Deposition of Variable Bead Diameter Arrays by Self-Focusing Electrohydrodynamic Jets

Electrohydrodynamic (EHD) processes were used for direct writing of bead arrays with controllable bead sizes. Experiments were conducted to align layers of bead-on-string structures in an effort to create three-dimensional patterns. The results show that the jet focuses on previously deposited droplets allowing for the selective deposition of material over already deposited patterns. Jet attraction to already deposited solutions on the substrate is attributed to the charge transport at the liquid ink–metal collector interface and the dielectric properties of the water/poly(ethylene oxide) (PEO) solution under an electric field. The deposition process consists of three steps: (1) deposition of a layer of bead-on-string structures, (2) addition of extra volume to the beads by subsequent passes of the jet, and (3) evaporation of the solvent resulting in an array of beads with varying sizes. Patterns with up to 20 passes were experimentally obtained. The beads’ height was seen to be independent of the number of passes. The process reported is a simple, fast, and low-cost method for deposition of bead arrays with varying diameters.

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The local increase in the electric fields to drive electric flows is also available in drop by drop e-jet printing. Galliker et al. use auto-focusing of the electric field while constructing nanopillars that are a single drop wide [19]. This super high-resolution technique is limited to a maximum deposition speed of 3 μm/s. Han et al. use phase changing inks that can be printed as liquids while hot, but solidify upon cooling [20]. This technique has a limited number of compatible inks with low melting points and can only stack ~10 layers due to electric field shielding as the wax ink stacks up. To expand this approach, An et al. use inks containing a solvent that is sintered after deposition [21]. This printing method is limited to printing speeds of 2 μm/s.

This study reports on the direct writing of droplet arrays by using multiple passes of an electrohydrodynamically driven jet. This new technique overcomes the limitations of other two-dimensional and 3D micro-additive manufacturing techniques due to its higher printing velocity (>100 mm/s), low-cost, and multi-material capability. The jet displays a self-focusing behavior on previously deposited droplets, allowing for increase in droplet volume with the number of passes. The effects of the number of passes on the area and height of the patterns are explored. The mechanisms of the deposition process are studied using a high-speed camera. A mechanism that leads to the self-focusing of the jet is proposed based on experimental results and finite element modeling (FEM) of the process.

The paper is organized as follows: First the experimental setup and experimental parameters are described in Sec. 2. In Sec. 3, the deposition and self-focusing mechanisms are introduced followed by the analysis of the effects of the process parameters on the deposited patterns in Sec. 4. In Sec. 5, a proposed mechanism of self-focusing behavior is described. Finally, Sec. 6 contains the conclusions of this work.

2 Experimental Details

Experiments were performed using the setup shown in Fig. 1. A direct current power source capable of applying 2000 V was connected to a 33 gauge (inner diameter: 108 μm, outer diameter: 210 μm, length: 50 mm) stainless steel needle. The tip of the needle was 5 mm away from the grounded collecting substrate. The substrate was held on a stage operated by a Delta Tau motion controller, and capable of following patterns programmed in LabVIEW. No pumping was used in these experiments. Copper plates were manually sanded using 400 grit sandpaper and used as substrates.

An aqueous solution of poly(ethylene oxide) with a molecular weight of 600,000 (Sigma Aldrich) was used for the experiments. For all results reported, the solution concentration was 10 g/L (1.0 wt %). The choice of polymer molecular weight and concentration resulted in a low viscosity solution that would allow for the formation of beads. Higher molecular weight and higher polymer concentrations will result in more fibrous patterns due to the additional viscosity. Very low concentrations will result in electrosprey due to insufficient viscosity to form a continuous jet [8].

A Zeiss Stemi 2000-C Microscope was used to capture videos of the emanating jet during the experiments. The jet behavior during pattern deposition was observed by a high-speed camera. The camera used was a FASTCAM Mini UX100 type 800K-M-16G, recording at 4000 frames/s. Imaging of the finished patterns was performed with an Alicona G4 Infinite Focus optical microscope. A Zygo NewView 7300 light interferometer was used for 3D imaging of the deposited beads. The interferometer was also used to measure the surface roughness of the copper substrates. Scanning electron microscopy (SEM) was performed using a LEO Gemini 1525 on uncoated samples. Low accelerating voltages (2 kV) were used for SEM to prevent charging or damage to the polymer beads.

The viscosity of the PEO solution was measured by an Anton Paar MCR 301 Rheometer using a Couette fixture. The electrical conductivity of the ink was determined by using a four-point probe method. A Kruss Easy Drop goniometer was used to determine the contact angle of water on the copper substrate. The current measurements were performed using a pre-amplifier (DL Instruments model 1212) connected to a national instruments data acquisition system.

