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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. For a specified electric field strength, E , flow rate, Q , and conductivity, K , the total measured current is shown empirically to scale as $I_{\text{TOTAL}} \sim EQ^{0.5}K^{0.4}$, for a wide variety of polymer solutions with different electrical conductivities. It is also shown that I_{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 electro spray emanating from the surface of the jet. The consequence of this secondary electro spray 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.¹⁻³ 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 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 point 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 rearranges 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.⁴ The accelerating jet decreases in diameter as the external applied field and surface charge repulsion continually draw on it, until a point is reached where the axis of the jet bends, and the jet begins to fluctuate rapidly in a “whipping” motion⁵. The thinning of the jet continues, and as the jet cools or 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.^{1,6,7} 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 revisit the behavior of the measured current in typical electrospinning experiments, motivated by recent work that demonstrates the important role played by the current on the jet in determining the diameter of the fibers obtained in electrospinning.⁸⁻¹⁰ We show that in some cases 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. At these small concentrations, the stability of the solutions was unaffected by the addition of salt, and no de-mixing was observed under quiescent conditions. 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, 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.⁸

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 $25\mu\text{S/cm}$. 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 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 reported previously^{8,11}, are also shown to follow 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 Gañán-Calvo¹², 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 γ , ϵ_0 and ρ 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.^{10,13} For a polymer solution of $K = 50\mu\text{S/cm}$, $\gamma = 30\text{mNm}^{-1}$ and $\rho = 1000\text{ kgm}^{-3}$, for instance, we determine, $Q_0 = 5.3 \times 10^{-14}\text{ m}^3\text{s}^{-1}$, $I_0 = 2.8 \times 10^{-9}\text{ A}$, and $E_0 = 3.9 \times 10^8\text{ V/m}$. Figure 3(a) shows that $I^* \sim E^* Q^{*0.5}$ in all cases. Different solutions with similar conductivities tend to group together in this plot. All of the data presented here is for homopolymer solutions that are non-polyelectrolytic in nature. Polyelectrolytes such as polyethylene oxide in water typically demonstrate more complicated functional behavior for the measured current. 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) are rescaled using the behavior of the glycerol system as a reference, denoted by subscript “ref”; E_{ref} , Q_{ref} and I_{ref} correspond to the values of E_0 , Q_0 and I_0 , respectively, for glycerol. For glycerol with density 1261 kg/m^3 , surface tension 64 mN/m , and conductivity is $0.01\text{ }\mu\text{S/cm}$, we obtain $E_{\text{ref}} = 3.0 \times 10^7\text{ V/m}$, $Q_{\text{ref}} = 4.5 \times 10^{-10}\text{ m}^3/\text{s}$, and $I_{\text{ref}} = 5.3 \times 10^{-9}\text{ A}$. Unlike E_0 and Q_0 and I_0 used in Figure 3(a), E_{ref} , Q_{ref} and I_{ref} are constants that do not vary with conductivity, K . To investigate the conductivity dependence, the exponent for (K/K_{ref}) is treated as an adjustable parameter. With an exponent of 0.4 ± 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 \sqrt{K} .^{10,14} Our results indicate a scaling that is within 20% of this value. Previous attempts to correlate current with electric field and flow rate suggested non-unique linear¹¹ or power law¹⁵ dependences

In electrospinning the equation for the charge balance on the jet is as follows:

$$I = \pi h^2 K E_1 + (2\sigma_0 Q/h). \quad (1)$$

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, σ 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 electrospaying process, where the current scales as the $Q^{0.5}$ as well.¹⁶ However, in contrast to electrospaying, and as noted previously¹⁷, 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 ($A1 = A2 = 225\text{cm}^2$). The size of the collector A1 was chosen to be large enough to ensure that electrospun fibers were deposited exclusively on A1 during each experiment. The current on each electrode was measured in the usual way⁸, 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} and 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 preclude 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, polymer-free electrospay that occurs simultaneously during electrospinning. Indeed, numerous photographs exist in the literature that document secondary jetting from the surface of the electrospinning jet.^{1,18,19} The possibility for secondary jetting from a straight jet has been explored theoretically.¹⁸ 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*¹⁸ 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*²⁰. If the charge density in such regions exceeds the Rayleigh threshold²¹, 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 electrospay is composed primarily of the solvent, because scanning electron micrographs of the slide surface failed to reveal any significant polymeric deposits. This surprising observation can be understood from recent reports showing that under extensional flow conditions, such as those encountered in electrospinning, polymer solutions may de-mix and form polymer-rich and solvent-rich regions.²² Under these conditions, electrospaying of solvent-rich droplets from a demixed polymer solution is possible. 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 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 of 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) 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.¹² 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. To date, we have not been successful in configuring our apparatus to measure separately the individual flow rates and currents associated with the primary electro spinning jet and the secondary electro spray. Published photographs suggest that secondary jets may emanate anywhere along the contour of the whipping jet.^{1,18,19} 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 fraction of the current due to 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 electrospray is collected at A1. Furthermore, the fraction of the spray that collects on A2 versus A1 is likely to depend on fluid and operating parameters like 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^{21,23} 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, θ) where s is the arc length and θ is 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, $f_n(\theta)$. For radii larger than $h_c = 4\epsilon_0 EQ/I$, the normal stress is

