

# ON THE MEASURED CURRENT IN ELECTROSPINNING

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## ABSTRACT

The origin and scaling of the current measured during steady electrospinning of polymer solutions in organic solvents is considered. It is demonstrated that, for a specified electric field strength,  $E$ , flow rate,  $Q$ , and conductivity,  $K$ , the total measured current scales as  $I_{\text{TOTAL}} \sim EQ^{0.5}K^{0.4}$ , for a wide variety of polymer solutions with different electrical conductivities. The exponent of the conductivity dependence differs from the theoretically expected value by 20%. It is also shown that  $I_{\text{TOTAL}}$  is composed of two distinct components, one that varies linearly with  $E$ , and another that is independent of  $E$ , but varies with the conductivity,  $K$ , of the fluid and the flow rate  $Q$ . The experimental evidence suggests that the latter component arises due to a secondary electrospay emanating from the surface of the jet. The consequence of this secondary electrospay mechanism on the final fiber size achieved during the electrospinning process is also discussed.

## I. INTRODUCTION

Electrospinning is a technique that can be used to manufacture polymeric nanofibers of various morphologies and sizes, inexpensively and in large quantities. The burgeoning interest in nanoscience and nanotechnology has led to significant research into the technique in recent times.<sup>1-3</sup> In a typical electrospinning operation, a small amount of a viscoelastic liquid is electrified to a high potential difference with respect to a grounded counter electrode and is subsequently extruded through a capillary. The electrification leads to an accumulation of charges on the surface of the meniscus at the tip of the capillary. When enough charge accumulates on the meniscus, the mutual repulsion among the charges on the surface destabilizes the meniscus and competes with the surface tension force, which tends to stabilize the meniscus. As the surface charge increases, a critical condition is reached at which surface charge repulsion dominates. At this stage the meniscus is drawn into a conical shape, and a jet emanates from the apex of the cone. With the onset of jetting, the meniscus immediately changes shape and the process enters what is commonly called the “cone-jet” regime, which operates at steady state given a constant rate of supply of fluid.<sup>4</sup> The accelerating jet decreases in diameter as surface charge repulsion continually draws on it, until a point is reached where the axis of the jet bends, and the jet begins to rapidly fluctuate in a “whipping” motion<sup>5</sup>. The thinning of the jet continues, and as the solvent evaporates the jet solidifies to form thin fibers, with diameters often in the sub-micrometer range, that are deposited on the electrically grounded counter electrode.

Comprehensive reviews on the technique and its applications are now available.<sup>1,6,7</sup> In these applications, the diameter of the fibers used is often of critical

importance, and recent work has focused on predicting the fiber diameter obtained from electrospinning processes. Here, we have revisited the behavior of the measured current in typical electrospinning experiments, motivated by recent work which has demonstrated that the current on the jet plays a dominant role in determining the diameter of the fibers obtained in electrospinning.<sup>8-10</sup> We show that the measured current includes a component that represents a leakage of charge from the surface of the jet. We also discuss how the leakage of charge impacts the diameter of the fibers obtained during electrospinning.

## II. EXPERIMENT

In this work, experiments were conducted primarily on solutions of polymethyl methacrylate (PMMA), having molecular weight  $M_w = 5.4 \times 10^5$  Da, in dimethyl formamide (DMF), with polymer concentration of 15% by weight. A 5%, by weight, solution of polystyrene (PS) of molecular weight  $M_w = 1.9 \times 10^6$  Da in DMF was also used. The conductivities ( $K$ ) of the solutions were adjusted by dissolving small quantities (approximately 0.01 to 0.16 wt % in solution) of tetrabutyl ammonium chloride salt in DMF. The conductivities were measured using a hand-held conductivity meter (model 42609, Cole-Parmer, Vernon Hills, Illinois) and ranged from 2.5 to 400  $\mu\text{S}/\text{cm}$ .

