

# Understanding Dynamic Relaxation of Inks at a Timescale Relevant to High Frequency Drop-On-Demand Printing

Nick Jackson, Tri Tuladhar, Maëlle Douaire, John Tatum, Angus Condie  
 Xaar plc, Cambridge, UK

## Abstract

*As the drop-on-demand (DOD) inkjet industry moves towards higher print frequencies to achieve higher productivity, the nozzle recovery rate and turnover time becomes increasingly important, in that attempting to jet from a nozzle that has not fully recovered results in meniscus instability and poor reliability [1] [2].*

*We have developed a new, simple, and rapid quantitative technique to measure the microsecond relaxation time of inks at a timescale relevant to DOD inkjet waveforms by exploiting the Piezo-Axial Vibrator (PAV) [3]. This microsecond relaxation has been found to be directly relevant to the maximum inkjet print frequency achievable. This has allowed for inks of any type to be screened, compared for batch variations and tailored for suitability for specific high-frequency jetting applications.*

*The results show that this relatively inexpensive and compact equipment can detect changes in the microsecond relaxation with a high degree of sensitivity, with the effect of dynamic fluid properties beyond surface tension, viscosity or density able to be detected and quantified, allowing for new formulations to be developed with higher print frequencies in mind.*

## Introduction

The biggest remaining limitation in productivity for industrial inkjet processes such as labels and coding & marking is the line speed; meaning that there is a continual push towards higher speeds and consequently higher print frequencies. While much progress has been made in the actuator design by increasing resonant frequencies through smaller actuators such as thin-film MEMS [4], and single-cycle actuator technologies [5] including Alternate Line Active (ALA) [6], the recovery time and therefore maximum print frequency of the inks being jetted is often overlooked.

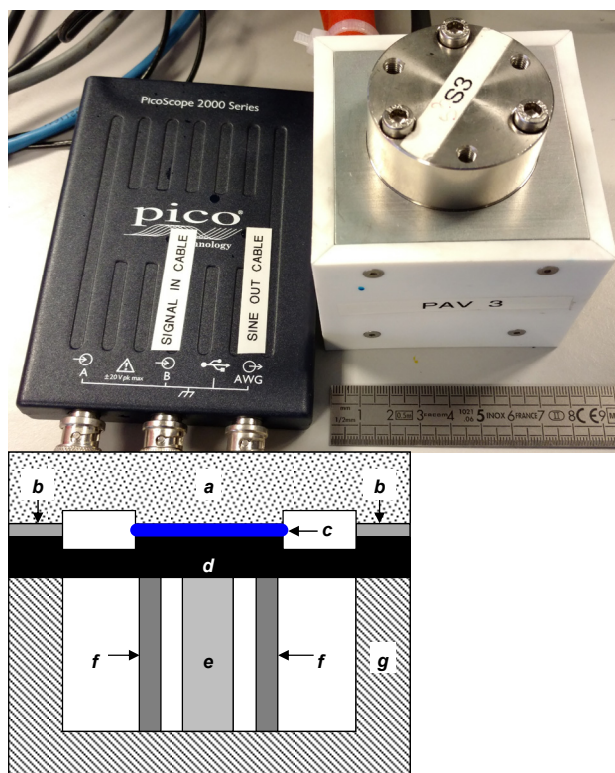
Presented here is a new measurement technique using the Piezo-Axial Vibrator (PAV) where the relaxation profile of an ink can be measured in response to a step-strain, allowing for the expected channel recovery time to be predicted. The extremely low sample volume required and instant result feedback also allows for rapid formulation development targeting reduced recovery times, while printhead manufacturers and integrators can screen inks for suitability with high speed digital presses.

## Piezo-Axial Vibrator

The PAV consists of active and passive piezoelectric elements bonded to a 20 mm diameter circular metal plate, with a top cover bolted in position. A calibrated spacer is used to simulate an inkjet channel of the desired width. A schematic view is presented in Figure 1. During operation, the active element is driven by a signal generator, while the response from the passive element is measured with a suitable data acquisition device.

In this new technique, the active element is driven by a low frequency square wave (approximately 5 Hz) from an Arbitrary Waveform Generator (AWG) with the total step voltage set to 4 V. The response from the passive element, in the region of 0.15 V, is recorded using an oscilloscope. The 4 V input signal was chosen to give a total deflection of the PAV sample plate (Figure 1d) of 5-10 nm to match the deflection of the walls in a printhead under standard operating conditions.