Data analysis was performed using Image J software for the measurement of the areas and centers of mass of the resulting bead arrays [22]. For ease of interpretation, the area results are typically presented in terms of equivalent diameter. The equivalent diameter is defined as the diameter of a circle with the same area as the bead. Gwyddion was used to analyze the surface profile data and calculate the height of the beads in the resulting patterns [23]. In all graphs, the error bars denote the standard deviations.

3 Deposition Process

The deposition is started by allowing the formation of a droplet at the tip of the needle. As the volume increases, the droplet climbs up the walls of the needle due to capillary action. After the droplet is formed, the high voltage supply is turned on. The applied electric field causes the migration of the droplet to the tip of the needle. Eventually, the droplet falls from the tip of the needle due to gravity and electrostatic forces. A jet is formed immediately after the droplet falls due to the viscous drag of the falling fluid on the solution in the syringe. The jet is continuous and originates from within the needle. The initiation process is shown in Fig. 2.

After the jet is formed, the stage is commanded to start its motion. The deposition of the first layer takes place in three steps: (1) adhesion of the jet to the substrate, (2) continuous deposition at the particular location, and (3) jumping of the jet to a new location on the substrate. The deposition process of the first layer is like that described by Bu et al. [16]. After the first pass, an array of discrete droplets is obtained. This process is shown in Fig. 3(a).

Subsequent passes show that the jet is attracted to the array of the previously deposited droplets. The jet follows the same steps as for the first layer except that it adheres to the droplets instead of to the substrate. First, the jet is pinned to a droplet present on the substrate. The high-speed videos show that the jet makes contact near the highest point of the droplet. The jet continuously adds material to the droplet causing it to increase in volume. As the stage moves, the jet continues to bend. After the substrate travels some distance, the jet jumps to the next droplet in the deposition direction and the deposition process repeats. This deposition mechanism was observed for samples with up to 20 passes. The
self-focusing mechanism is shown in Fig. 3(b). A lower magnification version of the process is shown in Fig. 4, while Fig. 5 summarizes the process mechanism.

4 Results and Discussion

Experiments were conducted to study the morphology and behavior of the beads and the effect of different experimental parameters. Optical microscopy and light interferometry were used to evaluate the effect of the number of passes on the diameter and the height of the beads. The relation between the deposition process mechanism, as observed using a high-speed camera, and the resulting structure is described. Section 4.1 presents the characterization of the ink properties and of the copper collector used. These properties are essential to the morphology of the beads. Section 4.2 describes the deposition of beads along linear and circular trajectories. Section 4.3 is a parametric study of the effects of collector speed and nozzle diameter on bead size.

4.1 Characterization of the Ink and the Substrates. The conductivity of the 1.0 wt% PEO solution was 62 μS/cm at room temperature. The viscosity of the solution was 20 mPa·s at 20 °C. The solution exhibits a Newtonian behavior for shear rates up to 50 s⁻¹—the maximum shear rate studied. The lack of shear thinning can be explained by the low concentration of the polymer, which prevents entangling and limits polymer–polymer interaction.

The roughness of the sanded copper substrate was measured using a white light interferometer. The $R_a$ and $R_t$ values were $320 \pm 40$ nm and $2700 \pm 550$ nm, respectively. The advancing contact angle of water on the substrate was $105 \pm 3.5$ deg. For comparison, the contact angle on mirror-finished copper ($R_a = 24 \pm 5$ nm) is $78 \pm 1.4$ deg. The increased roughness of the sanded copper substrate leads to a significant increase in contact angle. This is important, as the ink–substrate interactions will determine the morphology of the deposited beads.

4.2 Effect of Deposition Trajectory. One of the main advantages of the deposition of patterns via micro-additive
manufacturing processes is the possibility of depositing structures along freeform trajectories. The experimental setup used has a three-axis stage so it can be used to deposit beads along arbitrary patterns. Most arbitrary trajectories can be built as a combination of linear and circular sections, so this study focuses on two specific cases: linear and circular trajectories. The linear trajectories are characterized by reciprocating motion and acceleration and deceleration at the corners. Circular trajectories maintain constant speed but undergo constant accelerations as the direction of motion is constantly changing.

4.2.1 Deposition of Linear Patterns. The effect of the number of passes on the deposited structures was studied. Samples with 1, 5, 10, and 20 passes were deposited using a back-and-forth (reciprocating) motion of the stage. The lines had a total length of 50 mm and were deposited with a substrate speed of 100 mm/s. The resulting patterns are shown in Fig. 6. The patterns show circular and ellipsoidal beads. For the ellipsoidal beads, the long axis is always along the deposition direction. This is a result of the viscous forces from the jet dragging the bead along this direction. In general, the geometries are similar to those reported by Bu et al. for deposition on a silicon substrate [16]. The bead geometry was not completely homogeneous. Some deviations were expected due to the higher surface roughness of the copper substrate.

