

Ink preparation and inkjet printing of eutectic gallium indium nanodroplets

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Abstract

Interest in rapid prototyping and additive manufacturing techniques has grown immensely in the last few years, and such processes and techniques have the potential to revolutionize electronics manufacturing. Inkjet printing has attracted particular attention, and has already been used to fabricate electronic devices ranging from thin-film transistors to solar cells. Here, we design a process for inkjet printing eutectic gallium indium (eGaIn) to serve as flexible, moveable electrical contacts, with applications in extreme environment electronics, and soft and flexible electronics. We demonstrate how to formulate and systematically characterize the ink for printing with ExFab's Dimatix materials printer, and show that our ink is jettable using the printer. Though the ink design and characterization techniques in this report are described in the context of patterning eGaIn, they can easily be generalized to develop processes for inkjetting arbitrary materials.

1 Introduction

Inkjet printing is an additive manufacturing process capable of highly scalable, maskless, cleanroom-free patterning of unconventional materials, and has previously been used to pattern electronic devices like solar cells and thin-film transistors [1]. Using an inkjet printer to rapidly and scalably pattern eutectic gallium indium (eGaIn), a room-temperature liquid metal with composition of 75% gallium and 25% indium by mass [2], is of particular interest, with potential applications as moveable electrical contacts for devices subject to substantial thermal expansion, or as a flexible conductor for soft or flexible electronic devices. Several research groups have recently demonstrated inkjet patterning nanodroplets of eGaIn (figure 1(c)) [3] and its cousin galinstan (figure 1(b)) [4]. However, this process has never previously been performed at Stanford. In this report, we demonstrate how to develop an inkjet printing process to pattern eGaIn using ExFab's Dimatix materials inkjet printer. We describe the capabilities and limitations of the printer, and provide general techniques to efficiently design and characterize the nanoparticle/nanodroplet size, ink viscosity, and ink stability for use with the Dimatix printer. We use these techniques to formulate and characterize a variety of eGaIn inks, and demonstrate successful inkjetting of an ethylene glycol-based eGaIn ink.

2 Dimatix printer capabilities and limitations

The Dimatix inkjet printer in ExFab is a piezoactuator inkjet for printing user-supplied inks, and is capable of depositing materials ranging from nanoparticles to proteins. Our particular printer is

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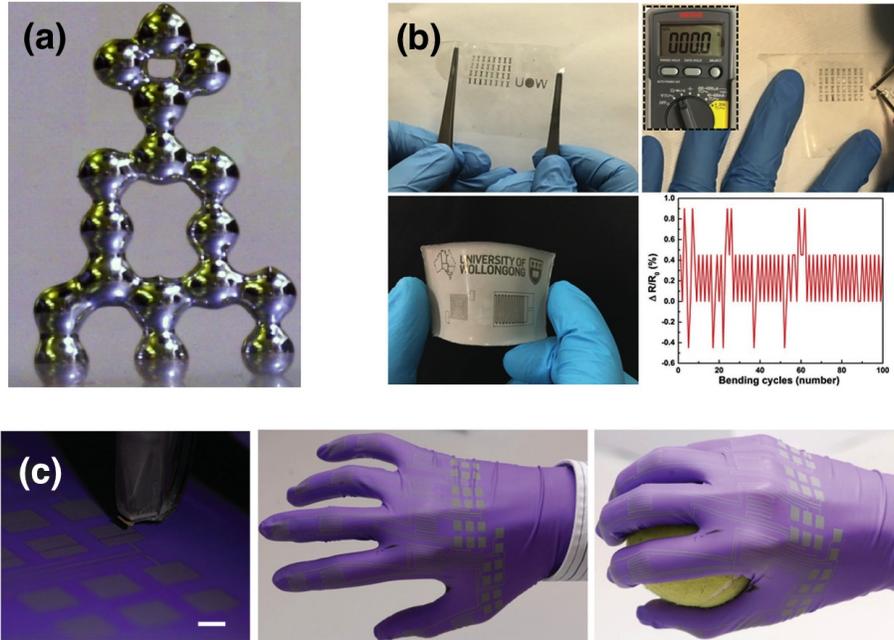


Figure 1: (a) 3D-printed eGaIn from [5], demonstrating the small-scale moldability and patternability of eGaIn. Each sphere has a diameter of approximately $500 \mu\text{m}$. (b) Inkjet printed galinstan from [4]. (c) Inkjet printed eGaIn from [3]

capable of printing spot sizes of around $40 \mu\text{m}$ with a repeatability of about $25 \mu\text{m}$ [6].

2.1 Required ink properties for the Dimatix printer

The primary challenge in developing inkjet printing processes for the Dimatix printer is formulating a jettable ink. In order for an ink to be jettable, it must satisfy several specific physical and rheological properties, like maximum particle size, surface tension, and viscosity. These properties are highly dependent on the specific model of printer being used, and this information is supplied by the manufacturer. In the case of ExFab's Dimatix inkjet, inks must satisfy the following properties to be printable [7]:

- Dynamic viscosity must be between 2 and 30 cP. Dimatix further recommends that the ideal ink have a viscosity between 10 and 12 cP.
- Surface tension should be between 28 and 33 dynes/cm, though surface tensions up to around 70 dynes/cm can be printed.
- Suspended particles in the ink must be much smaller than the printer nozzle diameter to prevent nozzle clogging. Dimatix recommends particles be 100x smaller than the nozzle diameter. If using the the $21.6 \mu\text{m}$ nozzle, particles should be around 200 nm in diameter, and if using the $9 \mu\text{m}$ nozzle, particles should be around 90 nm in diameter. In practice, slightly larger particles can be printed.
- Suspended particles in the ink cannot sediment or agglomerate during the printing process, so that the ink is uniform and so particle aggregates do not clog the printhead.

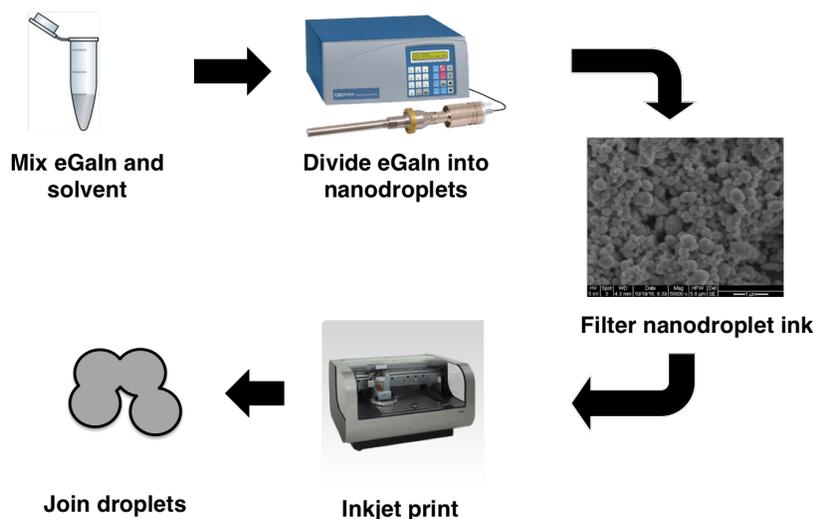


Figure 2: High level schematic of the eGaIn inkjet process. After mixing the ink components together in a glass vial, a probe sonicator is used to disperse the bulk eGaIn into nanoscale droplets and suspend these droplets in a carrier solvent. The ink is then filtered to remove debris and excessively large eGaIn droplet, and then loaded into the Dimatix inkjet for patterning. After patterning, the nanodroplets are then merged back together by mechanical means or with heat.