The results presented below were obtained using a Picoscope 2204A USB-based oscilloscope with a built-in AWG (Figure 1, top left), thus driving and reading from the same equipment with no additional electronics or external power supply required. The low voltage and nanoscale displacement of the PAV means that the drive signal can be continuously active such, that the results can be obtained as soon as the top cover is bolted in position, with the oscilloscope trace exported in CSV (comma separated values) format for further processing.

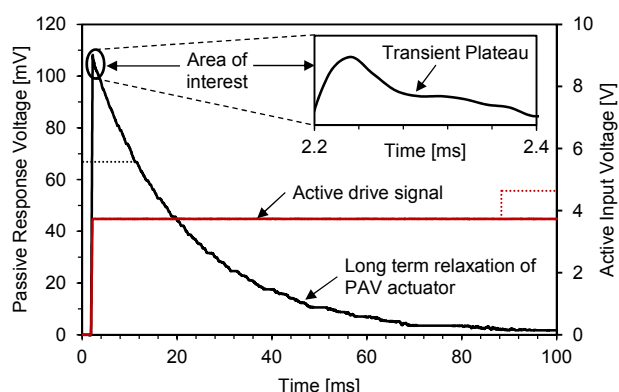


**Figure 1.** Top: Photograph of equipment used showing combined USB oscilloscope and AWG (left) and Piezo-Axial Vibrator (right) with centimetre ruler for scale. Bottom: Cross-section schematic of Piezo-Axial Vibrator showing a) top cover, b) calibrated spacer foil, c) fluid sample, d) metal plate with overflow gutter, e) active piezo element, f) passive piezo elements, g) temperature-controlled chassis casing.

For fluids with non-ambient operating temperatures such as UV-curable inks designed to jet at 45 °C, a heat exchanger jacket can be included to maintain a constant, controlled temperature of the metal sample plate.

## Data Processing

The response for commercial inks generally returns completely to rest after 100 to 200 ms despite the constant application of the active input signal, however there is a high frequency ‘transient plateau’ within the first 400  $\mu$ s after the initial peak, where the first-order oscillations from the initial step-strain decay down to the background relaxation of the PAV equipment itself (see Figure 2). The ink is considered to have relaxed sufficiently for the next firing event when this transient plateau has been reached. This transient plateau can also be calibrated using a “blank” measurement to remove the long-scale drift of the PAV.



**Figure 2.** Main graph: Full relaxation profile showing long-term relaxation of the PAV actuator in the passive response (left axis) while active drive signal remains constant (right axis), with the area of interest for step-strain relaxation highlighted. Inset: Expansion of area of interest showing the transient plateau after the initial peak in the microsecond timescale.

The raw data exported from the oscilloscope were plotted starting at the maximum peak response and a relaxation threshold is set, below which the ink can be considered to be relaxed and the transient plateau reached. This threshold can be calibrated by comparing the resulting relaxation times for a set of reference inks with a known maximum reliable printing frequency in a real printhead, and accounts for background equipment ‘ringing’ effects.

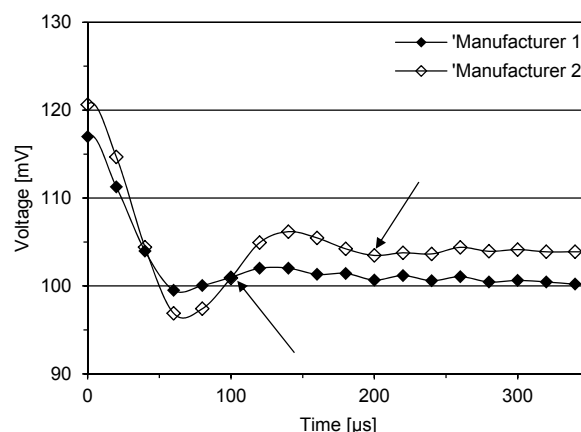
## Commercial Ink Results

Relaxation times were measured with a range of different inks of various families; UV-curable, volatile solvent and ceramic glaze (Table 1). For UV and Solvent inks, two different manufacturers were tested, as well as an additional solvent ink with a higher viscosity. The UV-curable and ceramic inks were all tested at 45 °C to match the recommended operating conditions, while the solvent inks were measured at 35 °C on the assumption that such inks would be loaded at room temperature, but then heated above ambient by the actuator during operation.