Electrospinning was conducted using a “plate-plate” geometry, with a distance of 0.53m between the electrodes, and at various voltages and flow rates. A schematic diagram of the electrospinning apparatus is shown in Figure 1. In a typical electrospinning experiment, a steady stream of a viscoelastic solution is extruded from a thin, uniform capillary tip (outer diameter = 1mm and inner diameter = 0.8mm) using a syringe pump (Model No. NE-1000, New Era Pump Systems Inc, Wantagh, NY). The top

plate is subjected to a large potential difference supplied by a DC power supply (Gamma High Voltage Inc) with respect to a grounded counter electrode. The electric field strength and the flow rate (infusion rate) are set, and the current ( $I$ ) is evaluated by measuring the voltage drop across a resistor that is in series with the grounded counter electrode. The product is collected as a non-woven mat, and the fiber sizes are determined from multiple scanning electron micrographs of samples of the mat.<sup>8</sup>

### III. RESULTS AND DISCUSSION

In Figure 2(a) representative data for  $I$  measured at different electric fields  $E$  and at different flow rates  $Q$  are presented for a PMMA solution having conductivity of 25 $\mu$ S/cm. Figure 2(b) shows that the data in Figure 2(a) collapses onto a single curve, with unit slope, when the x-axis is rescaled as with electric field,  $E$ , and the flow rate,  $Q^{0.5}$ , indicating that  $I \sim EQ^{0.5}$ . In Figure 3(a),  $I$  measurements in other systems, including those of other workers reported previously<sup>8,11</sup>, are also represented in terms of this scaling. The data is presented in terms of dimensionless current,  $I^* = I/I_0$ , flow-rate,  $Q^* = Q/Q_0$  and the electric field,  $E^* = E/E_0$ . The normalization was carried out according to the scheme suggested previously by Ganan-Calvo<sup>12</sup>, using the intrinsic scales  $I_0 = \epsilon_0 \gamma \rho^{-0.5}$ ,  $Q_0 = \gamma \epsilon_0 \rho^{-1} K^{-1}$ ,  $E_0 = (2\gamma \epsilon_0^{-1} d_0^{-1})^{0.5}$  and  $d_0 = (\pi^{-2} \gamma \epsilon_0^2 \rho^{-1} K^{-2})^{0.33}$ . In these equations  $\gamma$ ,  $\epsilon_0$  and  $\rho$  are the surface tension coefficient, the dielectric permittivity of the surrounding medium, and the density of the fluid, respectively. It has been shown that  $Q_0$ ,  $I_0$  and  $d_0$  are of the order of the smallest flow rate, current, and diameter possible in an electrohydrodynamic jet.<sup>13,14</sup> For a polymer solution of  $K = 50\mu$ S/cm,  $\gamma = 30$ mNm<sup>-1</sup> and  $\rho = 1000$  kgm<sup>-3</sup>, for instance, we determine,  $Q_0 = 5.3 \times 10^{-14}$  m<sup>3</sup>s<sup>-1</sup>,  $I_0 = 2.8 \times 10^{-9}$  A, and  $E_0 =$

$3.9 \times 10^8$  V/m. Figure 3(a) shows that  $I^* \sim E^* Q^{*0.5}$  in all cases. It can also be noted that different solutions with similar conductivities tend to group together in this plot. At this stage it is worth mentioning that all the data presented is for homopolymer solutions that are non-polyelectrolytic in nature. Polyelectrolytic systems with complex chain architectures and distributed charge along the chain typically demonstrate more complicated functional behavior for the measured current. Solutions of polyethylene oxide in water fall in this category. We have excluded these systems from the present discussion for simplicity, and focus on linear homopolymers in non-aqueous solvents.

In Figure 3(b) the data shown in Figure 3(a) is rescaled using the behavior of the glycerol system as a reference denoted by subscript “ref”. We estimate  $E_{\text{ref}}$ ,  $Q_{\text{ref}}$  and  $I_{\text{ref}}$  using the properties (density, surface tension, and conductivity) of the reference fluid, and the expressions suggested by Ganan-calvo and mentioned above. For Glycerol with density  $1261 \text{ kgs/m}^3$ , surface tension  $64 \text{ mN/m}$ , and conductivity is  $0.01 \text{ } \mu\text{S/cm}$ , we estimate  $E_{\text{ref}} = 3.0 \times 10^7 \text{ V/m}$  and  $Q_{\text{ref}} = 4.5 \times 10^{-10} \text{ m}^3/\text{s}$ , and  $I_{\text{ref}} = 5.3 \times 10^{-9} \text{ A}$ . Thus, once the reference fluid is chosen,  $E_{\text{ref}}$  and  $Q_{\text{ref}}$ ,  $I_{\text{ref}}$  are constants, unlike  $E_0$  and  $Q_0$  and  $I_0$  used in Figure 3(a). The experimental values of  $E$ ,  $Q$ , and  $I$  are normalized by  $E_{\text{ref}}$ ,  $Q_{\text{ref}}$ , and  $I_{\text{ref}}$ . To investigate the conductivity dependence, the exponent in  $(K/K_{\text{ref}})$  is used as an adjustable parameter that is altered to obtain an overlap of all other data with the reference data set. With an exponent of  $0.4 \pm 0.01$ , the available data collapse onto a single curve over approximately four orders of magnitude in conductivity. Recent simulation results suggest that the dependence in conductivity should scale as  $K^{0.5}$ .<sup>15</sup> Our results indicate a scaling that is within 20% of this value.