3 eGaIn nanodroplet ink formulation and preparation

Although eGaIn is liquid at room temperature, its extremely high surface tension of 600 dynes/cm [2] makes it unsuitable for inkjet printing in its bulk form. Based on the work of Boley *et al.* [3], we designed an ink preparation and inkjet printing process, using a probe sonicator to divide bulk eGaIn into nanodroplets suspended in a continuous phase carrier solvent and then using the inkjet printer to pattern the resulting ink. After patterning, these eGaIn nanodroplets are then merged back together either mechanically [3] or with low temperature sintering to improve conductivity. A high level overview of this process is shown in figure 2.

Based on the work of Boley *et al.* [3] and on correspondence with the Rebecca Kramer group at Purdue, we prepared inks with formulations of 90 mg eGaIn per mL of ethanol continuous phase solvent, with concentrations of 0 mM, 1 mM and 3 mM of either 3-mercapto-N-nonylpropionamide (abbrev. 1ATC9) (Sigma-Aldrich) or 1-dodecanethiol (abbrev. C12) (Sigma-Aldrich) thiol surfactant. These thiol surfactants form a self-assembled monolayer (SAM) on the surface of the eGaIn particles during the sonication process, slowing the formation of gallium oxide. This controls the rate at which the eGaIn is divided into smaller droplets, and should yield more uniformly sized nanodroplets [8]. Later on, we replaced the ethanol continuous phase with ethylene glycol, because of the unprintably low viscosity of the ethanol inks. The concentrations of eGaIn and of the thiol SAM surfactants remained the same in the ethylene glycol inks.

To prepare eGaIn nanodroplet inks, we used the following process, using the probe sonicator in ExFab. Note that identical steps and tool settings were used for all of our inks, regardless of continuous phase solvent.

1. Measure out 90 mg of eGaIn, and transfer it into a 20 mL glass vial. We used a 1 mL syringe and a mass balance for this, as eGaIn is extraordinarily difficult to move around with a micropipette.
2. Measure out the appropriate amount of SAM surfactant, either with a mass balance or mi-

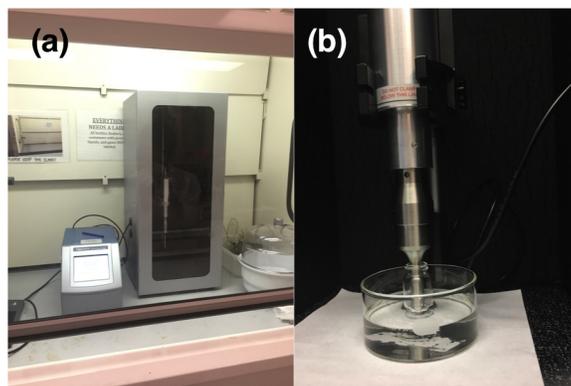


Figure 3: Probe sonication setup in ExFab. (a) The sonicator is located in a soundproof cabinet. (b) To prevent the sonicator tip from overheating, and to prevent an excessive amount of solvent from evaporating, the vial is placed in a cold water bath during sonication.

cropipette, and add it to the glass vial. Because the SAM surfactants are thiol-terminated, this should be done in a fume hood.

3. Add 10 mL of the continuous phase solvent (either ethanol or ethylene glycol) to the glass vial.
4. Prepare a cold water bath in a low-sided beaker. Place the 20 mL glass vial containing the ink precursors into this water bath, and then load this into the probe sonicator, as shown in figure 3b. The cold water bath is necessary so that the heating during the sonication process doesn't damage the sonicator tip, and so that we don't evaporate an excessive amount of the continuous phase solvent during the sonication process.
5. Close the door of the soundproof cabinet containing the sonicator, for hearing protection (figure 3a).
6. Program the sonicator to run at power setting 30, with a 1 hour sonication time, a pulse-on time of 3 seconds, and a pulse-off time of 3 seconds. This corresponds to a 2 hour sonication process, with a 6 second long sonication period and 50% duty cycle. When running the sonicator with these settings, approximately 45 W of power is dissipated into the ink when the sonicator is on.
7. Remove the ink from the sonicator, and empty the water bath.
8. To clean the sonicator of accumulated eGaIn nanodroplets, immerse the tip in ethanol and sonicate for at least 20 minutes. After sonication, wipe off the tip with an ethanol-soaked wipe.

4 Tools and processes for general ink characterization

In order to screen potential inks for their suitability for inkjet printing, we need to characterize nanodroplet size distribution, viscosity, and stability. Because of the potentially large number of different formulations to be tried, and the high potential cost of ink components, we focus on simple, fast characterization methods and tools requiring relatively ink sample volumes. While some of these methods are limited in precision, their simplicity and relative ease greatly accelerates the ink formulation and screening process. Though we use these tools and techniques to characterize inks containing eGaIn nanodroplets, they can easily be generalized to characterize nanoparticle inks.

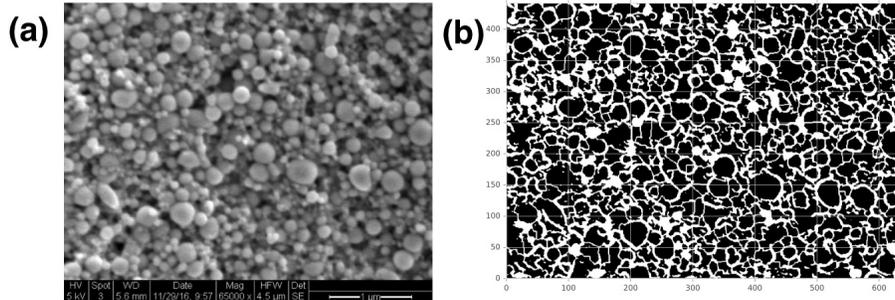


Figure 4: (a) Raw SEM, taken with Sirion in SNSF. (b) Segmented SEM, using our custom Python software tool for sizing nanodroplets. Each of the black regions corresponds to a nanodroplet, and the white lines borders correspond to the edges of nanodroplet.

4.1 Estimating eGaIn nanodroplet size with scanning electron microscopy

The size distribution of eGaIn nanodroplets in an ink must be characterized to minimize the chance of clogging the inkjet printhead. In particular, for the Dimatix materials printer in ExFab, we would like a narrow size distribution of nanodroplets with diameters below approximately 500 nm. There exist several methods to size nanodroplets in ExFab, including tools like the Malvern DLS. However, we chose to use scanning electron microscopy (SEM) to size nanodroplets, because of its relative ease and because knowledge of the nanodroplet size distribution (in addition to mean and median) is of great importance in determining if the nanodroplets are appropriately sized.

Our process to characterize nanodroplet size distribution was as follows:

1. Use a bath sonicator to redisperse the nanodroplets. This is to ensure that the small volume of ink taken is a representative sample of the entire ink.
2. Drop-cast 5 μL of ink onto a silicon wafer piece.
3. If necessary, put the sample on a hot plate to slowly and carefully bake off the continuous phase of the ink. In the case of eGaIn nanodroplets, special care needs to be taken to prevent the eGaIn nanodroplets from sintering together and ruining the measurement.
4. SEM the wafer piece, at a high enough magnification such that an image processing program can distinguish the boundaries of nanodroplets.
5. Use image processing tools like ImageJ [3] to segment the SEM image into distinct nanodroplets and extract nanodroplet diameters.