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

In Eq. (2) R is the radius of curvature, $\chi \sim R/h$ is the local aspect ratio of the thinning jet and ϵ_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 is insufficient to balance the normal Maxwell stress, i.e. where the electrical Bond number $Bo_E = f_n(\pi)/(\gamma/h)$ 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 beyond the scope of this analysis. Nevertheless one can speculate that the relevant modes are similar to small-scale unstable perturbations of the kind discussed by Yarin *et al.*¹⁸ In that work, however, perturbations were considered for a θ -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:

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

For typical experimental parameters ($h = 10^{-5}$ m, $E = 10^5$ V/m, $I = 10^{-8}$ A and $Q = 10^{-10}$ m³/s), the radius h_c at which the surface charge effect begins to dominate over effects of the induced field is approximately 5×10^{-8} m $\ll h$, so that Eq. 2 is valid and $Bo_E \approx 2$. Thus, the experimental system is indeed operating close to criticality²⁴. Curvature can enhance the local Bo_E by 10% or more, so that curvature effects can push the system locally into the unstable regime and initiate secondary jetting. These considerations suggest that secondary jetting, if occurring, would be observed at the first bends of the

whipping jet, where the jet radius is still large (since $Bo_E \propto h^3$) and curvature of the center line first becomes relevant. Evaporation of solvent should be insignificant up to this point. 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 then transported by secondary sprays 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. Fridrikh *et al*⁸ 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 $\chi = R/h$ is the dimensionless wavelength of the instability. The $-2/3$ scaling of h_t with Σ was confirmed experimentally for solutions of poly(ϵ -caprolactone) in a 3:1 mixture of chloroform and methanol, by volume. Quantitative agreement between observed and predicted fiber diameters, however, was found in some, but not all, cases. In order to explain this discrepancy, Fridrikh *et al* speculated that charge might be carried away from the jet by the evaporating solvent, resulting in overestimation of the current on the jet. Later, Korkut *et al* demonstrated that

ionization of the surrounding medium could also lead to overestimation of the charge on the jet²⁵. 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 Σ can result in a systematic overestimation of the charge on the jet. In Figure 8 the data for $h_t = d_f/c^{0.5}$, where d_f is the experimentally observed fiber diameter, are plotted versus Σ for solutions of PMMA (15% by weight in dimethylformamide) having various conductivities. Figure 8 shows that the relationship $h_t \sim \Sigma^{-0.66}$ holds only for these solutions at small values of the conductivity K . For higher values of K , the slope becomes progressively smaller. The inset in Figure 8 shows the same data in comparison with the predictions of the theoretical model proposed by Fridrikh *et al*⁸ (solid line); the theory predicts smaller diameter fibers for all cases. Leakage of charge due to secondary jetting leads to overestimation of Σ , which affects both the slope and magnitude of the curve for h_t versus Σ . At low conductivity, only the magnitude is affected, but at high conductivity the scaling relationship itself is altered. The data for the 400 μ S/cm solution in Figure 8 serves to emphasize that in cases where the leakage current is large, the fiber diameter can be almost independent of Σ .

IV. CONCLUSION.

We have demonstrated that the current, I_{TOTAL} , measured in electrospinning scales as $EQ^{0.5}K^{0.4}$, for a wide variety of 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 is a “leakage” current that arises

from secondary jetting and results in a superposed electrospray. 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.

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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

$$\sigma(s, \theta) = \sigma_0(s) + \sigma_D(s) \cos(\theta) \quad (\text{A1})$$

with a monopole σ_0 and a dipole σ_D contribution. As in Hohmann *et al.*,²⁰ 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 ϕ_∞ 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, ξ 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 ϕ . The assumed linear charge densities λ and P can be expressed in terms of the electrical field at the jet surface and the physical charge densities σ_0 and σ_D for which additional conditions are required to close the problem.

The monopole contribution follows from a charge balance

$$I = \frac{2Q\sigma_0}{h} + \pi h^2 \langle E_1 \rangle K, \quad (\text{A4})$$

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, $h \ll (2Q\sigma_0/\pi\langle E_1 \rangle K)^{1/3}$ bulk conduction can be neglected and we get

$$\sigma_0 = \frac{hI}{2Q} = \frac{h}{2} \Sigma \quad (\text{A5})$$

for the monopole charge density. Here Σ 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 σ_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, ϵ_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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- 24 Note that the precise location where the instability sets in depends on the details
of both $\sigma(z)$ and $h(z)$ {see ref [17] and ref [20]}. Previous work has shown that
due to Ohmic contributions to the current the charge density σ starts out small
near the nozzle, reaches a maximum and subsequently decreases asymptotically
as $\sigma = (I/Q) h$. {see ref [20] and in Feng, *Physics of Fluids*, 14, 3912 (2002)}
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FIGURE CAPTIONS

FIG. 1. A schematic representation of the experimental electrospinning apparatus used in this study.

