Electrospinning and electrically forced jets. II. Applications

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Electrospinning is a process in which solid fibers are produced from a polymeric fluid stream (solution or melt) delivered through a millimeter-scale nozzle. This article uses the stability theory described in the previous article to develop a quantitative method for predicting when electrospinning occurs. First a method for calculating the shape and charge density of a steady jet as it thins from the nozzle is presented and is shown to capture quantitative features of the experiments. Then, this information is combined with the stability analysis to predict scaling laws for the jet behavior and to produce operating diagrams for when electrospinning occurs, both as a function of experimental parameters. Predictions for how the regime of electrospinning changes as a function of the fluid conductivity and viscosity are presented. © 2001 American Institute of Physics. [DOI: 10.1063/1.1384013]

I. INTRODUCTION

In the previous article we developed a theory for the stability of electrically forced jets. The theory predicts the growth rates for two types of instability modes of a charged jet in an external electric field as a function of all fluid and electrical parameters, generalizing previous works2–6 to the regime of electrospinning experiments. The first type of mode considered is a varicose instability, in which the centerline of the jet remains straight but the radius of the jet is modulated; the second type is a whipping instability, in which the radius of the jet is constant but the centerline is modulated. It was demonstrated that there are three different modes which are unstable: (1) the Rayleigh mode, which is the axisymmetric extension of the classical Rayleigh instability when electrical effects are important; (2) the axisymmetric conducting mode, and (3) the whipping conducting mode. (The latter are dubbed “conducting modes” because they only exist when the conductivity of the fluid is finite.) Whereas the classical Rayleigh instability is suppressed with increasing applied electric field or surface charge density, the conducting modes are enhanced. The dominant instability strongly depends on the fluid parameters of the jet (viscosity, dielectric constant, conductivity) and also the static charge density on the jet. In particular, for a high conductivity fluid, when there is no static charge density on the jet, the varicose mode dominates the whipping mode. When there is a large static charge density, the whipping mode tends to dominate; the reason for this is that a high surface charge simultaneously suppresses the axisymmetric Rayleigh mode and enhances the whipping mode.

The aim of this article is to apply the results of the stability analysis to electrospinning and (in less detail) to electrospaying. Electrospinning is a process in which nonwoven fabrics with nanometer scale fibers are produced by pushing a polymeric fluid through a (millimeter-sized) nozzle in an external electric field.7–13 A schematic of a typical apparatus is shown in Fig. 1. In the conventional view, electrostatic charging of the fluid at the tip of the nozzle results in the formation of the well-known Taylor cone, from the apex of which a single fluid jet is ejected. As the jet accelerates and thins in the electric field, radial charge repulsion results in splitting of the primary jet into multiple filaments, in a process known as “splaying.” In this view the final fiber size is determined primarily by the number of subsidiary jets formed.

We argue, by comparing theory and experiments, that the onset threshold for electrospinning as a function of applied field and flow rate quantitatively corresponds to the excitation of the whipping conducting mode.14 This rigorously establishes that the essential mechanical mechanisms of electrospinning are those of the whipping mode. The idea is that the whipping of the jet is so rapid under normal conditions that a long exposure (>1 ms) photograph gives the envelope of the jet the appearance of splaying subfilaments.

In order to achieve the quantitative comparisons that establish this conclusion, it is necessary to extend the theoretical discussion of Part I to apply to electrospinning experiments, where both the jet radius and charge density change away from the nozzle. To this end, this article is organized as follows. First, we review the first article by discussing phase diagrams, a way of summarizing the stability calculations that facilitates comparison with experiments. To make use of
the phase diagrams, it is necessary to compute the steady-
state shape and charge density of the jet as a function of the
axial coordinate, \( z \), a task turned to in Sec. III. Our discus-
sion builds on previous work in electrospraying for the shape
of the steady jet in an electrospray,15–19 but differs from the
previous work in several important respects that were neces-
sary to understand our experiments. At the close of Sec. III
we use this information to present scaling laws for the de-
pendence of the maximum growth rate, whipping frequency,
and wave numbers on the imposed electric field and fluid
parameters. Section IV shows how the combined information
can be used to rationalize a set of observations from high-
speed movies for the destabilization of an electrospraying jet.
Finally, Sec. V presents operating diagrams. These diagrams
summarize the behavior of the jet (stable, dripping or whip-
ning) as a function of applied electric field and volumetric
flow rate. We argue that experimental measurements of the
onset of electrospraying correspond quantitatively to the on-
set of the whipping conducting mode, thereby establishing
this mode as the essential mechanism of electrospraying. We
also study how these results depend on fluid viscosity and
conductivity. In the limit of low viscosity and high conduc-
tivity, the operating diagrams qualitatively resemble those
measured by Cloupeau and Prunet-Foch20 in studies of elec-

trospraying.