To accelerate and automate calculation of nanodroplet size distributions from multiple SEM images, we developed image processing software in Python using the package `scikit-image` [9] to automatically segment SEM images into constituent nanodroplets, estimate the diameter of these nanodroplets, calculate mean and median nanodroplet diameters, and plot a histogram of nanodroplet diameters (figure 4). In brief, the algorithm detects edges in the image, and calculates the distance to the nearest edge for every pixel. The watershed algorithm iteratively fills in the image, starting from pixels that are local maxima in distance to an edge. This assumes that these maxima in distance correspond approximately to the center of a nanodroplet. The filled-in regions formed by the watershed algorithm then correspond to nanodroplet, and the boundaries of these regions correspond to the boundaries of segmented nanodroplets. A more complete description of the algorithm is provided below:

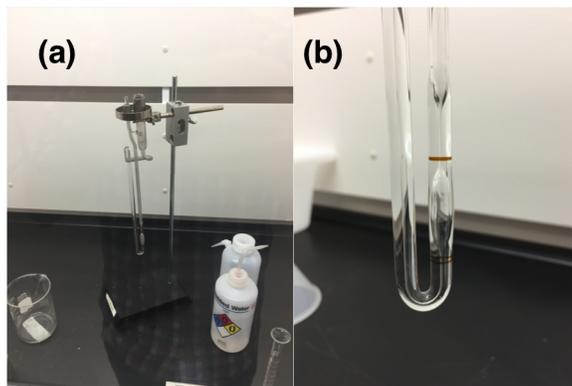


Figure 5: Zeitefuchs Cross-Arm capillary viscometer. (a) The full viscometer setup. Care must be taken to ensure that the viscometer is perfectly vertical. (b) The lines used to time fluid travel in the viscometer.

Algorithm 1: Nanodroplet image segmentation algorithm

```

edges ← Sobel(image)                                ▷ Detect edges using Sobel detector
binaryedges ← ThresholdIsodata(edges)                ▷ Isodata thresholding to binarize edges
distances ← EdgeDistance(binaryEdges)                ▷ calculate distance to nearest edge for every pixel
localmax ← LocalMaxima(distances)                   ▷ find pixels that are local maxima for distance to edge
particleList ← Watershed(localmax)                  ▷ segment into nanodroplets with watershed algorithm
for particle ∈ particleList do
    numPixels ← CountPixels(particle)                 ▷ Determine size in pixels
    area ← numPixels · pixelArea                       ▷ Determine area
    diameter ← 2√(area/π)                             ▷ Calculate diameter assuming spherical nanodroplets

```

The software tool takes in as input a CSV file containing the paths and scale-bar for each image to be processed. The source code for the tool is provided in a separate link, and more detailed documentation about how to install and operate the tool is provided there.

4.2 Measuring viscosity with a capillary viscometer

Because inks must have dynamic viscosities within the 2-30 cP range to be jettable by the Dimatix printer, characterizing the viscosity of inks is critical to formulating inks. Viscosity measurements can be performed with a variety of tools such as the rheometer in SMF and glassware like viscometers.

The rheometer offers the potential for very precise viscosity measurements for a range of shear stress values and with precise temperature control. However the need to expend large ink sample volumes makes the rheometer less than ideal for rapid ink characterization. Fluids with viscosities near that of a jettable ink are difficult to accurately characterize with the rheometer’s parallel-plate and cone geometries because the measured torque values fall very near the minimum threshold value of the instrument. For these fluids, the cup-and-bob geometry is strongly recommended for accurate and reproducible measurements, at the cost of requiring in excess of 10 mL of ink. This was unsuitable for our eGaIn ink preparation process, due to the limited volume of ink that could be prepared in a single batch and the excessive cost of materials, and so we moved to using a capillary viscometer to characterize ink viscosities.

A viscometer is a piece of glassware consisting of a thin capillary tube and a bulb, and is used to make time-based measurements of viscosity. This simple viscometer measurement does

have drawbacks, namely that (1) precise and accurate measurements are difficult to obtain, due to the manual timing of fluid flow and the lack of precise temperature control; and (2) cleaning the viscometer is time and labor intensive. These drawbacks do not pose problems for screening ink viscosity, since extreme precision and accuracy are not necessary.

4.2.1 Buying and using a capillary viscometer

We purchased a Cannon ZCAC-RO-3 Zeitfuchs Cross-Arm size 3 calibrated viscometer. The size and shape of a viscometer determine the viscosity range that it can measure. Although fluids outside that range can still be measured, there will be more error. A calibrated viscometer is more expensive but preferred, since it can be used immediately out-of-the-box without having to determine the calibration constant. The process for measuring viscosity is as follows:

1. Mount the viscometer so that it is perfectly vertical.
2. Verify that the viscometer is completely dry and clean. Measurements with a wet or dirty viscometer will likely be inaccurate.
3. Load the sample into the bulb end of the viscometer with a pipette. The minimum sample volume for our setup was 3 mL.
4. Use the timer to measure the amount of time needed for the sample to travel between the lines on the viscometer, as shown in 5b.
5. Calculate the kinematic viscosity ν (units centistokes [cSt]) of the fluid using the calibration constant provided by the viscometer manufacturer.
6. Use a mass balance to measure the density ρ of the ink.
7. Use the kinematic viscosity and the fluid density to calculate the dynamic viscosity μ (units centipoise [cP]).

It is worth repeating that the viscosity range for inks specified by Dimatix is for the dynamic viscosity, and that the relationship between dynamic and kinematic viscosities is

$$\mu = \nu\rho.$$

4.2.2 Cleaning the viscometer

It is critical that the viscometer be perfectly clean and dry before measuring in order to ensure accurate viscosity measurements. Cleaning the viscometer of moderately viscous inks proved to be a bit of a challenge. There exist a number of resources online [10] with suggestions for cleaning viscometers. Based on these processes, we found a simple but labor intensive method for cleaning the viscometer without nasty chemicals:

1. Empty out as much of the ink as possible. Compressed air or a pipet bulb may be helpful.
2. Fill the viscometer with ethanol, and use a bath sonicator to sonicate the viscometer for a few minutes. Take the ethanol out of the pipette with compressed air or a pipet bulb, and repeat this process until the viscometer is clean.
3. Use a volatile solvent like acetone to wash out the remaining ethanol. The acetone can then be removed with a pipet bulb or with compressed air. This accelerates the viscometer drying.

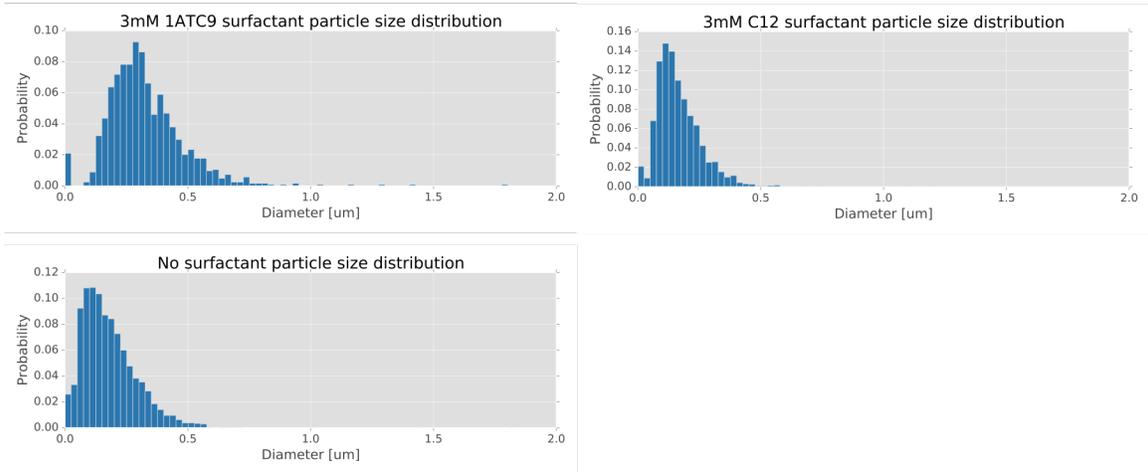


Figure 6: Size distributions of eGaIn nanodroplets in ethanol. The eGaIn nanodroplets have reasonably tight size distributions well below the $21.6 \mu\text{m}$ nozzle diameter, which suggests that these nanodroplets are printable. eGaIn nanodroplet size does not appear to depend on surfactant concentration.