**Table 1. List of commercial inks tested**

Ink	$T$ [°C]	$\rho$ [g/cm <sup>3</sup> ]	$\sigma$ [mN/m]	$\eta$ [mPas]
UV Mfg. 1	45	1.08	21.7	16.1
UV Mfg. 2	45	1.09	22.4	9.0
Solvent Mfg. A	35	0.96	23.8	8.9
Solvent Mfg. B	35	0.94	26.2	8.0
Solvent High $\eta$	35	0.97	24.8	13.5
Ceramic 0.6 $\mu$ m D <sub>90</sub>	45	1.19	28.7	12.6
Ceramic 1.2 $\mu$ m D <sub>90</sub>	45	1.44	30.4	18.9
Ceramic Aqueous	45	1.40	33.4	19.4

The two UV-curable inks show different relaxation profiles, with the oscillations for ‘Manufacturer 1’ (Figure 3a) stabilising after approximately 100  $\mu$ s, while the ink from ‘Manufacturer 2’ stabilises after 200  $\mu$ s (Figure 3b). For the reference printhead used, this represents a reduction in print frequency of 17 % for ‘Manufacturer 2’, however given that this relaxation time is fixed regardless of waveform used, the changes to the print frequency depends on the length of the waveform.

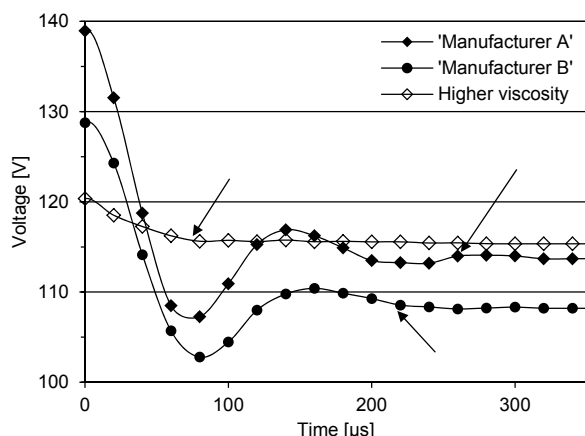


**Figure 3.** Relaxation profile at 45 °C for two UV-curable inks from different manufacturers showing a) shorter ( $\blacklozenge$ ) and b) longer ( $\diamond$ ) relaxation times as marked by arrows.

The differences between the volatile solvent inks measured are much less pronounced, with the relaxation time for ‘Manufacturer A’ only 18 % greater than ‘Manufacturer B’, at 260  $\mu$ s vs. 220  $\mu$ s respectively (Figure 4a).

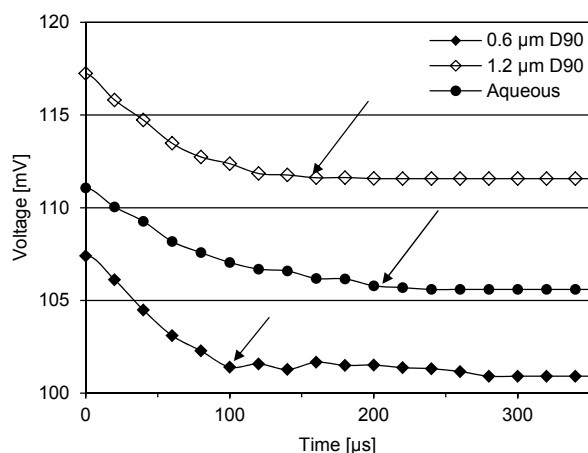
Compared to UV inks, solvent inks tend to include higher molecular weight polymeric components such as resins for greater adhesion to the substrate, leading to a higher degree of elasticity (0.03 % vs. 0.015 % for UV-curable). It is likely that this elasticity means that more energy is absorbed from the step-strain, requiring longer to dissipate during the subsequent relaxation.

A further solvent ink from ‘Manufacturer A’ modified to increase the viscosity shows a dramatic reduction in the relaxation time down to 80  $\mu$ s (Figure 4b). The additives used to modify the physical properties of solvent-based inks are usually polymeric, thus demonstrating that changes to these polymers can have a significant effect on the ink relaxation.



**Figure 4.** Relaxation profile at 35 °C for a) two volatile solvent based inks from different manufacturers (♦ and ●), and b) a modified ink with higher viscosity (◇), with relaxation times marked by arrows.