II. STABILITY ANALYSIS

A. Phase diagrams

First, we summarize the results of the stability analysis
presented in part I. Since both the surface charge density and
the jet radius vary away from the nozzle, the stability char-
acteristics of the jet will change as the jet thins. To capture
this, we plot phase diagrams as a function of the most im-
portant parameters that vary along the jet: the surface charge,
\( \sigma \), and the jet radius, \( h \). [As we will see in the next sec-
tion, the electric field also varies along the jet; however, in the
plate–plate experimental geometry that we use (Fig. 1) the
field everywhere along the jet is dominated by the externally
applied field produced by the capacitor plates, so it is safe to
neglect the field’s variance. To apply the present results to
experiments in the point–plate geometry, it would be neces-
sary to include the variation of the field along the jet as well.] Figures 2 and 3 show examples of phase diagrams, which
give the logarithm of the ratio of the maximum growth rate
of the whipping conducting mode to the maximum growth rate
of all axisymmetric modes as a function of \( \sigma \) and \( h \) for
various external field strengths \( E_\infty \). We saturate this ratio at
2 and \( \frac{1}{2} \) so that the detail of the transition can be seen. In the
white regions, a whipping mode is twice or more times as
unstable as all varicose modes; in the black regions, the vari-
cose mode is more unstable. Generically, the whipping
modes are more unstable for higher charge densities (to the
right), whereas the axisymmetric modes dominate in the low-
charge-density region (to the left).

Phase diagrams are shown for three different fluids: Fig.
2 shows a comparison between glycerol (high viscosity, \( \nu = 14.9 \text{ cm}^2/\text{s} \), and low conductivity, \( K = 0.01 \mu \text{S/cm} \)) and an
aqueous solution of polyethylene oxide (PEO; high viscosity,
\( \nu = 16.7 \text{ cm}^2/\text{s} \), and high conductivity, \( K = 120 \mu \text{S/cm} \))
seeded with KBr. Figure 3 shows a comparison between
glycerol with \( K = 0.58 \mu \text{S/cm} \) and water (\( \nu = 0.01 \text{ cm}^2/\text{s} \)) for
the same conductivity. For the two high-viscosity fluids, the
structure of the diagrams is qualitatively similar over the
entire range of electric field strengths and for different con-
ductivities. (However, it should be noted that the absolute
magnitude of the growth rates of both the axisymmetric and
whipping modes increases with the electric field strength.
Hence, at higher field strengths the jet is more unstable and
the oscillation frequency is greater.) The phase diagram for
water differs quantitatively from those for glycerol at high
field \( \prec 2 \text{ kV} \): when the jet radius is larger than \( 10^{-2} \text{ cm} \), for
all charge densities the whipping instability strongly domi-
nates the axisymmetric instability. Thick water jets whip
more strongly than they undergo axisymmetric instability.

B. Jet paths

The stability of the jet not only depends on the structure
of the phase diagram, but also the path the jet follows in the
diagram. This is determined by the \( (h(z),\sigma(z)) \) profiles,
summarizing the properties of the jet at distance \( z \) from the
nozzle. The types of instabilities that the jet undergoes (ei-
ther whipping or breaking) strongly depend on this path, and
this path through the diagram strongly depends on both the
external field strength and the conductivity of the fluid.