The scaling behavior of the jet current in electrospinning has been previously studied.<sup>11,16,17</sup> and typically, linear or power law dependencies between the measured current and the operating parameters are inferred from experiments. The empirical correlations, however, vary significantly amongst each other. A distinguishing feature of the present work is that the scaling law reported here is capable of representing experimental measurements of the current, from different literature sources, in a unified manner and with unprecedented clarity. However the physical processes responsible for the observed scaling behavior in the jet current remain unclear. In electrospinning the equation for the charge balance on the jet is as follows.

$$I = \pi h^2 K E_1 + (2\sigma Q/h). \quad (1)$$

In Eq. (1),  $I$  is the total current in the jet,  $h$  is the local radius of the cross section of the jet,  $K$  is the conductivity of the fluid,  $E_1$  is the “local” electric field strength,  $Q$  is the flow rate used in the experiment and,  $\sigma$  is the surface charge density. The first term in Eq (1) is due to conduction and the second term is due to surface charge advection with the axial flow of the fluid. As the radius of the jet decreases, the advection term dominates, and the current is expected to follow a linear relationship with  $Q$ . This contrasts with the experimental observations reported here. Interestingly however, the measured dependence of the current on the flow rate is identical to that observed in the electrospraying process, where the current scales as the  $Q^{0.5}$  as well.<sup>18</sup> However, in contrast to electrospraying, and as noted previously<sup>17</sup>, the measured current in electrospinning also possesses a distinct dependency on the imposed electric field.

To understand the observed current scaling better, the counter electrode configuration in the experiments was modified, such that it consisted of two concentric

square electrode plates, denoted A1 and A2, separated by a thin sheet of rubber. The distance between the top plate and the counter electrodes was maintained at 0.53m. The exposed surface area for the two electrodes were equal ( $A_1=A_2=225\text{cm}^2$ ). The size of the collector A1 was chosen to be large enough to ensure that all of the electrospun fibers were deposited on A1 during each experiment. The current on each electrode was measured in the usual way<sup>8</sup>, using the voltage drop across a  $1\text{M}\Omega$  resistor in series with each electrode and ground. The total current  $I_{TOTAL}$  in this configuration is then the sum of the currents measured at each collector:  $I_{TOTAL}=I_{A1}+I_{A2}$ . A schematic diagram of the modified electrospinning set up is shown Figure 4(a). Remarkably, a current  $I_{A2}$  is recorded from the plate A2 even though no fibers deposit on it. Tests were also conducted to ensure that ground loops or other residual charging problems did not contribute to  $I_{A2}$ . In Figure 4(b) the current  $I$  measured in the original configuration (Fig 1) is compared with the sum of the currents measured on plate A1 ( $I_{A1}$ ) and A2 ( $I_{A2}$ ). Figure 4(b) confirms that addition of the two independently measured contributions,  $I_{A2}$  to  $I_{A1}$ , recovers the magnitude of the current measured in the conventional experimental configuration. Figure 4(c) demonstrates that the overall behavior of  $I_{TOTAL}$  remains identical to that reported previously in Figures 2(b) and 3. In Figure 5(a) the additional current  $I_{A2}$  from the outer (fiber free) collector is plotted as a function of flow rate for two solutions having different conductivities. The current  $I_{A2}$  increases substantially with an increase in the conductivity of the solution. The variation of  $I_{A2}$  with changes in the flow rate and electric field is shown in Figure 5(b). Although  $I_{A2}$  increases linearly with increasing flow rate, it is independent of the applied electric field. The observed

dependencies of  $I_{A2}$  on flow rate  $Q$  and conductivity  $K$  precludes the possibility of the current originating from corona discharge or solvent evaporation, respectively.