In contrast to the UV-curable and commercial solvent inks, the relaxation profiles of all three tested ceramic inks decayed smoothly to rest with no additional oscillations, however the time taken to plateau was different for each ceramic ink tested, with the standard commercial ceramic ink ( $D_{90} \approx 0.6 \mu\text{m}$ ) relaxing in 100  $\mu\text{s}$  (Figure 5a) similar to the faster UV-curable ink from Figure 3a. The larger particle ink ( $D_{90} \approx 1.2 \mu\text{m}$ ) has a slightly longer relaxation time of 150  $\mu\text{s}$  (Figure 5b), while the aqueous ceramic ink tested took 200  $\mu\text{s}$  to relax (Figure 5c).



**Figure 5.** Relaxation profiles at 45 °C for three ceramic inks showing the difference between a) standard (♦), b) large particle (◇) and c) aqueous (●) formulations, with relaxation times marked by arrows.

This shows that the trend towards higher colour densities from larger pigment particles, and the use of water as a carrier solvent to reduce harmful evaporated organic compounds may compromise the ability to print at the full line speed unless the relaxation time is considered and optimised during formulation.

The small volume required for the PAV (approximately 0.5 mL) means that the formulation can be checked in the benchtop stage of development before large-scale production, potentially reducing material consumption.

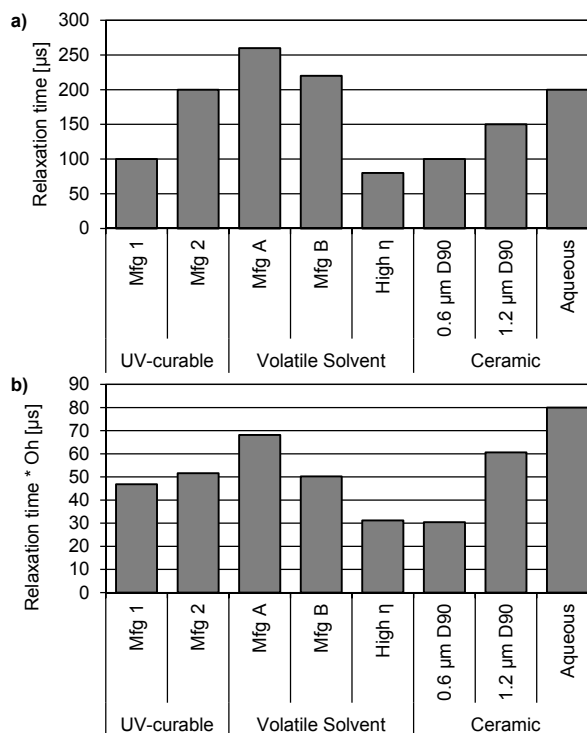
### Effects of viscosity and surface tension

The collected relaxation times shown in Figure 6a show that there are significant differences between the different inks, however there are also significant differences in the bulk

physical properties and chemical properties as seen in Table 1. The relaxation time was therefore multiplied by the dimensionless Ohnesorge number, ( $Oh$ ) [7] to take into account the surface tension ( $\sigma$ ), viscosity ( $\eta$ ), density ( $\rho$ ), and the width of the actuator ( $L$ ):

$$Oh = \sqrt{We} / Re = \eta / \sqrt{\rho \times \sigma \times L} \quad (1)$$

This should ensure that there is a high degree of flexibility to match the measurement to the application.



**Figure 6.** a) Relaxation times for all inks tested (top), b) Relaxation time multiplied by the Ohnesorge number for each ink (bottom).

Scaling the relaxation times by  $Oh$  (Figure 6b) shows that the difference seen between UV-curable ink manufacturers is almost entirely due to viscosity given that the surface tension and density in Table 1 are almost identical. Testing these two inks with a real printhead shows that both inks do have very similar maximum print frequencies despite the significantly different raw relaxation times.

The difference seen between raw and scaled relaxation times for the high viscosity solvent ink shows that even when the viscosity is factored out, there are still noticeable differences, implying that additional characteristics of the formulation are responsible for the differences and not simply the increased viscosity.

The scaled ceramic inks results show that there are clearly significant additional interactions, which are most likely entirely due to the pigment particles. The higher density for the larger particle ink ( $1.44 \text{ g/cm}^3$  vs.  $1.19 \text{ g/cm}^3$ ) is likely due to the higher solid loading for increased colour density on the printed tile, which will result in more energy absorption from the step-strain. The larger particles will also require more polymeric rheology network structures to prevent sedimentation, increasing elasticity and therefore increasing the energy absorbed and subsequently released during relaxation.