To proceed further, we therefore need a theory for the
jet’s shape and charge density as it thins away from the
nozzle. Such theories have been described extensively in the
electrospraying literature;21,16–19 in the next section, we review
this work and present the modifications that we found nec-

dessary to obtain quantitative agreement with our own experi-

tments. To anticipate the results, Ganan-Calvo22 and Kir-
ichenko et al.23 independently demonstrated that when the
jet is sufficiently thin, the conduction current becomes neg-
ligible and a very simple formula applies: the surface charge
is linearly proportional to the radius, \( \sigma = Ih/(2Q) \) in physi-
cal units. This implies that the ultimate path of a jet through
the phase diagrams is a straight line with unit slope. The
intercept of the line is determined by the ratio of current and
flow rate:
Note that the asymptotic path depends strongly on the ratio $2Q/I$. When the current is higher (flow rate lower) the intercept of the line decreases. Qualitatively, this implies that the jet has to spend more time in a regime where the whipping instability dominates, before approaching the ultimate axisymmetric-instability-dominated regime. A crucial question is, therefore: what is the current $I$ that flows through the jet? We will see below that the current is a globally defined quantity, depending in a nontrivial way on the jet shape and electric field strengths. Experiments reveal that the current increases strongly with the conductivity $K$, the imposed electric field $E_x$, and the flow rate $Q$. The paths swept by fluids of different conductivities therefore vary substantially. The typical currents for low-conductivity glycerol and high-conductivity PEO differ by three orders of magnitude ($0–200$ nA and $0–200$ μA, respectively); hence, the paths they

$$
\log_{10} h = \log_{10} \sigma + \log_{10} \left( \frac{2Q}{I} \right).
$$

FIG. 2. Contour plots of the logarithm (base ten) of the ratio of the growth rate of the most unstable whipping mode to the most unstable varicose mode, comparing glycerol ($v = 14.9 \text{ cm}^2/\text{s}$, $K = 0.01 \mu \text{S/cm}$) and PEO ($v = 16.7 \text{ cm}^2/\text{s}$ and $K = 120 \mu \text{S/cm}$). The ratio is cut off at 2 and 1/2 so that the detail of the transition can be seen. In all cases, axisymmetric modes prevail at low charge density and whipping modes at high charge density. An experimental jet in the asymptotic regime will follow a straight line of unit slope through these log–log domain plots.
sweep out differ substantially. The glycerol jet is confined to the regime where $\sigma < 10^{-1}$ esu/cm, whereas the PEO jet is confined to $\sigma < 10^3$ esu/cm.

It will also be important to understand what the jet does before reaching this asymptotic regime. We will see in the next section that nearer to the nozzle, before the jet reaches its asymptotically thinning state, some of the current is carried by conduction. In this region $\sigma$ will be smaller than the asymptotic formula predicts, and the path will describe a curve that lies above the asymptotic line. How far above the line it curves greatly influences the stability properties of the jet.

III. DETERMINATION OF THE JET SHAPE AND SURFACE CHARGE DENSITY

The conclusion of the stability analysis is that the way an electrically forced jet destabilizes (at high enough fields so that the classical Rayleigh mode is suppressed) depends critically on both the surface charge density and the radius of the jet. We can calculate these quantities as a function of $z$ (the axial coordinate) using the conservation of mass, charge, and force-balance (Navier–Stokes) equations presented in the previous article, together with a way of calculating the electric field strength. A more detailed discussion and derivation
of these equations is presented in that article, as well as cone-jet electrospraying studies where similar equations have been applied.\textsuperscript{24,17–19,16,25} We will express the equations in dimensionless form: The equations are nondimensionalized by choosing a length scale \( r_0 \) (determined by the nozzle radius), a time scale \( t_0 = \sqrt{\rho r_0^3 / \gamma} \), an electric field strength \( E_0 = \sqrt{\gamma / (\epsilon - \bar{\epsilon})r_0} \) and a surface charge density \( \sigma_0 = \sqrt{\gamma / \bar{\epsilon}r_0} \), where here \( \gamma \) is the fluid surface tension, \( \epsilon \) and \( \bar{\epsilon} \) are the dielectric constants of fluid and air, respectively, and \( \rho \) is the fluid density. Denoting the radius of the jet as \( h(z) \) and the fluid velocity parallel to the centerline \( v(z) \), then conservation of mass gives

\[
h^2v = Q,\tag{1}
\]

where \( Q \) is the volume flow rate.