Figure 6(c) shows that in some cases there was not perfect overlap between the different passes. In these cases, the patterns show multiple tracks of beads of smaller sizes instead of a single track. The tracks merge and divide at multiple points along the deposition direction. In all cases when limited overlap was seen, the deposited pattern followed a sinusoidal trajectory despite the stage being programmed to run in a straight line. The sinusoidal path was caused by perturbations of the jet in the direction perpendicular to the deposition direction. The perturbation resulted in an oscillatory motion of the jet. Oscillations impede jet focusing by altering the system dynamics resulting in structures that do not consistently overlap. The origins of the perturbation could be jet–substrate interactions, or perturbations of the system by vibrations or air flow. The magnitude of the perturbations could also be magnified by the vibrations of the needle due to its high slenderness ratio of 210.

To verify whether the origin of the oscillation was due to the needle slenderness, the experiments were repeated using a 12.7 mm long 25-gauge needle (inner diameter: 260 μm, outer diameter: 508 μm) and a 30-gauge needle (inner diameter: 150 μm outer diameter: 300 μm). These nozzles have a slenderness ratio of 25 and 41.6, respectively, and did not exhibit the oscillations. Therefore, it was determined that oscillation originated due to the long and thin nozzle used in the experiments.

The most significant morphological difference in comparison with previous reports in the literature is the lack of fibers or "strings" in the deposition of the bead-on-string structures. Fibers connecting the beads were not seen in any of the samples analyzed, not even after 20 passes. The fibers can be seen in the high-speed camera images during deposition (Fig. 3) but not on the resulting structures. This indicates that they were either too small to be detected by the microscope or that they were removed at some point during the process. We hypothesize that due to the liquid state of the deposition, the fibers break into small droplets or diffuse toward the larger beads by Rayleigh instability. This behavior of low concentration PEO solutions has been observed in silicon [7]. The higher surface energy of copper when compared to silicon should further enhance the instability of the deposited liquid ribbons. Huang et al. showed that for a PEO/silicon system, no satellite droplets, small beads present between larger beads, formed when the spacing between beads was small, on the order of 25–65 μm [7]. If all of the material between the beads does not migrate toward the beads, we hypothesize that very small droplets will form. Previous reports in the literature show large bead width to string diameter ratios, on the order of ~10 at low collector speeds [7]. As the polymer concentration decreases, viscosity decreases, resulting in larger bead width to fiber diameter ratios [22]. Given the low collector speed and the low polymer concentration used in the experiments, it is expected that large ratios of bead width to fiber diameter will be obtained. If a ratio of ~10 is assumed, then fibers should be on the order of ~1 μm. This is comparable to the surface roughness of the copper substrate used.

To further analyze the morphology, SEM was performed on a 20-pass sample shown in Fig. 7. The image shows that the beads have a coffee ring structure. This structure is the result of the evaporation of the solvent of the droplet. Coffee ring structures are commonly seen in the deposition of wet inks [24]. The SEM image also shows that as the diameter increases, the coffee ring effect becomes more defined, i.e., the height difference between the edge of the bead and the center becomes more noticeable. Smaller beads do not show the coffee ring structure and are also less circular. Their morphology results from a larger interaction with the high surface roughness of the sanded copper. The copper substrate can be seen through the deposited droplet in Fig. 7(b) despite the low accelerating voltage of 2 kV, indicating that very thin beads were obtained. No fibers or small droplets were seen connecting the beads in the SEM images. This serves as further evidence of the migration of the liquid material in the strings toward the beads during deposition. Although it is possible that the surface roughness of the substrate prevents the detection of nanosized droplets.

The bead area was quantified to estimate the effects of the number of passes. Figure 8(b) shows the results for multiple different runs for each of 1, 5, 10, and 20 passes. A single data point for the five-pass sample is shown because the two other runs presented
insufficient overlap to quantify the effect of the number of passes on bead area. The average equivalent diameters were 16.1 μm, 27.5 μm, 69.1 μm, and 104.8 μm for 1, 5, 10, and 20 passes, respectively. The data show that the area increases with increasing number of passes. The increase in area suggests that as additional material is added into the droplet, the footprint of the droplet expands. This behavior was also captured by the high-speed camera video, which shows droplets increasing their diameter as the number of passes increases (Fig. 4). The large increase in droplet size as the number of passes increases is also explained by the joining of adjacent droplets during the deposition process. Droplets merge once their volumes are large enough to come into contact with one another. In addition, when the jet is depositing additional material on a droplet, it can exert a viscous drag force in the direction of motion causing it to join the droplet downstream. The merging process can be seen in Fig. 9. The high-speed camera sequence shows how the dragging and joining of droplets happens. The resulting structure is also seen. When beads merge, the resulting bead has an ellipsoidal shape with a ratio of the long to short axis of about 2. The ratio is due to the conservation of the width of the bead along the axes perpendicular to the deposition direction.