To further investigate the origin of the current measured at the outer electrode A2, a small amount of a nonvolatile UV sensitive dye (Fluorescent Brightener 28, Sigma-Aldrich, St. Louis, Missouri) was dissolved in the polymer solution, and electrospinning was conducted under identical conditions. Addition of the dye did not measurably change the conductivity of the solutions. A clean glass slide was also placed on the electrode A2 during the experiment, while the current  $I_{A2}$  was measured as before. After about 15 minutes the glass slide was removed and inspected using a fluorescence microscope (Axiovert 200, Zeiss). Fluorescent clusters were visible on the glass slide as shown in the inset in Figure 5(b). When a sample from the same area was inspected for deposits of polymer under the SEM, however, no deposits were visible. These experiments suggest that  $I_{A2}$  results from a secondary electro spray of the solvent that occurs simultaneously during electrospinning. Indeed, numerous photographs exist in the literature that document secondary jetting from the surface of the electrospinning jet.<sup>1,19,20</sup> The possibility for secondary jetting from a straight jet has been explored theoretically.<sup>19</sup> The physical picture that emerges from these theoretical considerations suggests a smooth jet with a circular cross-section is stable only at low electric fields. As the electric potential difference between the electrodes is increased, undulations can occur on the surface of the jet. Yarin *et al*<sup>19</sup> argue that these undulations grow in amplitude, giving rise to secondary jets that emanate from the surface of the main jet. Alternatively, the onset of whipping creates the possibility for the redistribution of charge density to regions of the jet characterized by highest curvature, as described in the model of the nonlinear jet



derived by Hohman *et al*<sup>21</sup>. If the charge density in such regions exceeds the Rayleigh threshold<sup>22</sup>, secondary jetting may occur, as suggested by the image (Fig.5.82) in Ref 20.

The results presented here for the PMMA solutions suggest that the electro spray might be composed primarily of the solvent, because scanning electron micrographs of the slide surface failed to reveal any significant polymeric deposits. Recent reports have shown that under extensional flow conditions, such as those encountered in electrospinning, polymer solutions may de-mix and form polymer-rich and solvent-rich regions.<sup>23</sup> Under these conditions, electro spraying of solvent-rich droplets from a demixed polymer solution would not be surprising. Therefore, the presence of dye but absence of polymer collected on the plate A2 provides strong evidence for the secondary jetting mechanism, giving rise to an additional electro spraying contribution that would explain the current measured on A2.

Figure 6(a), shows the behavior of the contributions of  $I_{A1}$  and  $I_{A2}$  to the total current as functions of  $Q$  and at constant  $E$  for two different values of the solution conductivity,  $K$ . The current  $I_{A1}$  has a much weaker dependence on  $Q$  than does  $I_{A2}$ . This distinction becomes clearer in the higher conductivity solution shown in the upper panel Figure 6(a). In Figure 6(b) the mean values of  $I_{A1}$  observed at different  $Q$  are plotted for various values of the accelerating voltage ( $V$ ) and at constant electrode separation distance  $d_g=0.53\text{m}$ .  $I_{A1}$  increases almost linearly with increase in  $V$  (or  $E=V/d_g$ ).

The measured current in an electro spray is known to scale with the square root of the flow-rate.<sup>12</sup> In the present measurements the current on A2, on the contrary, scales linearly with  $Q$ , while the current observed on A1 is independent of  $Q$ . However,  $Q$  in

this case is the total flow rate or infusion rate of the combined jet and spray. At present, we have not been able to configure our apparatus to measure separately the individual flow rates and currents associated with the primary electrospinning jet and the secondary electro spray. Published photographs suggest that secondary jets may emanate all along the contour of the whipping jet.<sup>1,19,20</sup> Under these circumstances, the charge and mass collected on A1 is likely to comprise not only the jet but also some portion of the spray arising from secondary jetting, so that  $I_{A2}$ , measured at A2, represents only a part of the contribution due the electro sprayed droplets. The lower limit on the size of A1 is set by the amplitude of the whipping instability at the collector, in order to ensure that all of the mass and charge carried by the fiber is collected on A1. Even using the smallest A1 collector, it is unavoidable that a portion of the electro spray is collected at A1. Furthermore, the fraction of the spray that collects on A2 versus A1 is likely to be dependent on other operating parameters including  $Q$  and  $K$  (see below). For these reasons, we cannot separately analyze the current versus flow rate relationships for the jet and the spray, respectively, but can confirm only that such secondary jetting occurs.