Letting the surface charge be \( \sigma(z) \), conservation of charge gives

\[
\sigma hv + \frac{K^*}{2} h^2 E = I,\tag{2}
\]

where \( K^* = K \sqrt{\rho_0 / (\gamma \beta)} \) is the dimensionless conductivity of the fluid (with \( \beta = \epsilon / \bar{\epsilon} - 1 \)), and \( I \) is the current passing through the jet. Force balance gives

\[
\frac{v^2}{2} = -\left( \frac{1}{h} \frac{h''}{h} - \frac{E^2}{8\pi} - 2\pi \sigma^2 \right) + g^* + \frac{2\sigma E}{\sqrt{h}} + \frac{3v^*}{h^2} (h^2)'',\tag{3}
\]

where \( g^* = g \rho r_0^3 / \gamma \) is the dimensionless gravitational acceleration and the dimensionless viscosity is \( \nu^* = \sqrt{\nu / r_0^2} \) with the viscous scale \( l_v = \nu^2 / (\rho \gamma) \). In these equations \( Q \) is related to the experimental flow rate, \( Q_{\exp} \), measured in \( \text{cm}^3 / \text{s} \), and \( I \) is related to the physical current measured in esu/s as follows:

\[
Q = \frac{Q_{\exp}}{\pi r_0^2} r_0,\tag{4}
\]

\[
I = \frac{I_{\exp}}{2 \pi r_0^2 \sigma_0} r_0.\tag{5}
\]

To these equations we must add an equation for the electric field. We previously\textsuperscript{1} introduced asymptotic equations for the field that were valid in the slender jet. These equations will not be useful for our present purposes because of the difficulty in specifying the physical boundary conditions in the approximate equations. Instead we will use an asymptotic version of Coulomb’s law, specified later.

In this section we will construct solutions of these equations and quantitatively compare them to the jet profiles in our electrospinning experiments. We will then use these solutions in the subsequent sections to assess the stability of the jet solution. There have been several groups\textsuperscript{16,17} who have previously compared solutions of equations similar to the above with experimental profiles of jets for the purpose of developing an understanding of current–voltage relations in electrospraying. Ganan-Calvo has also determined the surface charge along the jet in an electrospay study, by measuring the jet profile and current in an experiment, and then using equations similar to those written above to deduce the surface charge density.\textsuperscript{26} The approach that we follow here differs from these studies in several important respects, which were necessary to understand our electrospinning experiments.

These steady-state equations give solutions as a function of three parameters: the imposed flow rate \( Q \), current \( I \), and the voltage drop between the plates. However, our electrospinning experiments have only two independent parameters: given an imposed flow rate and field strength, the current is determined dynamically. As an illustration, Fig. 4 shows measurements of the current passing through a jet as a function of both applied field and applied flow rate.
Two sets of experiments are shown: a glycerol jet, with a conductivity \( K = 0.01 \, \mu \text{S/cm} \), and a PEO/water jet, with a conductivity of \( 120 \, \mu \text{S/cm} \). In both cases, the current increases monotonically with the electric field strength and with the volume flow rate passing through the jet. There is approximately a 100-fold difference between the currents passing through the two jets. Note that the current–voltage characteristic is roughly linear, except at higher voltages in the more conducting fluid, where it increases at a faster rate. The current is also a roughly linear function of the flow rate. The prediction of this current should follow from the theory. It is clear that the above equations are not capable of doing this without including additional physics. It should be remarked that the \( I-V \) characteristics in our electrosprinning experiments disagree with those usually studied in electrospraying, where the current is both independent of the voltage (e.g., Ref. 17), and scales like \( I \sim \frac{1}{h^2} \).

For the mathematical problem, the determination of the current is equivalent to specifying boundary conditions on the equations. The current at the nozzle is \( I = 2 \pi h(0) \sigma(0) + K \pi h(0)^2 E(0) \). If the charge density at the nozzle is specified, then the electric field can be determined everywhere so the current is fixed. Hence, determining the current is equivalent to specifying the charge density at the nozzle. Since this charge density is fixed by the mechanisms of charge transport down the capillary to the nozzle, we believe this is a physically meaningful way of posing this problem.

Many electrospraying studies have focused on understanding “universal” current–voltage relationships, which were first explored by de la Mora.\(^{27,21}\) In these studies, electrospraying from an isolated needle at high potential relative to ground tends to produce a current that is independent of the voltage. To rationalize this, Ganan-Calvo and others\(^{17,22,16,18,19}\) have proposed that the current is determined as a matching condition of the jet onto a perfectly conducting nozzle. Namely, the boundary condition on \( \sigma \) discussed above is that the jet shape is matched to a perfectly conducting Taylor cone. Ganan-Calvo showed that this leads to a current that independent of the voltage, which is quantitatively in good agreement with experiments.\(^{17,22}\)

We were not able to utilize these results for the present study because our electrospinning experiments do not show a current independent of the voltage drop between the capacitor plates. In fact, an experimental study of the factors besides the voltage drop setting the current (and hence the shape and charge density on an electrosprinning jet) revealed that detailed factors (such as the shape and material properties of the nozzle) had a strong influence on the jet behavior. We therefore needed to develop a methodology which could take these effects into account.