The variation in droplet area also increases as the number of the passes increases. The average standard deviations in equivalent diameter for 1, 5, 10, and 20 passes were 13 μm, 24 μm, 46 μm, and 63 μm, respectively. The very significant increase in variation is partially due to the added volume but the deposition mechanics also play a very important role. The deposition time per droplet, and thus the deposition volume, is related to the length of the deposition direction. More elongated beads will receive additional material in every pass than smaller beads. This will lead to even larger and more elongated beads that still receive smaller volumes. These trends are self-promoting and are intrinsic to the process. In addition, as the number of passes increases, and the possibility of adjacent beads merging increases, a wider variation in the bead areas can be observed. The merged beads themselves will also benefit from the “large becomes larger process.”

The effect of the number of passes on bead spacing was also calculated (Fig. 8(a)). The average spacing between beads was defined as the distance between their area centers. The average spacing values for the 1-, 5-, 10-, and 20-pass samples were 70 μm, 61 μm, 136 μm, and 178 μm, respectively. The constant spacing between the one-pass and five-pass values is due to a constant number of beads at this stage. The droplets are too small to merge so they only grow in area in each pass due to the additional volume brought by the jet. For the 10-pass and 20-pass samples, merging is more common. Merging causes the centers of the areas of two droplets to move to a point in between, and hence further away from the droplets on either side. This causes bead spacing to be significantly affected by the number of passes.

The relation between bead spacing and bead area was also studied. Figure 8(c) shows that there is a linear trend between the equivalent diameter of the beads and the spacing. The linear trend is a result of the larger droplet becoming larger mechanics. The larger droplets are more likely to grow and merge with nearby neighbors, resulting in increased spacing. The one-pass and five-pass samples show that their spacing is similar but the area increases with the number of passes. At a low number of passes, droplets do not grow enough to merge.

The variations between samples with the same number of passes can be partially attributed to the effects of the size of the jet and its flow rate. The flow rate should depend mostly on the magnitude of the electric field which remains constant throughout the process. Nonetheless, variations in jet diameters and in the initiation process could also affect the flow rate. This effect of variations in the initiation process on jet diameter is commonly seen in near-field electrospinning [25]. Changes in the jet diameter were difficult to measure due to its small size and the limitations of the microscopic camera used to observe the deposition process. We estimate the jet diameter to be on the order of single-digit microns in agreement with published literature on continuous jet electrohydrodynamic methods [14].

4.2.2 Deposition of Circular Patterns. The back-and-forth motion of the stage leads to significant acceleration and deceleration effects along the deposition line. The local speed of the collector affected the size and spacing of beads near the edges. In general, beads near the edge have a much larger area expected from a longer deposition time resulting from the lower stage speed. Figure 10 shows that beads are larger near the edge of the patterns, where the direction of the motion is reversed, than near the center where a constant maximum speed is achieved. The analysis shown above studied only the constant velocity regimes of the deposition process. Even in the constant velocity regions,
the back-and-forth motion also leads to uneven temporal spacing between passes. After the turning point, the droplets that had additional volume added most recently by the jet will be once again contacted by the jet. This leads to an increased likelihood of beads merging when they are close to the turning points as pairs of passes will happen more often.

In order to overcome the limitations of back-and-forth deposition, a circular deposition pattern was used for further experimentation. Circular patterns have a constant speed regardless of the number of passes. They also allow for equal time spacing between the different passes. Figure 11(a) shows the pattern chosen. The needle was positioned at the center of the circle. Once the droplet fell and the jet was observed, the stage moved 7.5 mm to the edge of the circle. The stage traced a circle with a diameter of 15 mm at 50 mm/s for 1, 5, or 10 passes and then returned to the center of the circle. The voltage was turned off once the stage finished its motion.

Figure 11 shows the resulting patterns for the different number of passes. The figures show that the beads followed a circular pattern that matched that programmed trajectory of the stage. The path is not a perfect circle as the programmed curved trajectories in a three-axis stage will have some following errors from the motion controller. The trajectories are expected to be reproducible so that stacking of multiple passes is possible. The viscous nature of the polymer solution will also affect the accuracy of the deposited pattern. There will be a lag between the stage motion and the deposition of the beads. Ink-substrate interactions will also generate deviations in the deposited geometry due to the roughness of the sample. The manual sanding of the copper substrate results in a random surface. Local peaks and valleys affect the electric field and solvent-collector interactions.

The beads show a circular to ellipsoidal geometry. In all cases, a single track of beads was seen. The bead spacing and bead area were measured for two different runs each with 1, 5, and 10 passes. The results are shown in Fig. 12. The bead spacing does not increase with the number of passes, while the bead equivalent diameter is seen to increase monotonically with the number of passes. The one-pass sample for the first run was an outlier in terms of area and spacing.