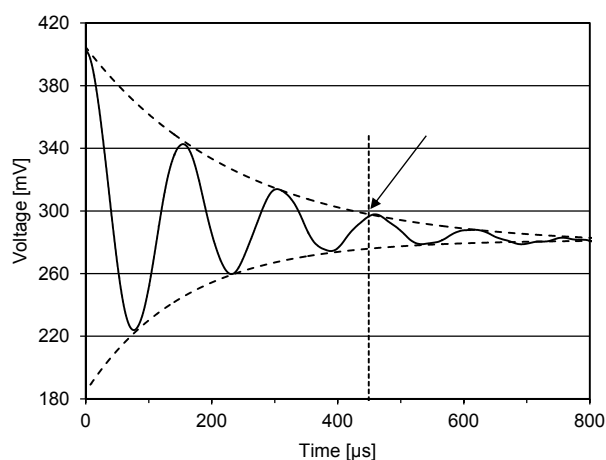
Testing has shown that this larger particle ink is not reliable at the same print frequency at which the smaller particle ink is stable, thus showing the unintended consequence of the increased particle size formulations, which would not necessarily be detectable using conventional measurement techniques.

## Model Fluids

A range of model fluids, including common base solvents for inkjet inks, were tested using the new PAV technique over a range of temperatures to further investigate the effects of viscosity, surface tension, and molecular mass:

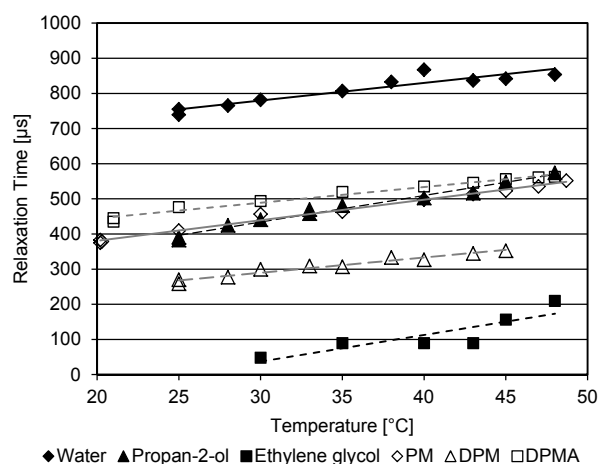
- Water
- Propan-2-ol
- Ethylene glycol
- Propylene glycol methyl ether (PM)
- Dipropylene glycol methyl ether (DPM)
- Dipropylene glycol methyl ether acetate (DPMA)

To speed up analysis and more reliably obtain the relaxation time, a script was created that identifies all of the peaks and any troughs in the relaxation profile, then fits an exponential curve to both by least squares minimisation to create a “decay envelope”. The relaxation time was then taken as the point at which the decay envelope had reached 10% of the envelope size at the maximum peak response. Figure 7 shows the example relaxation profile, decay envelope, and relaxation time for DPMA at 25 °C.



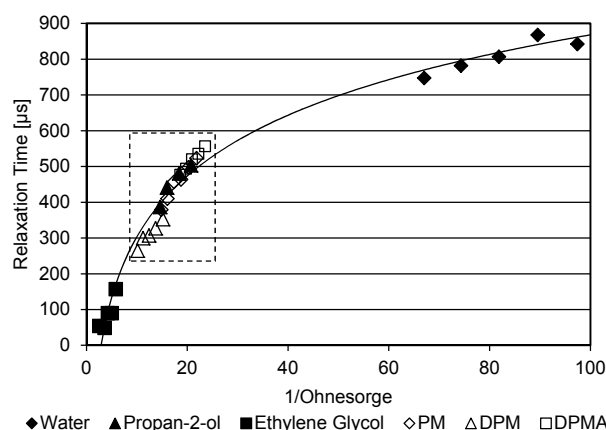
**Figure 7.** Example relaxation profile for Dowanol™ DPMA at 25 °C, aligned to the maximum peak response, with decay envelope curves fitted and 10% relaxation threshold marked.

Plotting the relaxation times for all fluids tested for the range of temperatures (Figure 8) shows that there are some significant vertical offsets between the fluids, while in all cases the relaxation time increases as the temperature increases, as expected given the linked decrease in viscosity. This clearly demonstrates the need to account for the base physical properties of the test fluids as too many parameters are changing at once.



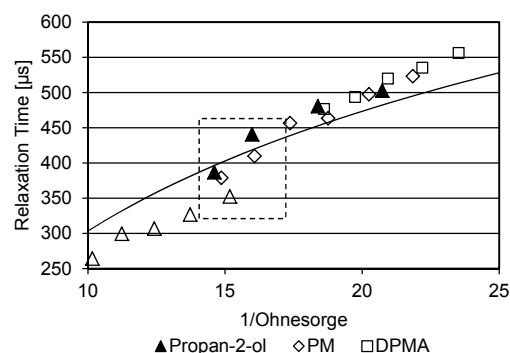
**Figure 8.** Relaxation times for test fluids over a range of temperatures showing significant differences between the fluids due to the varied bulk physical properties.