4.3 Settling tests to determine ink stability

Nanodroplets in the ink must remain suspended before and during the printing process. To characterize the long-term stability of prepared inks, we performed a settling test, which consisted of letting the inks sit undisturbed for 24 hours, and photographing before and after. Inks that visibly separate are unsuitable for printing, as an ink that separates easily will be highly nonuniform and difficult to print consistently. In addition, ink separation may suggest that the nanodroplets in the ink have aggregated, which increases the likelihood of clogging the printhead.

5 Characterizing ethanol-based inks

We prepared ethanol inks with the formulations of 90 mg/mL eGaIn to ethanol, with concentrations of 0 mM, 1 mM, and 3 mM of 1ATC9 or C12 thiol SAM surfactant, and characterized these inks using the processes described above. These inks showed promising eGaIn nanodroplet size distributions, but their viscosities proved to be too low to effectively print. Some of these inks also separated in relatively short periods of time, further suggesting that ethanol-based eGaIn inks are unsuitable for patterning with the Dimatix inkjet.

5.1 Ethanol-based inks have small enough eGaIn nanodroplets to print

We characterized the size distributions of ethanol-based inks with SEM and image processing. The eGaIn nanodroplet sizes were consistently in the submicron range, and while they had diameters larger than the Dimatix-recommended values, these droplets are printable. Contrary to the result in Hohman *et al.* [8] we did not observe a dependence of eGaIn nanodroplet diameter on thiol SAM surfactant concentration. This may be due to the different methods of sonication used in this project (probe sonication) and Hohman *et al.* (bath sonication). Size distributions for various ink formulations are shown in figure 6, and mean and median sizes are shown in table 1.

Ink formulation	Mean diameter [nm]	Med. diameter [nm]
ethanol, 3 mM C12, 90 mg/mL eGaIn	334	302
ethanol, 3 mM 1ATC9, 90 mg/mL eGaIn	170	147
ethanol, neat, 90 mg/mL eGaIn	184	157

Table 1: Mean and median size distributions for eGaIn nanodroplets in ethanol.

Ink formulation	Flow time [s]	Kinematic viscosity [cSt]	Density [g/mL]	Viscosity [cP]
ethanol	44	1.4	0.82	1.1
ethanol, 3 mM 1ATC9, 90 mg/mL eGaIn	40	1.2	0.93	1.1
ethanol, 3 mM C12, 90 mg/mL eGaIn	41*	1.2*	0.90	1.1*
ethanol, 90 mg/mL eGaIn	41*	1.2*	0.90	1.1*

Table 2: Viscosities for various formulations of ethanol inks. The measured flow times for ethanol inks through the viscometer are shown. The reference dynamic viscosity for ethanol is 1.144 cP at 20°C, and 1.040 cP at 25°C [11], showing that the viscometer measurements are reasonably accurate. * indicates that the ink separated in the viscometer during the measurement, and that the measured viscosity is likely inaccurate.

5.2 Ethanol-based inks are not viscous enough to print

We characterized the viscosity of ethanol inks using the viscometer. 3 mL of ink was used for each trial, and each ink was measured once. Neat ethanol without any eGaIn was also characterized and compared against the reference value, showing that the viscometer measurements are reasonably accurate. The results of these measurements are shown in table 2.

The viscosities of the eGaIn-in-ethanol inks is nearly identical to that of neat ethanol, and is out of the 2-30 cP jettable range for the printer. In addition, two of the inks separated in the viscometer during the viscosity measurement (figure 7), further suggesting that these inks are unsuitable for printing.

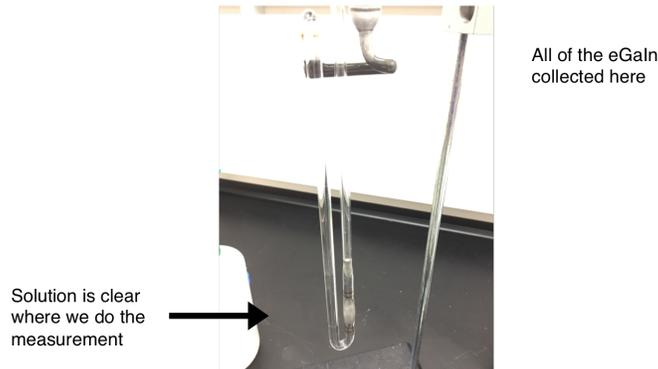


Figure 7: Ink separation during the viscosity measurement. All of the eGaIn nanodroplets sediment at the top of the viscometer, and only ethanol makes it through the capillary to the bulb. This measurement is likely inaccurate.

Ink formulation	Stability
ethanol, 3 mM C12, 90 mg/mL eGaIn	unstable
ethanol, 1 mM C12, 90 mg/mL eGaIn	unstable
ethanol, neat, 90 mg/mL eGaIn	unstable
ethanol, 1.5 mM 1ATC9, 90 mg/mL eGaIn	stable
ethanol, 3 mM 1ATC9, 90 mg/mL eGaIn, trial 1	unstable
ethanol, 3 mM 1ATC9, 90 mg/mL eGaIn, trial 2	stable

Table 3: Settling test results for ethanol-based eGaIn inks. eGaIn nanodroplet settling not appear to depend on surfactant concentration. Settling behavior is also inconsistent for identical inks formulated in different batches.

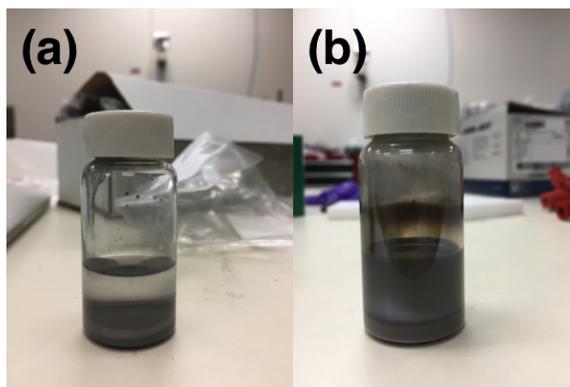


Figure 8: Results of two ink settling experiments for ethanol, 3 mM 1ATC9, 90 mg/mL eGaIn ink formulation. (a) The ink settles. (b) A different batch of the same ink is stable.

5.3 Ethanol-based inks are unpredictably unstable

We performed ink settling experiments to determine the stability of ethanol-based eGaIn inks. Inks were allowed to settle for 24 hours on the benchtop, and were photographed before and after. The ethanol-based eGaIn inks were unpredictably unstable – different batches ink with the same formulation both settled and remained suspended (figure 8). In addition, we did not observe a clear dependence on thiol SAM surfactant concentration on settling. The complete settling data for the settling experiments is shown in table 3. Because the ethanol-based inks tend to settle relatively quickly, they are unprintable. In addition, settling may suggest that the eGaIn nanodroplets are aggregating together, another undesirable behavior for printing.

6 Characterizing ethylene glycol-based inks

Because of the low viscosity of and lack of consistent stability in ethanol-based inks, we replaced the ethanol continuous phase with ethylene glycol. An ethylene glycol continuous phase ink offers several potential advantages. Ethylene glycol’s room temperature viscosity is approximately 18 cP [11], well within the printable range for the Dimatix printer. In addition, by using the Dimatix printer’s built-in ink cartridge heating, the viscosity of ethylene glycol can be lowered into the recommended 10-12 cP viscosity range, which should improve ease of printing (figure 9). Furthermore, because of the higher viscosity, the eGaIn droplets should stay suspended for much longer, and ethylene glycol-based inks should be significantly more stable. Characterization of these inks confirms these advantages, and demonstrates that ethylene glycol can be used to formulate jettable eGaIn inks.

