

Computation of the transition points between the regimes, in terms of molecular weights, is of obvious practical interest. Data for polystyrene in DEP [2] were used in Figure 2 as shown below. The model assumptions fail for $L < \sim 5$ ($M_w \approx 10$ kDa).

Relaxation time (μs) is approximated by $\tau = M_w^{3\nu}/(5.4\times10^7)$. Finite extensibility L is estimated from $L^2 = (9.2\times10^{-3})\, M_w^{2(1-\nu)}$. Weissenberg number Wi is evaluated from equations (1) and (2), using U_0 associated with the jetting speed at the start of necking, which is 1.5-2 times the final drop speed (as we observe in our numerical simulations and experiments).

The first transition point is at Wi = ½, becoming a limit on τ and hence M_w.

$$M_w = \left(\frac{1}{2}\frac{D}{U_0}5.4\times10^7\right)^{1/3\nu} \qquad (3)$$

The first transition for a $D = 50$ μm diameter nozzle occurs above 64 kDa (54 kDa) for $U_0 = 1.5(2) \times$ the final 6 m/s drop speed.

The second transition point is at Wi = L, hence

$$M_w = \left(\left(9.2\times10^{-3}\right)^{1/2}\frac{D}{U_0}5.4\times10^7\right)^{1/(4\nu-1)} \qquad (4)$$

The second transition for $D = 50$ μm occurs at ~760 kDa (~610 kDa) for $U_0 = 1.5(2) \times 6$ m/s drop speed.

Equations (3) and (4) can be used, with appropriate numerical values for other polymer-solvent systems, for other DoD jetting scenarios. As an example, we consider the data of de Gans *et al* [6] for PS in ATP from a 70 μm diameter nozzle producing a final drop speed of ~2 m/s. The 5.4 numerical factor in both these equations is then ~6 times larger than for DEP because of the viscosity ratio of DEP to ATP, while the D/U_0 ratio is a factor of 4.2 larger because of the larger nozzle and slower ATP drop speed. These transitions for PS in ATP are raised to 260 kDa (220 kDa) for entering the elastic regime and to ~ 3300 kDa (~ 2600 kDa) for entering the stretched chain regime. These predictions appear consistent with the data of de Gans *et al* [6], as shown in Figure 3 above.

A further application of equations (3) and (4) is to the data of A-Alamry *et al.* [15], to jetting of linear polymers PS and PMMA in γ-butyrolactone (GBL), for which $\nu = 0.55$ is a reasonable choice. The 5.4 numerical factor change is again by a factor of 6 for solvent viscosity ratio DEP/GBL, but the D/U_0 ratio is only affected by the drive voltage used (hence by U_0 and the target speed). For 50 V drive, A-Alamry *et al.* measured final speeds of 4±1.5 m/s, so that D/U_0 should be increased by a factor of 1.5 for GBL. The first transition is at ~340 kDa (~290 kDa), while the second transition is predicted at molecular weights well beyond the data, despite apparent agreement in Figure 4 with the stretched scaling law (which may be due to polymer chain scission [15]).

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References

[1] I.M. Hutchings, G.D. Martin & S.D. Hoath, High speed imaging and analysis of jet and drop formation, *JIST* **51** (2007) pp 438-444.

[2] C. Clasen, J.P. Plog, W.M. Kulicke, M. Owens, C. Macosko, L.E. Scriven, M. Verani, G.H. McKinley, How dilute are dilute solutions in extensional flows? *Journal of Rheology* **50** (2006) pp 849-881.

[3] S.D. Hoath et al, Drop-on-demand jetting of dilute polymer solutions, 3rd International Workshop on Ink-jet Printing, Eindhoven (2007)

[4] S.D. Hoath, I.M. Hutchings, G.D. Martin, T.R. Tuladhar, M.R. Mackley and D.C. Vadillo, Links between fluid rheology and drop-on-demand jetting and printability, *JIST* **53** (2009) 041208.

[5] N.F. Morrison & O.G. Harlen, Viscoelasticity in inkjet printing, *Rheologica Acta* **49** (2010) pp 619-632.

[6] B.J. de Gans, E. Kazancioglu, W. Meyer, U.S. Schubert, Ink-jet printing polymers and polymer libraries using micropipettes, *Macromolecular Rapid Communications* **25** (2004) pp 292-296

[7] J.R. Castrejón-Pita, G.D. Martin, S.D. Hoath, I.M. Hutchings, *Review of Scientific Instruments* **79** (2008) 075108

[8] D.C. Vadillo, S.D. Hoath, W.-K. Hsiao, M.R. Mackley, The effect of inkjet ink composition on rheology and jetting behaviour, NIP27, Minneapolis, Minnesota, USA October 2nd-6th (2011) pp 568-572

[9] S.D. Hoath, O.G. Harlen and I.M Hutchings, Jetting behaviour of polymer solutions in drop-on-demand inkjet printing, *Journal of Rheology* **56** (2012) DOI: 10.1122/1.4724331

[10] A.V. Bazilevski, J.D. Meyer, A.N. Rozhkov, Dynamics and breakup of pulse microjets of polymeric liquids, *Fluid Dynamics* **40**, (2005) pp 376-392

[11] W.-K. Hsiao, S.D. Hoath, G.D. Martin and I.M. Hutchings, Jetting, In-Nozzle Meniscus Motion and Nozzle-Plate Flooding in an Industrial Drop-on-Demand Print Head, NIP27 Minneapolis, Minnesota, USA October 2nd-6th (2011) pp 66-69

[12] T.R. Tuladhar & M.R. Mackley, *J. Non-Newtonian Fluid Mechanics* **148** (2008) pp 97-108

[13] D.C. Vadillo, T.R. Tuladhar, A.C. Mulji, S. Jung, S.D. Hoath, M.R. Mackley, Evaluation of ink jet fluids performance using the "Cambridge Trimaster" filament stretch and break-up device, *Journal of Rheology* **54** (2010) pp 261-282

[14] D.C. Vadillo, W. Mathues, C. Clasen, Microsecond relaxation processes in shear and extensional flows of weakly elastic polymer solutions, *Rheologica Acta* **50** (2012) pp

[15] K. A-Alamry, K. Nixon, R. Hindley, J.A. Odel, S.G. Yeates, Flow-induced polymer degradation during ink-jet printing, *Macromolecular Rapid Communications* **32** (2011) pp 316-320.

[16] B.J. de Gans, L.J. Xue, U.S. Agarwal, U.S. Schubert, Ink-jet printing of linear and star polymers, *Macromolecular Rapid Communications* **26** (2005) pp 310-314.

[17] X.J. Yan, W.W Carr, H.M. Dong, Drop-on-demand drop formation of polyethylene oxide solutions, *Physics of Fluids* **23**, (2011) 107101.

[18] S. Jung, S.D Hoath, G.D. Martin, I.M. Hutchings, A new method to assess the jetting behavior of drop-on-demand ink jet fluids, *JIST* **55** (2011) 010501

[19] O.G. Harlen, N.F. Morrison, S.D. Hoath, Jet break-up of polymeric fluids in inkjet printing, 16th International Conference on Rheology, Lisbon (2012)

[20] N.F. Morrison, O.G. Harlen, W.-K. Hsiao, S.D. Hoath, J.R. Castrejón-Pita, Drop ejection in industrial inkjet printing, ICIAM Vancouver (2011)

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