Our methodology is most similar to two other studies: first, a recent study of Hartmann et al.\(^{28}\) on the cone-jet shapes in electrospraying. Second (in an unpublished work we learned of after completing this study), Ganan-Calvo carried out an electrospraying study between two parallel plates, and achieved good agreement with his experiments.\(^{29,30}\) Both studies focus on a regime of electrospraying where the current is apparently independent of the voltage. Like these authors, to obtain quantitative agreement with experiments we were forced to take account of experimental details. However, the way in which we fixed some of the most subtle problems differs from their approaches; the major issues are noted later in this work.

### A. Asymptotics

The asymptotic behavior of steady-state solutions provides a good estimate of the radius and surface charge density of a thinning jet given its experimental parameters. As the jet thins it better approximates a cylinder. For a cylinder in an axially applied electric field, the electric field within the jet is purely axial and equal in magnitude to the applied field. This implies the equation for the current is

\[
\frac{Q \sigma}{h} + \frac{K E_{\infty}}{2} h^2 = I. \tag{6}
\]

The leading order balance has the current asymptotically dominated by advection, \( Q \sigma/h = I \), because the conduction current vanishes as \( h \rightarrow 0 \). The physical reason that the surface charge density decays (as \( h \)) as the jet thins is that though the radius decreases, the velocity increases to conserve volume flow rate, and the net effect stretches any given patch of advected jet surface.

The dominant balance in the Navier–Stokes equation is between inertia, tangential electric stress, and gravity,

\[
\frac{\nu^2}{2} = \left( \frac{Q^2}{2 h^3} \right) \left( \frac{g^*}{\sqrt{\beta h}} \right) + \frac{2 \sigma E}{\sqrt{\beta h}} g^* = \frac{2 I \Omega_0}{\sqrt{\beta Q}}. \tag{7}
\]

We can see that asymptotically \( h \sim z^{-1/4} \), or

\[
h \sim \left( \frac{2 g^*}{Q^2} + \frac{4 I \Omega_0}{\sqrt{\beta Q}} \right)^{-1/4} z^{-1/4}. \tag{8}
\]

This law was derived independently by Kirchenko et al.\(^{23}\) and by Ganan-Calvo\(^ {22,17,29}\) in his universal theory of electrospraying. Since \( \sigma \sim h \), the jet follows a line in the phase diagrams of unit slope, with an offset determined by the values of the current and volume flow rate.

### B. Numerical solutions

We now proceed to calculate the steady states numerically, in order to obtain the path of the jet before entering the asymptotic regime. In the process of working out these calculations and comparing the resulting solutions with experiments, we encountered many difficulties that had to be surmounted. We will now list and discuss these issues.

To calculate the electric field near the jet, it is necessary to impose the correct boundary conditions (of a constant potential drop) between the two capacitor plates. This requires accounting for image charges caused by the charging and polarization of the jet. Our equation for the electrical potential is therefore
nonlinear equations are solved using Newton’s method. In integration scheme. At each step of the iteration, the resulting using the previously calculated solution as a guess in our calculations of the shape while gradually increasing gravity, using as an initial guess the analytic solution of a perfect
cretization of the equations. Without an electric field, we can calculate the solution of a purely gravity driven thinning jet,
uses a standard second order in space finite difference dis-
cally as a function of all parameters. The numerical scheme
We have developed algorithms to solve these equations
where is the electrostatic potential that gives the constant electric field produced by the capacitor plates, and is the effective charge density on the jet (see Sec. II of Ref. 1). This cascade ensures that the surface \( z = 0 \) and \( z = d \) will be the proper equipotentials, since all integrals terms vanish on those surfaces, leaving just \( \bar{\phi} = \bar{\phi}_\infty \).