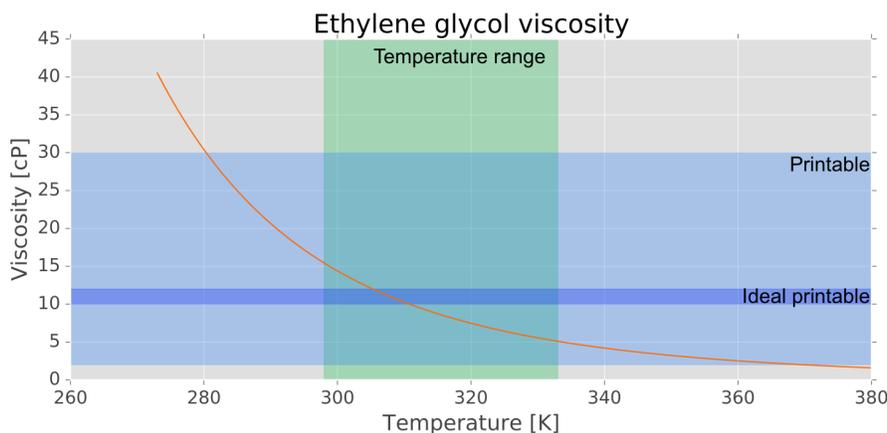


Figure 9: Dynamic viscosity vs. temperature for ethylene glycol. The light blue shaded region corresponds to the printable viscosity range for the Dimatix printer, and the dark blue shaded region corresponds to the manufacturers recommended viscosity range. The green shaded region corresponds to the ink temperature range that can be achieved with the Dimatix printer’s built-in cartridge heating. The room temperature viscosity of ethylene glycol is within the printable range, and raising the temperature lowers the viscosity into the ideal printable range.

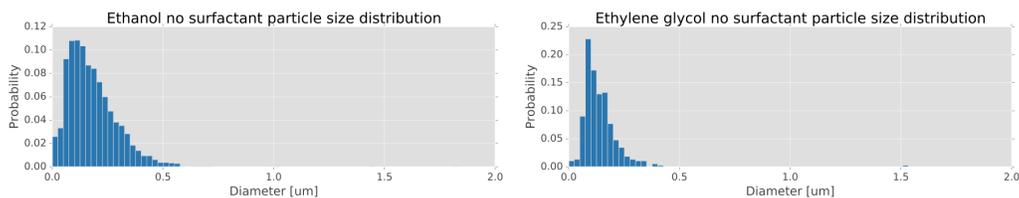


Figure 10: Nanodroplet size distribution of ethylene glycol-based eGaIn ink, with the equivalent ethanol-based ink in comparison. The size distribution of the ethylene glycol ink shows nanodroplets that are on average smaller and more tightly distributed in size than the ethanol ink.

6.1 eGaIn nanodroplet sizes are printable

We characterized the size distribution of a 90 mg/mL eGaIn to ethylene glycol no-surfactant ink with SEM and image processing. The eGaIn nanodroplet sizes were on average smaller than the equivalent ethanol inks, and were also somewhat more tightly distributed (figure 10), suggesting that these droplets are printable. The mean and median nanodroplet diameters were 142 nm and 125 nm, respectively. Because both nanodroplet size and size distribution width were satisfactory without the use of thiol SAM surfactants, we did not characterize surfactant inks for particle size.

6.2 Ink viscosities are within the printable range

We characterized the viscosity of ethylene inks using the viscometer. 3 mL of ink was used for each trial, and each ink was measured once. Neat ethylene glycol without any eGaIn particles was also characterized and compared against the reference value, showing that the viscometer measurements are reasonably accurate. The results of these measurements are shown in table 4.

The measured viscosity values of the ethylene glycol-based inks do not differ too much from that

Ink formulation	Flow time [s]	Kinematic viscosity [cSt]	Density [g/mL]	Viscosity [cP]
ethylene glycol	466	14.3	1.16	16.6
ethylene glycol 90 mg/mL eGaIn neat	508	15.6	1.18	18.4
ethylene glycol 90 mg/mL eGaIn 1 mM C12	443	13.6	1.22	16.6
ethylene glycol 90 mg/mL eGaIn 3 mM C12	381	11.7	1.24	14.5

Table 4: Viscosities for various formulations of ethylene glycol inks. The measured flow times for ethylene glycol inks through the viscometer are shown. The reference dynamic viscosity for ethylene glycol is 18.365 cP at 20°C, and 15.128 cP at 25°C [11], showing that the viscometer measurements are reasonably accurate.

Ink formulation	Stability
ethylene glycol, neat, 90 mg/mL eGaIn	stable
ethylene glycol, 1 mM C12, 90 mg/mL eGaIn	stable
ethylene glycol, 3 mM C12, 90 mg/mL eGaIn	stable

Table 5: Settling test results for ethylene glycol-based eGaIn inks. All of the inks were stable, and thus there was no observed dependence on surfactant concentration.

of bulk ethylene glycol, and, as predicted, are well within the printable 2-30 cP range required by the Dimatix printer.

6.3 Inks are consistently stable

We performed ink settling experiments to determine the stability of ethylene glycol-based eGaIn inks. Inks were allowed to settle for 12 hours on the benchtop, and were photographed before and after. As predicted, all of these inks were much more stable than the ethanol inks. Although the after photos were taken earlier than for the ethanol inks, the ethylene glycol inks remained stable for several weeks, suggesting that ethylene glycol-based inks are very suitable for inkjet printing. The complete data for the settling experiments is shown in table 5.

7 Removing large particles and debris

To mitigate the possibility of clogging the printhead during the inkjetting process, outlier extremely large particles and debris (figure 11) must be filtered out of the ink before inserting the ink into the printer cartridge. With a typical solid nanoparticle ink, this can be done by passing the ink through a single syringe filter, or through a series of syringe filters (i.e. filtering with a 5 μm pore diameter filter, followed by a 1 μm , followed by a 0.45 μm filter). For the ethylene glycol-based eGaIn inks described here, syringe filtration proved to be unsuitable for removing all but the largest of nanodroplets, and centrifugation was used to more finely filter the ink. The inks filtered with the centrifugation process satisfy the nanodroplet size criterion needed for inkjet printing.

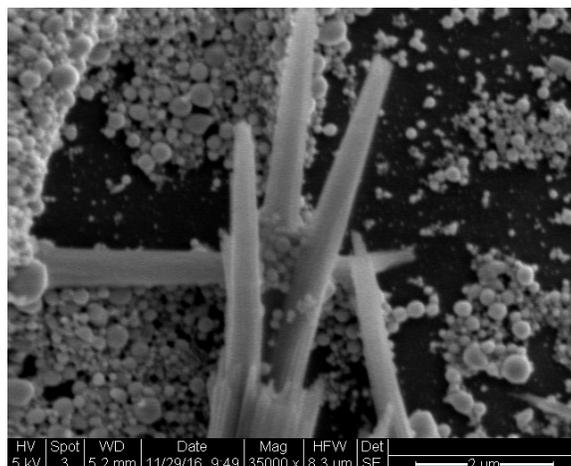


Figure 11: Debris in ethylene glycol ink. The debris was isolated by centrifuging the ink at 2500 RCF, and sampling from the sedimented material.