The effect of the number of passes on height was studied for the circular patterns. The transparency of the deposited material and the thinness of the film (on the order of a few microns) prevented the interferometer from obtaining complete information on the surface of the beads. The height data obtained had large gaps. Therefore, the height was defined as the difference between the maximal local height of the bead and the average height of the surrounding substrate. The highest point was located close to the edge and not near the center of the beads. This agrees with the coffee ring morphology expected for the samples. Figure 12(c) shows the average height for all the circular samples. The data show that the number of passes does not increase the height. Even the ten-pass samples show a height comparable to the one-pass samples. This indicates that additional volume leads only to an increase in deposition area and not deposition height. The resulting morphology of the beads after solvent evaporation is given by the size of the droplet after the final pass. As the number of passes increases, larger droplets form so that the final morphology will correspond to a larger bead. The low concentration of the polymer in the ink, 1.0 wt%, means that most of the droplet will evaporate leaving only a very thin bead. There is not enough polymer to produce taller beads.

Samples with the same number of passes show large differences in the average bead areas. The difference in area was expected to come from the differences in jet diameters and flow rates during deposition. The height data only show a big difference in one-pass samples. This difference in height can also be attributed to different jet flow rates. To normalize for the difference in the area of the jet, the total area of the beads between the center of the circle and the beginning of the circular path was measured. This area should work as a proxy for the jet area as the deposition time of this region should be the same for all of the samples. The jet traces...
this line twice regardless of the number of circles programmed, once at the beginning of the process and once at the end of the process. The normalized graph is shown in Fig. 12(d). The normalized area is unitless as it is the product of the average area of the beads for a given run by the total area of the beads between the starting point and the edge of the circle. The figure shows that the normalized area increases by the number of passes. The one-pass sample in run 1 is no longer an outlier in the trend. Normalization leads to a reduction in the spread of the sample averages about the mean for experiments with the same number of passes. The standard deviation of the average normalized bead area is between 0.04 and 0.06 for each pair of samples with equal number of passes.

In an attempt to capture the expansion of the beads as the number of layers increases, the edge-to-edge spacing was measured for the six circular samples. Four additional samples, two three-pass and two seven-pass, were also analyzed. The edge-to-edge spacing was defined as the minimum distance between adjacent beads. The results are summarized in Fig. 13(a). The edge-to-edge distance reduces with the number of layers showing an increase in the length of the beads along the deposition direction. As the beads grow, they get closer to one another.

The effect of the number of layers on the edge-to-edge spacing can also be studied theoretically. Three key assumptions are made: (1) the number of beads is constant throughout the process, i.e., no beads merge, (2) the bead’s shape can be approximated by a cylinder or radius and height , and (3) the beads maintain a constant height regardless of the number of layers. Assumptions (1) and (3) are in agreement with the data for the circular patterns. The second assumption is a valid approximation as beads are seen to be circular to ellipsoidal. Given these assumptions, the area and the volume of the first layer would be given by

\[
A_1 = \pi r_1^2
\]  
(1)

\[
V_1 = \pi r_1^2 h
\]  
(2)

where , , and are the area, volume, and radius of the bead, respectively, and is the height of the bead. The subscript denotes the number of passes. For subsequent passes, the added volume per pass should be the same as for the first pass as the deposition time per bead depends on the area of the beads and the deposition rate is constant, given a constant flow rate in the jet. Therefore, the total volume after passes would be:

\[
V_N = N\pi r_1^2 h
\]  
(3)

and given the constant height after passes, the area would be

\[
A_N = N\pi r_1^2
\]  
(4)

The radius of the bead after passes is

\[
r_N = \sqrt{Nr_1}
\]  
(5)

The edge-to-edge spacing after layers is defined as

\[
s_{edge,N} = s_{center} - 2r_N
\]  
(6)

where is the center-to-center distance between beads. will be constant under the assumption that the number of beads remains the same and, therefore, has no subscript for the number of layers. Substituting Eq. (5) in Eq. (6) results in

\[
s_{edge,N} = s_{center} - 2\sqrt{Nr_1}
\]  
(7)

The edge-to-edge spacing decreases with the square root of the number of layers. The average edge-to-edge spacing is plotted versus the square root of the number of layers in Fig. 13(b). A linear trend-line is included and shows good agreement with the data.

4.3 Effect of Deposition Speed and Nozzle Diameter. Some conclusions about the effect of speed on bead area and bead spacing can be drawn by comparing the results for the back-and-forth deposition at 100 mm/s and the circular deposition at 50 mm/s. The average spacing for the one-pass and five-pass samples of the back-and-forth samples, where little merging of droplets occurs, was 66 µm compared to 135 µm for all of the circular samples. This finding shows that a decrease in speed results in an increase in the spacing. The result is in agreement with the quadratic relation between speed and bead spacing reported by Bu et al. [14]. According to the quadratic relation, both speeds studied were in the monotonic decreasing region. The average equivalent diameter for the one-pass and five-pass samples for the back-and-forth motion were 13 µm and 24 µm compared to 45 µm and 42 µm for the circular depositions. A reduction in speed leads to an increase in area. This relation is expected as lower speeds allow for longer deposition times per unit length, which will result in larger deposition areas.