FIG.2. (a) Measured current (I) against the imposed electric field (E) for experiments conducted at various flow rates (Q). Symbols correspond to experiments done at 50 μ l/min (\diamond) 30 μ l/min (\blacklozenge) 20 μ l/min (\square) 10 μ l/min (\blacksquare) 7.5 μ l/min (\triangle). (b) Collapse of a data into a single curve upon rescaling $EQ^{1/2}$.

FIG. 3(a). Plot of dimensionless current I^* vs $E^*Q^{0.5}$, of solutions with various polymers and various solution conductivity. The symbols correspond to Glycerol, $K = 0.01 \mu\text{S/cm}$ (open diamonds), PCL [poly(ϵ -caprolactone)] $K= 0.6\mu\text{S/cm}$ (open triangles), 15%PMMA, $K = 2.5\mu\text{S/cm}$ (open circles), 5%PS, $K = 5\mu\text{S/cm}$ (filled circles), 15%PMMA, $K = 75\mu\text{S/cm}$ (open inverted triangles), 15%PMMA $K = 118\mu\text{S/cm}$ (+), 15%PMMA $K = 256\mu\text{S/cm}$ (*). The data on the PCL solution and Glycerol are from Ref [8] and [11] respectively. Normalization performed as in text. **(b)** Overlap of data obtained using Glycerol with $K_{\text{ref}}=0.01\mu\text{S/cm}$, as reference.

FIG.4. (a): Schematic of modified set-up for measurement of the contributions to the electrospinning current. The collector plate is divided into two parts A1 and A2, which are separated from each other by a thin insulator film. Current on the plates is determined using the voltage drops across $1\text{M}\Omega$ resistors (R1, and R2) measured by multimeters (M1 and M2) **(b)** Experimental data on 15%PMMA solution having $K = 400 \mu\text{S/cm}$,

comparing I (filled squares) and the sum of I_{A1} and I_{A2} , I_{TOTAL} (open circles). Experiments were performed at a voltage $V = 27\text{kV}$ and electrode separation $d_g = 0.53\text{m}$. The corresponding electric field $E = 5.09 \times 10^5 \text{ V/m}$. (c) Variation in the total current I_{TOTAL} against $EQ^{0.5}$ for various values of voltage, and a constant separation between the electrodes ($d_g = 0.53\text{m}$).

FIG. 5. (a) Variation in the current contribution I_{A2} with flow-rate, Q , for two values of solution conductivity, K at $E = 5.09 \times 10^5 \text{ V/m}$ and $d_g = 0.53 \text{ m}$. Filled symbols are for $K = 256 \mu\text{S/cm}$ and open symbols are for $K = 400 \mu\text{S/cm}$. The lines show linear fit to the data. (b) Variation in the current I_{A2} with flow-rate (Q) for several applied voltages and at constant electrode separation ($d_g = 0.53\text{m}$) for $K = 400 \mu\text{S/cm}$, showing that I_{A2} is independent of E . Inset shows fluorescent clusters seen on the glass slide. Magnification (20X).

FIG. 6. Individual contributions to the total current. (a) I_{A1} (filled circles) and I_{A2} (open circles) vs flow-rate for 15%PMMA, at $E = 5.09 \times 10^5 \text{ V/m}$ and $d_g = 0.53 \text{ m}$. top panel: $K = 400 \mu\text{S/cm}$; bottom panel: $K = 235 \mu\text{S/cm}$. The solid line in each panel represents the arithmetic mean of the I_{A1} values. (b) Average value of I_{A1} against applied voltage V for a 15% PMMA solution ($K = 400 \mu\text{S/cm}$) with fixed electrode separation ($d_g = 0.53 \text{ m}$).

FIG. 7. Local coordinates chosen for the computation. (a) \hat{t} is tangential to the jet center line (dashed) and the principal normal $\hat{\xi}$ points in the direction of maximum curvature.

(b) Cross section of the jet: A point on the surface is parametrized by the arc length s and the angle θ with respect to the principal normal.

FIG. 8. Terminal diameter h_t against $\Sigma = I_{\text{TOTAL}}/Q$. Symbols correspond to $2.5\mu\text{S}/\text{cm}$ (filled squares), $75\mu\text{S}/\text{cm}$ (open circles), $118\mu\text{S}/\text{cm}$ (filled triangles) $236\mu\text{S}/\text{cm}$ (open inverted triangles), $400\mu\text{S}/\text{cm}$ (open diamonds). Inset shows the same data compared to the diameter predicted using Equation 3 of Ref [8] (solid line).