To check the likelihood of emission of secondary jets under these conditions, we consider the local balance between electrical stresses and surface tension along the surface of the primary jet. Following the original argument proposed by Rayleigh<sup>22,24</sup> for the instability of a charged droplet, we expect that secondary jets occur when the normal Maxwell stress becomes so large that it can no longer be balanced by surface tension. Since the electrical relaxation processes are much faster than the rapid motion of the thinning and whipping jet, we consider the jet as quasi-stationary and compute the normal Maxwell stress on a bent jet, with circular cross-section, in an external electrical field.

The rationale of the calculation follows Ref. 17 and is summarized in the appendix. We introduce local orthogonal coordinates  $(\hat{t}, \hat{\xi}, \hat{y})$  with  $\hat{t}$  tangential to the center line of the jet and  $\hat{\xi}$  the principal normal pointing in the direction of maximal center line curvature as shown in Figure 7(a). A point on the surface is parametrized by  $(s, \theta)$  with  $s$  the arc length and  $\theta$  the azimuthal angle to the principal normal as shown in Figure 7(b). Solving for the surface charge density and the electrical field on the jet surface (see appendix) we can compute the normal Maxwell stress. For radii larger than  $h_c = 4\epsilon_0 EQ/I$ ,

$$f_n(\theta) \approx \frac{1}{2\epsilon_0} \left( \frac{hI}{2Q} \right)^2 \left( 1 - 2\ln(\chi) \frac{h}{R} \cos(\theta) \right). \quad (2)$$

In Eq. (2)  $R$  is the radius of curvature,  $\chi \sim R/h$  is the local aspect ratio of the thinning jet and  $\epsilon_0$  is the dielectric permittivity of the surrounding air. Thus, the local curvature of the center line of the jet introduces a considerable modulation of the local normal stress, which is maximized in a region pointing ‘away’ from the center of curvature ( $\theta = \pi$ ). Instabilities finally leading to secondary jetting are expected in regions where surface tension can not balance the normal stress, i.e. when the electrical Bond  $Bo_E = f_n/(\gamma/h)$  is of order unity or greater. Determining an exact stability threshold would require detailed information about the relevant breakup mode responsible for secondary jetting, which is currently not available. Nevertheless one can speculate the relevant modes to be similar to small-scale unstable perturbations of the kind discussed before by Yarin *et al.*<sup>19</sup> In that work, however, perturbations were considered for a  $\theta$ -independent surface charge density, and thus would need to be modified for the bent jet considered here.

For a straight jet ( $R \rightarrow \infty$ ), the electrical Bond number is as follows.

$$Bo = \frac{h^3 I^2}{Q^2 \gamma} \frac{1}{8 \epsilon_0}. \quad (3)$$

For typical experimental parameters ( $h = 10^{-5}$  m,  $E = 10^5$  V/m,  $I = 10^{-8}$  A and  $Q = 10^{-10}$  m<sup>3</sup>/s) surface charge effects dominate ( $h_c \approx 5 \times 10^{-8}$  m  $\ll h$ ),  $h_c$  being the radius at which the surface charge effect begins to dominate over effects of the induced field, so that Eq. 2 is valid and  $Bo \approx 2$ . Thus, the experimental system is operated close to criticality. Curvature can enhance the local  $Bo_E$  by 10 % or more, so that curvature effects can indeed push the system locally into the unstable regime and initiate secondary jetting. These considerations suggest secondary jetting would be observed at the first bends of the whipping jet, where the jet radius is still large (since  $Bo \propto h^3$ ) and curvature of the center line first becomes relevant. Since the local stress is maximized at the outward-facing part of the jet spiral, secondary jets should be predominantly ejected away from the main jet; this picture is compatible with experimental observations, and can account for the leakage of charge from the main jet which is transported by secondary jets in the two-electrode setup discussed above. The proposed instability mechanism is not dependent on the applied field strength  $E$  and thus suggests the leakage current  $I_{A2}$  to be independent of the applied field, in accord with experimental observation.