In practice we retain only the first term on each side. This means neither surface is exactly an equipotential; however, this is sufficient for unambiguously fixing the boundary conditions on the plate and enforcing the experimentally imposed potential drop up to a known error. Using these boundary conditions, the solutions for the electric field will ostensibly improve near the capacitor plates and thus (for the upper plate) near the nozzle. The behavior of the field near the nozzle is crucially important, as we will see below, for obtaining reasonable solutions.

Additionally, near the plate the locality assumptions that were used in an asymptotic approximation for the field in Ref. 1 for deriving the electric field equation break down. For this reason, we opted to solve the full integral equation numerically to determine the electric field. The integral equation that we use is

\[
\bar{\phi}(z,r = h(z)) = \bar{\phi}_\infty + \int_0^d dz' \lambda(z') \left[ \frac{1}{\sqrt{(z'-z)^2 + h^2(z)}} - \frac{1}{\sqrt{(z'+z)^2 + h^2(z)}} \right] \\
- \frac{1}{\sqrt{(2d-z'-z)^2 + h^2(z)}} + \frac{1}{\sqrt{-(2d+z'-z)^2 + h^2(z)}} \right] \right\}, \tag{9}
\]

FIG. 5. Change in jet shape with ramping electric field strength. As the electric field is ramped from 0 to 5 kV/cm, the jet thins substantially. The fluid is glycerol with \( \nu = 14.9 \text{ cm}^2/\text{s} \), with \( K = 0.01 \mu \text{S/cm} \).

As discussed earlier, the difficulty with this procedure is that it does not fix the current, which is mathematically equivalent to specifying the charge density near the jet. Since the current is a crucial factor in determining the stability of the jet, this conclusion implies that the detailed shape and material properties of the nozzle affects the stability of the jet, even when the jet is very far from the nozzle. By “detailed,” we do not mean something as mundane as a dependence on the nozzle radius, but we conjecture that even variations in the shape and material properties of the electrode, or the protrusion length of the nozzle through the ca-

cpacitor plates have a noticeable effect. Our own experiments

FIG. 6. Comparison of theoretical (dashed) and experimental (solid) radial jet profiles for a glycerol jet in a uniform applied field. The flow rate is \( Q = 1 \text{ mL/min} \) and the applied voltage is 30 kV over 6 cm. The characteristic decay lengths of the experimental and theoretical curves, normalized to the initial radius of the jet, are 1.28(3) and 3.26, respectively. See Fig. 8(c) for the considerable improvement that results when the correct fringe fields of the nozzle are used instead of a uniform applied field. There the two curves lie nearly on top of one another.

\[
\bar{\phi}(z,r = h(z)) = \bar{\phi}_\infty + \int_0^d dz' \lambda(z') \left[ \frac{1}{\sqrt{(z'-z)^2 + h^2(z)}} \\
- \frac{1}{\sqrt{(z'+z)^2 + h^2(z)}} - \frac{1}{\sqrt{(2d-z'-z)^2 + h^2(z)}} + \frac{1}{\sqrt{-(2d+z'-z)^2 + h^2(z)}} \right] \right\}, \tag{9}
\]

\[
\bar{\phi}(z,r = h(z)) = \bar{\phi}_\infty + \int_0^d dz' \lambda(z') \left[ \frac{1}{\sqrt{(z'-z)^2 + h^2(z)}} \\
- \frac{1}{\sqrt{(z'+z)^2 + h^2(z)}} - \frac{1}{\sqrt{(2d-z'-z)^2 + h^2(z)}} + \frac{1}{\sqrt{-(2d+z'-z)^2 + h^2(z)}} \right] \right\}, \tag{9}
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- \frac{1}{\sqrt{(z'+z)^2 + h^2(z)}} - \frac{1}{\sqrt{(2d-z'-z)^2 + h^2(z)}} + \frac{1}{\sqrt{-(2d+z'-z)^2 + h^2(z)}} \right] \right\}, \tag{9}
\]