The effect of nozzle diameter on bead morphology was explored by depositing single-layer samples with needles of 25, 30, and 33 gauge with inner diameters of 260, 159, and 108 µm, respectively. A 1.5 wt % PEO in water solution was used; samples were collected at 100 mm/s. As the needle diameter increased, the size of the beads increased as shown in Fig. 14(b). The center-to-center bead spacing also increased with increasing nozzle diameter as shown in Fig. 14(a). No significant changes in morphology were observed.

To understand the effect of collector, speed samples were collected at 25, 50, 75, 100, and 125 mm/s. The 33-gauge needle and a 1.5 wt % ink was used. The samples show some variability in the bead area but, in general, the size decreases as the speed increases.
drag exerted by the jet on the bead during formation. The order of 10 films of the same molecular weight was reported to be on the effects of different droplet sizes, droplet locations, and the number field near the collector. The simulations allowed for testing the into the effect of the polymer solution droplets on the local electric field [7,18]. The lack of residual charges would indicate that charges have been shown to overcome the difficulty in stacking of the fibers [26]. Recently, the deposition of fibers in semi-liquid state via near-field electrospinning has taken days to completely dissipate [26]. The complete discharge shows how the liquid nature of the ink immediately after deposition allows for charge removal. The diameter of the droplet in Fig. 15 is 2.5 mm, much larger than those seen during deposition with a fast-moving collector. For the smaller beads with larger surface area to volume ratios and lower volume charge, removal should be faster.

5 Proposed Self-Focusing Mechanism

The nature of the self-focusing mechanism that allows the jet to add additional volume to the deposited droplets is the key for the process described in this work. To understand the mechanism, experiments were performed to measure the charge removal at the droplet–collector interface (Sec. 5.1). In addition, two-dimensional (2D) FEM simulations of the electric fields of the setup were performed (Sec. 5.2). FEM simulations were used to provide insights into the effect of the polymer solution droplets on the local electric field near the collector. The simulations allowed for testing the effects of different droplet sizes, droplet locations, and the number of droplets on the electric field.

5.1 Charge Removal in Liquid Inks. Traditionally, in electrospinning, the fibers contain residual charges, which lead to repulsive forces between adjacent fibers and prevent the stacking of fibers. The residual charges are embedded in the polymer and can take days to completely dissipate [26]. Recently, the deposition of fibers in semi-liquid state via near-field electrospinning has been shown to overcome the difficulty in stacking of the fibers [7,18]. The lack of residual charges would indicate that charges are transported from the solution and into the collector substrate by the liquid medium. Mishra et al. describe the coalescence of multiple droplets when they are ejected at the same location over a period of 1 ms in an e-jet printing setup [11]. A similar process is taking place in the process reported here although the different droplets are added over timescales on the order of seconds.

The conductivity of the aqueous PEO solution used was 0.62 μS/cm. On the other hand, the conductivity of solid PEO films of the same molecular weight was reported to be on the order of 10−14 μS/cm [27]. The timescale of ionic conductivity in liquids is in nanoseconds while the timescale in between passes is in seconds [28]. The charge contained in the liquid ink should be quickly removed upon contact with the conductive copper. The liquid droplet should lose all its charge in the time between passes. The liquid state allows for the merging of the droplets and the removal of charges.

Figure 15 shows the current flowing through the collector when the voltage is turned on and off for the deposition of a single droplet with a stationary collector. Initially, there is no current flowing through the collector as there is an open circuit. When the voltage is turned on, the droplet migrates to the tip of the needle and falls to the collector. At this point, the current spikes and saturates the picammeter capabilities. While the voltage is kept on, a continuous current of ~200 nA is observed. The jet between the nozzle and the droplet is visible while the voltage is on. When the voltage is turned off, the jet collapses and the measured current begins to drop. After ~1 s, there is no charge flowing through the collector.

The complete discharge shows how the liquid nature of the ink immediately after deposition allows for charge removal. The diameter of the droplet in Fig. 15 is 2.5 mm, much larger than those seen during deposition with a fast-moving collector. For the smaller beads with larger surface area to volume ratios and lower volume charge, removal should be faster.

5.2 Jet Attraction to Droplets. The attraction of the jet to the top of the droplets can also be explained. Water has a high dielectric constant of 80 indicating that it is easily polarizable. In fact, solvents in electrospinning processes typically require high dielectric constants [29]. As water is present in the electric field, its molecules will polarize in the direction opposite to the electric field. Any charges present in the droplet will tend to migrate toward the boundary. In particular, negative charges will migrate toward the top of the droplet where the positive electrode, i.e., the needle, is closest. The charge migration and solvent polarization make the top of the droplet the point with the lowest electric potential. The top point is also the closest to the positively charged needle. Thus, the electric field will be the strongest between the tip of the needle and the top of the droplet. The charged jet will naturally tend to follow the path of the highest electric field and, therefore, will be attracted to the top of the droplets.