It is better, therefore, to plot the relaxation time against the inverse Ohnesorge number in order to compensate for the bulk physical properties changing:



**Figure 9.** Relaxation Time vs. the inverse Ohnesorge number, with region expanded in Figure 10 highlighted

The plot in Figure 9 shows that when the bulk physical properties are accounted for, most of the fluids follow the same overall trend, except for DPM, which has a lower relaxation time despite having similar Ohnesorge numbers (Figure 10).



**Figure 10.** Relaxation Time vs.  $1/Oh$  expanded to show the differing relaxation times for DPM and DPMA with similar Ohnesorge numbers to propan-2-ol and PM in the same region.

The Ohnesorge number only factors in the bulk, static properties of the fluids, meaning that any dynamic effects such as elasticity and the intermolecular interactions from functional groups would need to be considered and terms for these properties included in the dimensionless number expression.

The fluids tested here are all base solvents and do not take into consideration the effects from the addition of polymeric additives. Additives such as surfactants, dispersants, and resins could explain why the commercial inks have such pronounced differences compared to the model fluids tested here.

## Conclusion

We have developed a new measurement technique exploiting the Piezo-Axial Vibrator to measure the relaxation of an ink in the microsecond timescale in response to an applied step-strain. This new technique was used to measure the response of a range of commercial inks, with the relaxation times identified and scaled by the Ohnesorge number.

These results showed that there are different relaxation times from different ink types, even when the bulk physical properties have been taken into consideration, which can be explained by the unique chemical compositions of each ink. Solvent inks, for example, have a higher proportion of long-chain polymeric additives such as resins that increase the elasticity, while relaxation times of ceramic inks can be dramatically changed by the particle interactions as a consequence of the high solid loading and support networks to reduce sedimentation.

Measurements with model fluids show that the bulk physical properties of the base solvents cannot fully account for the differences in relaxation times, with additional effects from functional groups and molecular interactions resulting in detectable differences in the relaxation times even when the fluids have the same Ohnesorge number.

The threshold for the 'transient plateau', as well as the characteristic length in the Ohnesorge equation can be calibrated

for the printhead and intended application, meaning that this new measurement technique can be applied to a wide range of scenarios, while the rapid rate of data acquisition and extremely small sample volume required will benefit benchtop-scale ink formulation.

## References

- [1] W.-K. Hsiao, "Jetting, In-Nozzle Meniscus Motion and Nozzle-Plate Flooding in an Industrial Drop-on-Demand Print Head," in *Proc. Int. Conf. on Digital Printing Tech.*, Minneapolis, 2011.
- [2] J. de Jong, "Air Entrapment in Piezo-Driven Inkjet Printheads," *J. of Acoustic Soc. of America*, vol. 120, no. 3, pp. 1257-1265, 2006.
- [3] D. Vadiello, "The Rheological characterization of linear viscoelasticity for ink jet fluids using piezo axial vibrator and torsion resonator rheometers," *J. Rheology*, vol. 54, no. 4, pp. 781-795, 2010.
- [4] A. L. Brady, "The Impact of Silicon MEMS on the Future of Ink Jet Printhead Design and Performance," in *Proc. Int. Conf. on Digital Printing Tech.*, 2005.
- [5] P. Drury, "Three-fold Increase in Inkjet Speed of Piezoelectric Shared Wall," in *Proc. Int. Conf. on Digital Fab.*, 2009.
- [6] H. Watanabe, "New Developments of Shear-Mode Piezo Inkjet Heads for Industrial Printing Applications," in *Proc. Int. Conf. on Digital Printing Tech.*, 2011.
- [7] W. Ohnesorge, "Formation of drops by nozzles and the breakup of liquid jets," *J. Applied Maths and Mech.*, vol. 16, pp. 355-358, 1936.

## Author Biography

Nick Jackson is a member of the Technology Development team at Xaar plc, Cambridge. He received his degree in Natural Sciences (chemistry) from the University of Cambridge in 2007 and joined Xaar in 2008. In the past 8 years, he has built up extensive experience in printhead performance, developing several processes for product development and testing, and currently works on developing new technologies for use in future products.