Importantly, the measurement of the current of  $I_{A2}$  indicates a mechanism for dynamic removal of charge from the surface of the jet. Such a process can affect the final diameter of the fibers formed in electrospinning by reducing the stretch imposed on the

jet by the surface charge repulsion. An argument advocating the existence of a process for dynamic removal of surface charge in electrospinning was first made by Fridrikh *et al*<sup>8</sup>. Fridrikh *et al* provided a simple relationship between the terminal jet diameter  $h_t = d_f/c^{0.5}$ , where  $d_f$  is the measured fiber size and,  $c$  is the concentration of the polymer, and the volume charge density,  $\Sigma = I_{TOTAL}/Q$ , based on a balance between surface charge repulsion and surface tension forces. This equation is  $h_t = (2\gamma\epsilon_0/\pi)^{1/3} (2\ln \chi - 3)^{-1/3} \Sigma^{-2/3}$ , where  $\chi = Rh^{-1}$ , is the dimensionless wavelength of the instability. It was demonstrated theoretically, and confirmed experimentally for solutions of poly( $\epsilon$ -caprolactone) in a 3:1 mixture of chloroform and methanol, by volume, that  $h_t \sim \Sigma^{-0.66}$ . Quantitative agreement between observed and predicted fiber diameters, however, was not obtained in all cases. In order to explain this discrepancy, it was speculated that the charge on the jet might be overestimated, and that charge might be carried away from the jet by the evaporating solvent. Later, it was demonstrated that ionization of the surrounding medium could also lead to overestimation of the charge on the jet<sup>25</sup>. The present work provides evidence for yet another mechanism that can cause an overestimation of the charge on the jet during electrospinning. It follows from the discussion above that using  $I_{TOTAL}$  in estimating  $\Sigma$  can result in a systematic overestimation of the charge on the jet. In Figure 8 we present the data on the experimental fiber size in a plot of  $h_t$  versus  $\Sigma$ , as was proposed by Fridrikh *et al* for solutions of PMMA (15% by weight in dimethylformamide) and having various conductivities. Figure 8 shows that the relationship  $h_t \sim \Sigma^{-0.66}$  holds for solutions at small values of the conductivity  $K$ . For higher values of  $K$ , the slope becomes progressively smaller. Overestimation of  $\Sigma$  can indeed lead to changes in the slope of the curves shown in Figure 8. We have included the fiber size data for the 400 $\mu$ S/cm solution

in Figure 8 to emphasize that in cases where the leakage current is significant, the fiber diameter can be almost independent of  $\Sigma$ . The inset in Figure 8 shows the same data in comparison with the predictions of the theoretical model proposed by Fridrikh *et al*<sup>8</sup> (solid line). The theory predicts smaller diameter fibers for all the cases. Fridrikh *et al*<sup>8</sup> have also reported the underestimation of the experimental fiber diameters for non-conductive poly( $\epsilon$ -caprolactone) solutions, in methanol, and have suggested that the loss of charge from the surface can increase the measured current while not contributing to the stretch imposed on the jet. This can result in fibers with diameters larger than those predicted by their equation. We point out that the PMMA polymer, for which the fiber size data is presented in Fig. 8, are also inherently non-conducting and the charge is carried by the solvent molecules, in electrospinning PMMA solutions. We have also demonstrated here that a significant amount of charge can be lost from the jet due to secondary jetting. The observed discrepancy between the experimental and predicted fiber diameter can stem from such effects, although, the scaling is preserved for the solution with the lowest conductivity for which the charge removed through secondary jetting, might be significantly smaller in magnitude.

#### IV. CONCLUSION.

In summary we have demonstrated that the current,  $I_{TOTAL}$ , measured in electrospinning scales as  $EQ^{0.5}K^{0.4}$ , for a wide variety of linear homo-polymer solutions in organic solvent. We have also shown that the current measured at the collector can be composed of two components, one of which is the current carried by the main jet, and the second “leakge current” that arises from secondary jetting and results in a superposed electro spray. The latter component provides a mechanism for the removal of charges

from the jet dynamically and leads to a systematic overestimation of the actual current carried by the jet. It can be minimized by reducing  $Q$  or  $K$ . The effect of the leakage current on the final fiber diameter was also explored. The results discussed here are significant because they enable a better understanding of the nature of the current in electrospinning and provide guidelines for minimizing the leakage of charge from the jet. This in turn also allows identification of conditions where the process conforms to theoretical models better.