Finite element modeling of the electric fields was used to quantify the effect of the droplets on the electric field. Stationary studies were performed using the COMSOL MULTIPHYSICS software. A 2D
approximation was used for all models. The simulation used the same parameters as in the experiments, i.e., the nozzle to collector distance was 5 mm, the nozzle had an outer diameter of 210 μm, and the applied voltage was 2 kV. The nozzle was modeled as a rectangle made of steel. The collector was treated as a copper rectangle. The droplets were modeled as semicircles made of water with a dielectric constant of 80. The model simulated an 8 mm × 6 mm space of air surrounding the nozzle and the droplets. Three different configurations were considered: nozzle-collector (Fig. 16(a)), droplet array (Fig. 16(d)), and single droplet (Fig. 16(g)). In all cases, the origin was located at the intersection of the nozzle axis with the collector plane (Fig. 16(a)).

To quantify the effects of the droplets, the horizontal and vertical electric fields were analyzed. The horizontal electric fields were studied along a line parallel to the collector at a height one droplet radius above the collector. This line corresponds to the height of the droplet. The vertical electric field was studied along the nozzle axis. Figures 16(b) and 16(c) show the electric fields when no droplets are present. In this case, there is no horizontal electric field and the vertical electric field decreases monotonically from the nozzle to the collector. For the droplet array, 21 droplets each 50 μm in diameter with a 200 μm center-to-center spacing were modeled. These values are chosen as they are representative of those found experimentally. The horizontal electric field (Fig. 16(e)) shows oscillations between 150 kV/m and −150 kV/m. The electrostatic force on a charged particle is proportional to the electric field and the charge of the particle. Therefore, for the positively charged jet, the horizontal electric fields result in a net force toward the closest bead. The horizontal electric field is zero at the location of the droplets and at positions equidistant from adjacent droplets. This indicates that there is no horizontal electrostatic force experienced by the jet at either of these positions, making them points with electrostatic equilibrium. However, the points equidistant from the droplets are in an unstable equilibrium as any deviation in position will result in a force toward the nearest droplet. Therefore, the top of the droplets is the

Fig. 16 Electric potential models for: (a) nozzle-collector, (d) droplet array, and (g) single droplet configurations. (b) Horizontal and (c) vertical electric fields for nozzle-collector configuration. (e) Horizontal and (f) vertical electric fields for droplet array configuration. (h) Horizontal and (j) vertical electric fields for the diameter sweep of single droplet configuration. (k) Plot of horizontal electric field versus normalized distance from the center of the droplet. (l) Horizontal and (l) vertical electric fields for the displacement sweep of a single droplet with a 40 μm diameter.
preferred position for charged particles due to its stable equilibrium. At the top of the droplets, any deviations from this position will result in electrostatic forces that lead back to the center of the droplet. The vertical electric field for the droplet array (Fig. 16(f)) shows that there is a minor increase in the electric field near the top of the bead.

The single droplet model was used to determine how the electric field changes as beads increase in size or when the droplet’s center is offset from the axis of the nozzle. Droplet diameters ranging from 20 μm to 200 μm were considered. This diameter range was used to capture the behavior for droplets of different sizes that are obtained by the multiple passes of the jet. The horizontal electric field (Fig. 16(h)) shows that the maximal electric field does not change with droplet size; however, the reach of the electric field, i.e., how far away the horizontal electric field is disturbed, widely depends on the droplet diameter. Figure 16(i) shows that the horizontal electric field curves collapse into a single curve when the x-coordinate is normalized by the diameter of the droplet. The electric field of a droplet has an effect up to 2.5 diameters from its center. This result agrees well with the experimental parameters where the spacing is typically 2–3 times larger than the bead diameter. For a single droplet, the electric field is positive left (negative-x) of the droplet indicating that a positive charge would exert a force toward the right (a positive force) from where the droplet is located. The opposite is true for the electric field in the positive-x direction from the droplet: the electric field is negative and, therefore, the force points left (negative force) toward the droplet location. The effect of bead diameter on the vertical component of the electric field is shown in Fig. 15(c). In each case the electric field will increase in the vicinity of the droplet. Figures 16(a) and 16(l) show the horizontal and vertical electric fields for a 40 μm droplet as it is offset between 5 μm and 200 μm from the axis of the nozzle. The offset distance simulation investigated how the electric field changes when the droplets deviate from the axis of the nozzle. The offset causes an offset in the horizontal electric field, but the magnitude and shape of the curve are unaffected. The range of the electric field due each bead is still 2.5 diameters in each direction. The vertical electric field decreases as the offset increases. At offsets larger than 50 μm, a negligible effect is seen.