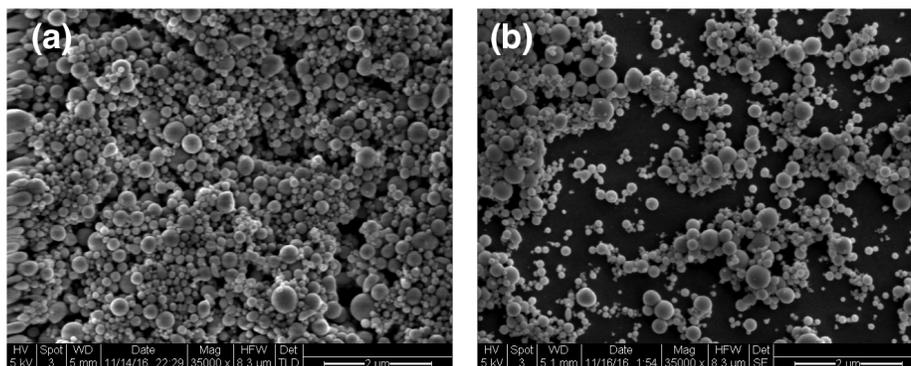


Figure 12: (a) Unfiltered ethylene glycol ink, showing original, high nanodroplet density. Scale bar is 2 μm . (b) Ethylene glycol ink filtered with 1 μm syringe filter, showing greatly reduced nanodroplet density. Scale bar is 2 μm .

7.1 eGaIn nanodroplets clog fine syringe filters

We first attempted to fine-filter ethylene glycol inks with a 1 μm syringe filter. With the vast majority of eGaIn nanodroplets having diameters well below 1 μm , we expected that the filtration process would be relatively effortless. Surprisingly, this turned out not to be the case. Due to filter clogging, syringe filtering required a large amount of force, in excess of what could be supplied with a single thumb, and sometimes so high that the filter itself would rupture. Filtered inks were limited to about 1 mL of total volume before the filter would stop up completely. eGaIn nanodroplet density also fell dramatically (qualitatively), as seen by comparing figures 12(a-b). Most curiously, some of the filtered ethylene glycol inks separated overnight, while the original unfiltered ink remained stable, suggesting that the fine filtration process may be causing the eGaIn nanodroplets to rupture and reflow. The combination of limited ink volumes, greatly reduced eGaIn nanodroplet densities, and unstable filtered inks suggests that fine filtration is unsuitable for eGaIn ink preparation.

7.2 Centrifugation can be used as a fine filter

The Fisher accuSpin 24C centrifuge is a new ExFab tool, having arrived in mid-November 2016, and is capable of centrifuging samples up to 3000 relative centrifugal forces (RCF, converts 1:1 with Earth’s gravity g). By using differential centrifugation to separate ink particles and debris by size and mass, the centrifuge can be used in place of a fine filter for inkjet ink preparation.

7.2.1 *A priori* determining centrifugation speed

We can *a priori* calculate the required centrifugation force and time to sediment particles of a given size and mass. Stoke’s law, which describes the behavior of very small spherical particles under a uniform gravitational force in viscous fluids,

$$V_{term} = \frac{2}{9} \frac{(\rho_p - \rho_f)}{\mu} ar^2$$

can be used to calculate a terminal velocity for a spherical particle with radius r and density ρ_p in a fluid with density ρ_f and viscosity μ under uniform acceleration a . Putting the acceleration in terms of number of Earth gravities $N \cdot g$, we can rewrite Stoke’s law as

$$V_{term} = \frac{2}{9} \frac{(\rho_p - \rho_f)}{\mu} Ngr^2$$

where N is the number of RCF applied by the centrifuge, and g is 9.8m/s^2 corresponding to Earth’s gravitation. If we have a centrifugation container with height H and a centrifugation time t , and assume that all particles reach their terminal velocity immediately, particles that satisfy the following criterion

$$V_{term}t \geq H$$

must sediment at the bottom of the container. If we fix the centrifugation time t , we can calculate how particles of varying size settle under varying numbers of RCF:

$$\begin{aligned} \frac{2}{9} \frac{(\rho_p - \rho_f)}{\mu} Ngr^2t &\geq H \\ r &\geq \sqrt{\frac{9}{2} \frac{H\mu}{(\rho_p - \rho_f)Ngt}} \end{aligned}$$

To check the sanity of this model, we fit the model’s predicted particle settling against the results of an eGaIn-in-ethanol differential centrifugation experiment in [12]. Plugging in known values for eGaIn density, ethanol density, and ethanol viscosity, and estimating approximate centrifuge container heights from the methods section of the paper, we demonstrate that the model predicts differential segregation behavior reasonably well (figure 13). Thus, by using Stoke’s law, we can *a priori* calculate the required amount of centrifugation needed to remove particles of a given size.

Of course, with all such models, there are assumptions that may affect the validity of the model. In particular, Stoke’s law makes the assumptions of laminar flow, spherical particles, smooth surfaces, and no interaction between particles. Furthermore, the calculations done here do not account for the differences in centrifugal force experienced at different locations in the fluid. In cases where the container height is much smaller than radius of the centrifuge rotor arm, this approximation holds, but corrections need to be made if this is not the case.

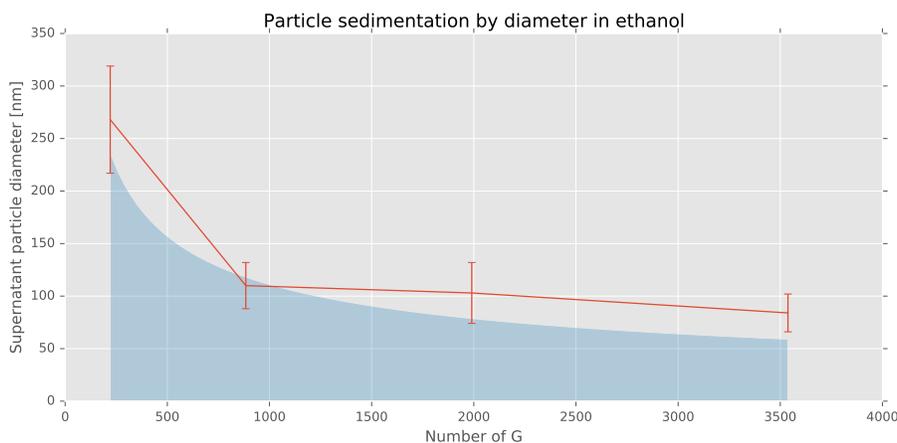


Figure 13: Fitting our Stoke’s law model of centrifugation to differential centrifugation done in [12]. The shaded region of the graph corresponds to particles that are predicted to still be suspended, and the unshaded region corresponds to particles that are predicted to have sedimented. The orange mean particle size and error bars being fitted are taken from the supplementary material of [12].

7.2.2 Using the centrifuge as a fine filter

Using our Stoke’s law model in combination with known values for eGaIn density, ethylene glycol density, and ethylene glycol viscosity, we determined the number of RCF needed to sediment eGaIn nanodroplets in ethylene glycol assuming a 10 minute centrifugation (figure 14). As shown in the graph, because of the high viscosity of ethylene glycol, the only way to use centrifugation as a fine filter for eGaIn nanodroplets is to sediment excessively large nanodroplets, and harvest the suspension as the filtered solution. Using this method, we chose an RCF value of 300, which should sediment all particles with a diameter greater than $1.6 \mu\text{m}$ (the original calculation had an error, and after performing the experiment the correct diameter was recalculated, hence the rather strange value of $1.6 \mu\text{m}$).

The filtration process we settled on was the following:

1. Centrifuge at 300 RCF for 10 minutes. Take the slurry off of the top of the centrifuge tube as the ink, taking care to not disturb the sediment at the bottom of the tube.
2. Coarsely filter the ink with a $5 \mu\text{m}$ syringe filter, to remove any large debris with low density.