## ACKNOWLEDGEMENTS

This research was supported (in part) by the U.S. Army Research Office through the Institute for Soldier Nanotechnologies, under contract W911NF-07-D-0004. TMS acknowledges support by the Deutsche Forschungsgemeinschaft.

## APPENDIX

In the following we outline the calculation of the normal Maxwell stress Eq. 2 that can destabilize the jet surface. A surface charge density that depends on azimuthal position can be written as

$$\sigma(s, \theta) = \sigma(s) + \sigma_D(s) \cos(\theta) \quad (\text{A1})$$

with a monopole  $\sigma$  and a dipole  $\sigma_D$  contribution. As in Hohmann *et al.*,<sup>21</sup> we use Coulomb's law to express the electrical potential outside the slender jet as

$$\phi(\vec{x}) = \phi_\infty(\vec{x}) + \int ds' \frac{\lambda(s')}{|\vec{x} - \vec{r}(s')|} + \int ds' \frac{\vec{P}(s') \cdot (\vec{x} - \vec{r}(s'))}{|\vec{x} - \vec{r}(s')|^3}, \quad (\text{A2})$$

where  $\vec{r}(s)$  is the position of the jet center line,  $\lambda(s)$  and  $\vec{P}(s)$  are linear monopole and dipole charge densities and  $\phi_\infty$  is the potential related to the externally applied field.

Close to the jet surface this integral may be approximated by

$$\phi(\vec{x}) \approx \phi_\infty(\vec{x}) + 2\lambda(s) \ln \frac{L}{r} + \frac{\xi \lambda(s)}{R} \ln \frac{L}{r} + \xi \frac{P(s)}{r^2}, \quad (\text{A3})$$

where  $R$  is the radius of curvature,  $r$  the distance from the center line,  $\xi$  the coordinate in the principal normal direction and  $L$  an axial length scale with  $L \sim R$  for a bent jet.

Applying boundary conditions for both the normal and tangential components of the electrical field at the jet surface ( $r = h$ ) we can relate the field inside the jet to the external field given by the gradient of  $\phi$ . The assumed linear charge densities  $\lambda$  and  $P$  can be expressed in terms of the electrical field at the jet surface and the physical charge densities  $\sigma$  and  $\sigma_D$  for which additional conditions are required to close the problem.

The monopole contribution follows from a charge balance

$$I = \frac{2Q\sigma}{h} + \pi h^2 \langle E_1 \rangle K, \quad (\text{A4})$$

where  $I$  is the current,  $Q$  the flow rate,  $K$  the conductivity of the liquid and  $\langle E_1 \rangle$  the averaged tangential field inside the jet. For a thin jet,  $h \ll (2Q\sigma/\pi \langle E_1 \rangle K)^{1/3}$  bulk conduction can be neglected and we get

$$\sigma = \frac{hI}{2Q} = \frac{h}{2} \Sigma \quad (\text{A5})$$

for the monopole charge density. Here  $\Sigma$  is the volume charge density as defined previously.



Assuming charge relaxation processes in a cross section perpendicular to the jet axis to be quasi-instantaneous, the normal field component inside the jet vanishes, which fixes  $\sigma_D$ . Expanding the resulting expressions in  $h/R$  we get

$$\sigma(\theta) = \frac{hI}{2Q} \left( 1 - \cos(\theta) \ln(\chi) \frac{h}{R} \right) + 2 \cos \theta \epsilon_0 \vec{E} \cdot \hat{\xi} + O\left(\left(\frac{h}{R}\right)^2\right), \quad (\text{A6})$$

where  $\chi \sim R/h$  is the local aspect ratio,  $\epsilon_0$ , the dielectric permittivity of the surrounding air and  $\vec{E} \cdot \hat{\xi}$  the projection of the external field onto the principal normal. The weak dependence on the arc length  $s$  has been dropped for simplicity.

For radii  $h \gg h_c = 4\epsilon_0 EQ/I$ , the contribution to charge density induced by the external field can be neglected. Applying the jump condition for the normal field component at the interface we can express the normal stress as

$$f_n(\theta) \approx \frac{1}{2\epsilon_0} \left( \frac{hI}{2Q} \right)^2 \left( 1 - 2 \ln(\chi) \frac{h}{R} \cos(\theta) \right) + O\left(\left(\frac{h}{R}\right)^2\right), \quad (\text{A7})$$

which reduces to Eq. 2 at first order in  $(h/R)$ .

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