The FEM model results support the thesis that self-focusing is caused by the electric field generated by the presence of liquid solutions at the collector. The local increase in the electric field will generate forces on the jet that will drive it to each individual droplet. The close spacing of the droplets guarantees that the jet will always experience an attraction force to the nearest bead.

In summary, the self-focusing mechanism works as follows: first, a charged droplet is deposited onto the collector. The droplet loses its charge in between passes of the jet due to the high conductivity of the liquid ink. When the nozzle returns to the proximity of the droplet, it experiences attraction forces toward the droplet due to the local electric field around the droplet. The jet comes into contact with the droplet and adds additional charged ink. When the jet jumps to the next droplet, the previous droplet will start to discharge its electric charge and the process will repeat for subsequent layers.

The fabrication method reported here offers several advantages over other systems currently available. It is a very low cost system that only requires a direct current source and a linear stage unlike pulsed e-jet systems [11]. It is a very simple system that requires no control mechanism beyond those necessary to drive the stage. The self-focusing phenomenon allows for simple control of the deposited volume and of the resulting bead area. The system could be easily extended to use multiple materials so that droplets with varying ratios of materials can be deposited. The deposition of polyacrylonitrile (PAN)/dimethylformamide (DMF) links on copper and of water/PEO on silicon and aluminum is shown in Fig. 17. The printing speeds used in the experiments are below the critical speeds reported by Bu et al., which means that the deposition speed could be significantly increased from the current 100 mm/s [14]. The throughput of the system can also be increased by the use of nozzle array systems, similar to those available for other EHD methods [30].

The work here presented sets the basis for the development of multilayer bead arrays. By controlling the evaporation rates of the solvents, and the time between passes it may be possible to deposit new droplets only when the previous layer has solidified or partially solidified. By changing the speed during subsequent passes, we hypothesize that pyramidal structures can also be built. Additional work is required to achieve these multilayer structures. A parametric analysis of the variables in the system, especially voltage, collector speed, and ink composition, is also required to be able to better understand the system behavior. The understanding of these variables can help with the choice of design parameters to achieve desired geometries. Additional work is necessary to increase the repeatability of the deposition process.

6 Conclusions

A new method has been proposed for the deposition of bead arrays through electrohydrodynamic methods using low concentration polymer solutions. The method was studied using aqueous poly(ethylene oxide) solutions. The deposition process works by first depositing a layer of bead-on-strings structures on a conductive collector. During subsequent passes, the jet is attracted to the already deposited droplets. This causes the jet to deposit additional volume of solutions on top of the previously deposited droplets, leading to an increase in droplet volume. After solvent evaporation, an array of circular to ellipsoidal solid PEO beads is obtained. The diameter of the beads depends on the number of passes but the height remains constant. The lack of height increase with number of paths is due to the lack of solvent evaporation between passes. The morphology of the bead was dictated by the final droplet size before evaporation and not by the size of intermediately droplets. The diameter of the beads was proportional to the square root of the number of passes. However, after a large number of passes, adjacent beads can merge creating very large beads that do not follow the square root growth.

The focusing of the jet to the droplets is the key phenomenon that allows the process to function. It was hypothesized that self-focusing is achieved by charge dissipation in the droplet upon contacting the grounded collector, followed by polarization of the solvent molecules and transport of the negative charged species to the boundary of the top of the droplet. These processes generate a strong local electric field at the droplet, which results in electrostatic forces that guide the charged jet to each of the droplets. These hypotheses were verified with the use of experimental current measurements and FEM models of the beads in the electric field.

The results show that beads with diameters ranging from 10 μm to 150 μm can be easily produced by controlling the number of passes. Further control can be achieved by changing the deposition speed and the nozzle diameter. The deposition speeds on the order of 100 mm/s that were used are faster than those of other electrohydrodynamic methods. The deposition of bead arrays along linear and circular trajectories was demonstrated. It was discovered that it is necessary to control the acceleration and deceleration of the substrate as well as time in between passes to obtain homogeneous bead arrays. The bead arrays can be patterned in

![Fig. 17](a) Deposition of PAN/DMF ink on copper. Deposition of PEO/water ink on (b) aluminum and (c) silicon.)
arbitrary patterns and can be deposited on conductive and semiconductor materials such as copper, aluminum, and silicon. A wide range of simple inks can be used as long as the polymer concentration is tuned so that beads are obtained and the evaporation is slow enough to allow for charge removal before solidification. This approach to deposition of polymer bead arrays opens the window for fast, large-scale, and multimaterial deposition in a simple and low-cost manner.

Two main limitations need to be addressed to develop a system that can be widely used. First, the repeatability of the system needs to be improved so that homogenous bead sizes can be obtained. Second, the evaporation process needs to be controlled so that convex bead morphology can be obtained and the height of the beads can be controlled.

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