We applied this filtration process to the most promising ink from the previous experiment, the 90 mg/mL eGaIn to ethylene glycol ink without surfactants. The filtration process does not significantly alter the mean and median nanodroplet diameters, but it does reduce the number of eGaIn nanodroplets at the 500 nm upper tail of the size distribution, as seen in 15(a-b). This claim can be more easily seen by comparing the SEM images in 15(c) and 15(d), and observing that there are indeed fewer eGaIn nanodroplets with diameters of around 500 nm in the (d) than in (c). Unfortunately, because our eGaIn nanodroplets are so small to begin with, we were unable to test our Stoke’s law model to verify that centrifugation eliminates all nanodroplets larger than $1.6 \mu\text{m}$.

Thus, by performing centrifugation and filtering, we were able to remove large eGaIn nanodroplets and debris, and thus satisfy the nanodroplet size criterion for using the Dimatix inkjet.

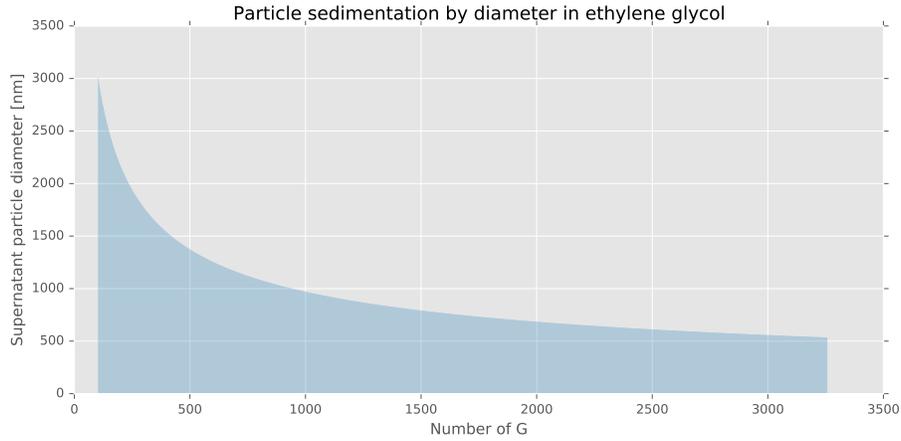


Figure 14: Fitting our Stoke's law model of centrifugation to differential centrifugation done in [12]. The shaded region of the graph corresponds to nanodroplets that are predicted to still be suspended, and the unshaded region corresponds to nanodroplets that are predicted to have sedimented.

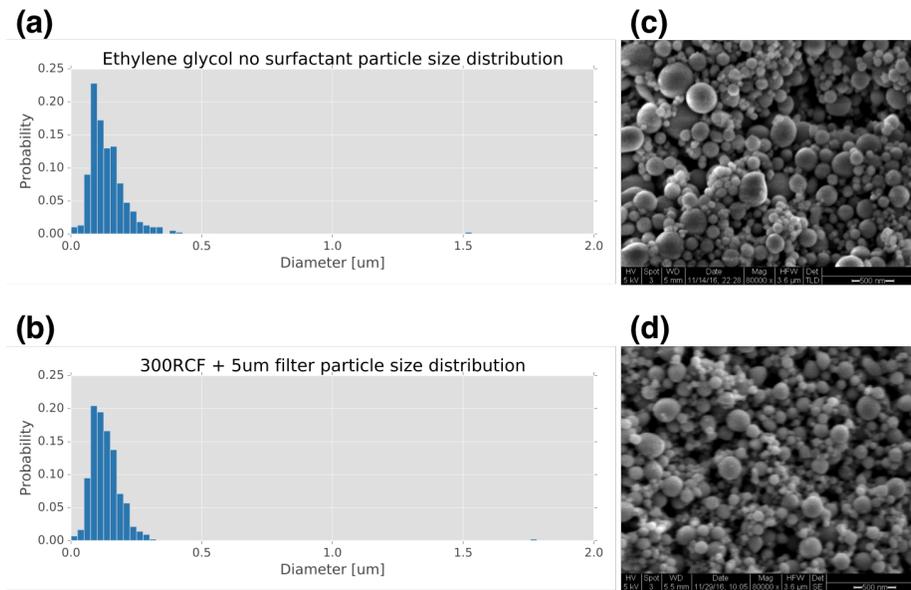


Figure 15: Comparing uncentrifuged and centrifuged ethylene glycol inks. (a) eGaIn nanodroplet size distribution of unfiltered ethylene glycol ink. (b) eGaIn nanodroplet size distribution of filtered ethylene glycol ink. There are fewer nanodroplets in the 500 nm diameter range. (c) SEM of drop-cast unfiltered ethylene glycol ink. The scale bar is 500 nm. (d) SEM of drop-cast filtered ethylene glycol ink. The scale is the same 500 nm as in (c), and directly comparing the images shows that there are indeed fewer large eGaIn nanodroplets.

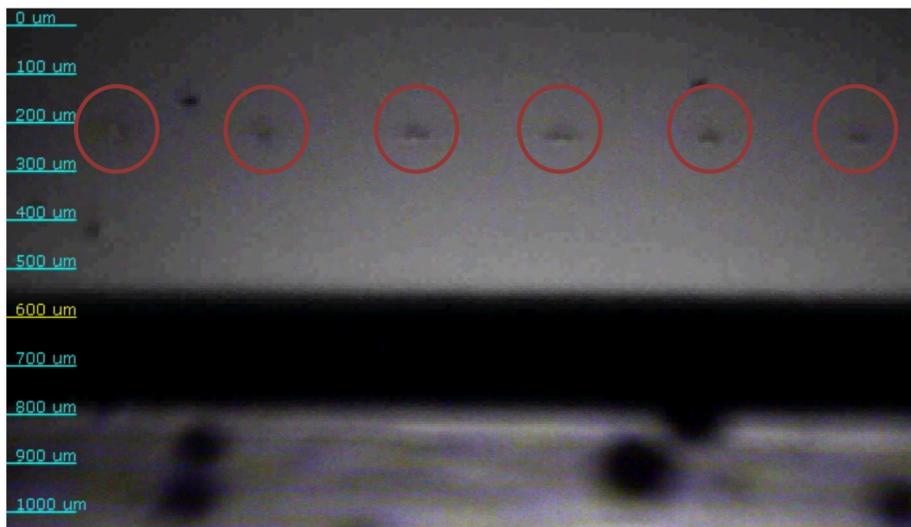


Figure 16: Droplet watcher camera. The printhead nozzles are circled. There are 16 total nozzles. The would-be substrate is located at the bottom of the image, and droplets travel from the nozzle downwards.

8 Inkjetting of ethylene glycol-based eGaIn inks

Using the no surfactant, 90 mg/mL eGaIn to ethylene glycol ink successfully characterized and filtered above, we used the Dimatix inkjet to conduct a preliminary jetting experiment to verify that our ink formulation is indeed jettable. Although we were able to successfully demonstrate controlled jetting of the ink out of the printer, we did not have the chance to use the inkjet to pattern eGaIn on a substrate due to time constraints and the limited amount of sample ink prepared for the test.

In order to optimize jetting, the Dimatix inkjet printer has a camera that allows the user to watch droplets jetting out of printhead. The camera is oriented vertically such that droplets ejected out of the nozzle and falling with gravity fall downwards in the image. By watching the camera, the user can adjust printer parameters appropriately to achieve the desired straight, controlled jetting needed to produce good patterns. The view provided by this camera without droplets is shown in figure 16.

The primary user-alterable variables for optimizing jetting in the Dimatix printer are ink cartridge temperature, and piezoactuator voltage. The primary purpose of raising the ink cartridge temperature is to lower the viscosity of the ink to facilitate printing. The Dimatix printer is capable of heating the ink cartridge from room temperature up to 70°C. The piezoactuator voltage amplitude controls the amount of force applied by the MEMS actuator to generate droplets, with a higher voltage amplitude corresponding to a larger amount of force. As expected, larger voltage amplitudes are required to jet higher viscosity inks. The shape (frequency, slew rate, width of constant regions) of the square-ish wave used to drive the piezoactuator can also be altered to optimize jetting.

The most important printer parameter for jetting our eGaIn ink was piezoactuator voltage amplitude. Because our ink is relatively viscous, a large 30V voltage must be applied in order to jet the ink (the upper limit on voltage is 40V). Below this voltage, the ink fails to jet at all (figure 17). Above this voltage, ink begins to jet out of the cartridge, though somewhat uncontrollably (figure 18). After tuning the waveform shape, we were able to achieve straight, controlled jetting (figure 19), demonstrating that our eGaIn ink formulation is indeed inkjettable.

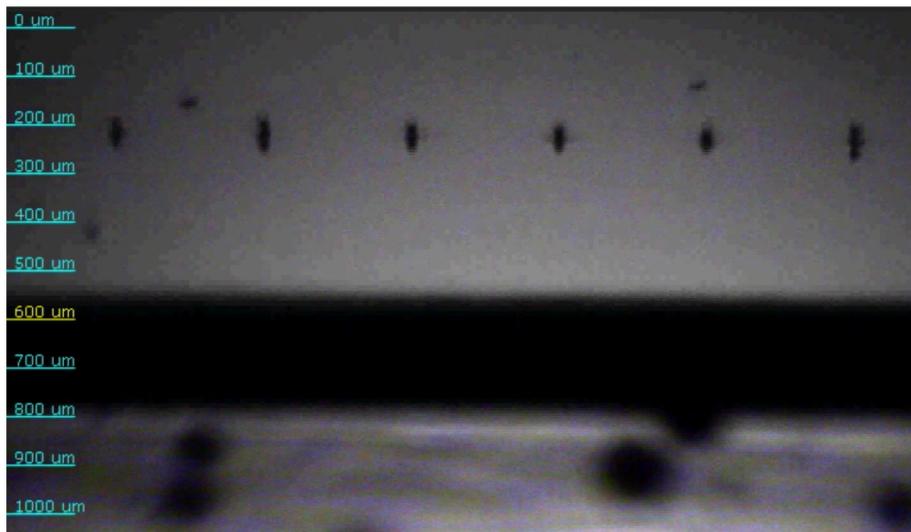


Figure 17: Droplet watcher camera view when piezoactuator voltage is too low. Ink is visible in each of the nozzles, but because of the high ink viscosity and low actuator voltage, the ink has not started to jet.

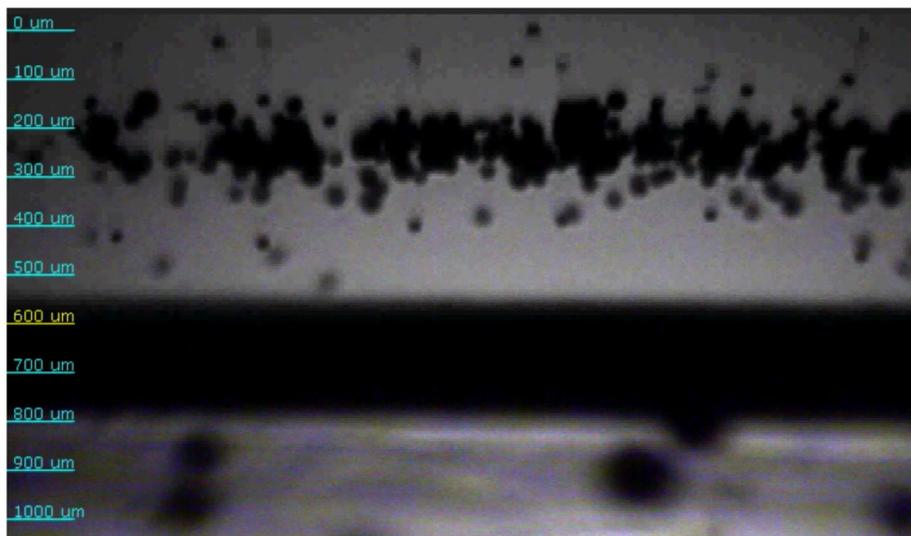


Figure 18: Droplet watcher camera view when piezoactuator voltage is high enough to jet the ink. Ink is jetting out of the nozzle. Droplets are scattered randomly, however, suggesting that the jetting is uncontrolled and not ideal for patterning.

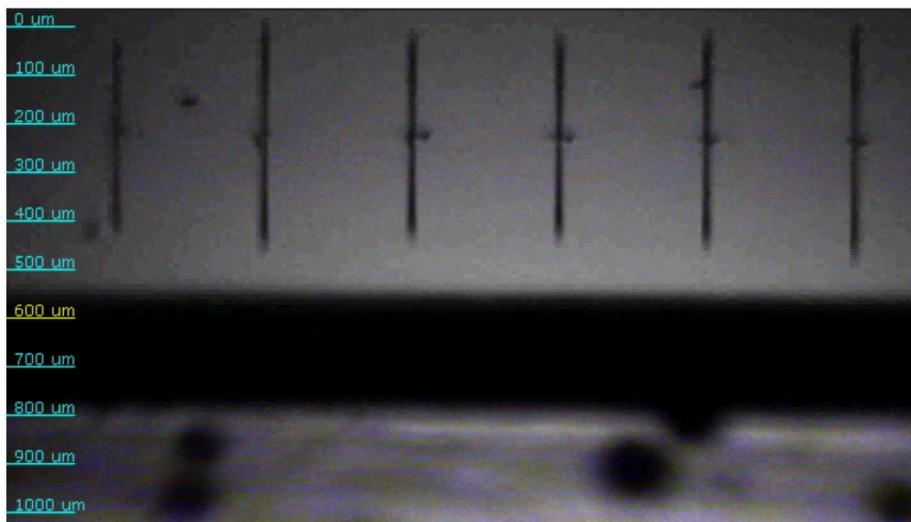


Figure 19: Droplet watcher camera view after optimizing the piezoactuator drive voltage waveform shape. The ink jets out of the printer in a straight and uniform manner, which is suitable for patterning.

9 Conclusion and future work

In summary, we have developed a process for preparing jettable eGaIn nanodroplet inks for use with the Dimatix inkjet printer, and demonstrated that our ink preparation process yields an ink that is jettable by the printer. We have found ways to quickly and systematically characterize critical ink properties like nanodroplet size, ink viscosity, and ink stability, and applied these techniques to screen and optimize inks. We also explored the methods of filtering and centrifugation to remove large nanodroplets and debris from the ink. Though the processes described here have been optimized for eGaIn, the tools and general techniques for inkjet ink formulation and characterization can easily be adapted to designing inks for patterning materials ranging from metallic nanoparticles to biomaterials.

We did not get to work on optimizing inkjet patterning or eGaIn nanoparticle sintering process due to time constraints. As HyeRyoung described it at the start of the quarter, the inkjet printing process is 90% ink formulation, and just 10% printing. If the experience of this project is any guide, there is more than a bit of truth to this.

A substantial amount of work remains to fully develop and characterize the eGaIn inkjet process. In the coming weeks, we plan on using the printer to pattern eGaIn on a variety of substrates, to further optimize printer parameters and improve the jetting of the ink. We will also characterize the resolution and linewidth achievable by the printer, and will optimize techniques to evaporate the ethylene glycol carrier solvent without sacrificing print quality. Lastly, we plan on exploring both mechanical and thermal means of sintering eGaIn nanodroplets together into conductive structures, and on characterizing the electrical resistivity of these structures.

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