\[
\bar{\phi}(z,r = h(z)) = \bar{\phi}_\infty + \int_0^d dz' \lambda(z') \left[ \frac{1}{\sqrt{(z'-z)^2 + h^2(z)}} \\
- \frac{1}{\sqrt{(z'+z)^2 + h^2(z)}} - \frac{1}{\sqrt{(2d-z'-z)^2 + h^2(z)}} + \frac{1}{\sqrt{-(2d+z'-z)^2 + h^2(z)}} \right] \right\}, \tag{9}
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\[
\bar{\phi}(z,r = h(z)) = \bar{\phi}_\infty + \int_0^d dz' \lambda(z') \left[ \frac{1}{\sqrt{(z'-z)^2 + h^2(z)}} \\
- \frac{1}{\sqrt{(z'+z)^2 + h^2(z)}} - \frac{1}{\sqrt{(2d-z'-z)^2 + h^2(z)}} + \frac{1}{\sqrt{-(2d+z'-z)^2 + h^2(z)}} \right] \right\}, \tag{9}
\]

\[
\bar{\phi}(z,r = h(z)) = \bar{\phi}_\infty + \int_0^d dz' \lambda(z') \left[ \frac{1}{\sqrt{(z'-z)^2 + h^2(z)}} \\
- \frac{1}{\sqrt{(z'+z)^2 + h^2(z)}} - \frac{1}{\sqrt{(2d-z'-z)^2 + h^2(z)}} + \frac{1}{\sqrt{-(2d+z'-z)^2 + h^2(z)}} \right] \right\}, \tag{9}
\]

\[
\bar{\phi}(z,r = h(z)) = \bar{\phi}_\infty + \int_0^d dz' \lambda(z') \left[ \frac{1}{\sqrt{(z'-z)^2 + h^2(z)}} \\
- \frac{1}{\sqrt{(z'+z)^2 + h^2(z)}} - \frac{1}{\sqrt{(2d-z'-z)^2 + h^2(z)}} + \frac{1}{\sqrt{-(2d+z'-z)^2 + h^2(z)}} \right] \right\}, \tag{9}
\]
confirm that changing the protrusion length of the nozzle changes the stability properties of the jet.

The idea that the detailed shape of the nozzle matters was previously recognized by Pantano et al. and Hartmann et al. in carrying out similar studies for electrospraying. This point of view is also consistent with experiments dating back to G. I. Taylor's original experiments describing the Taylor cone. In this experiment, Taylor found it necessary to machine a conducting nozzle with an opening angle of exactly the Taylor cone angle, 49.3°; presumably, his initial efforts using more ordinary nozzles failed, and he ascribed this failure to the fringe fields near the nozzle. In our own experiments, making the nozzle protrude by different distances from the equipotential conducting plate resulted in quantitative changes in the stability properties of the jet.

In order to compute the theoretical current and jet profiles, we need to figure out what is happening at the nozzle. For the long wavelength theory developed earlier, this translates into determining a relation between the electric field \( E(0) \) and the surface charge density \( \sigma(0) \) at the nozzle. Given such a boundary condition, the current is determined through a combination of the equation for the current equation (2) and the equation for the electric field (10). The determination of the current is inherently nonlocal, in that the current depends on the shape, charge density, and electric field along the entire jet.

We do not know from first principles what this boundary condition should be, because it is not clear what is the predominant charge transport mechanism near the nozzle. In order to determine the effective boundary condition, we chose to iterate between theoretical solutions for a variety of different boundary conditions and a carefully controlled set of experiments. The philosophy we followed was to find the set of boundary conditions for which quantitative agreement with experiments is obtained over a range of applied fields and flow rates. Using the apparatus outlined in Fig. 1, we measured the steady shapes of jets of several fluids over a range of electric field strengths. The currents from the jets were also measured independently.

We experimented with various possibilities for the effective boundary condition at the nozzle and found that we were only able to find steady solutions for the field strengths and flow rates observed experimentally when we used the boundary condition \( \sigma(0) = 0 \). Including a substantial amount of initial surface charge caused the jet to balloon outwards as it exited the nozzle due to self-repulsion of charge. This caused the solutions to destabilize at moderate fields, typically far below the field strengths where steady jets are observed ex-

**FIG. 7.** Typical nozzle fringe fields: the nozzle used to compute the field is a solid metal cylinder that protrudes 7.2 mm from the plate and has an outer radius of 0.794 mm. In these pictures the nozzle points upwards, and we only present the right half of it. All dimensions are in centimeters. We show lines of equal field strength on the top left and equipotentials on the top right. The bottom figure shows the extracted \( E_0(z) \), as described in the text.
perimentally. This difficulty did not exist when \( \sigma(0) = 0 \) (or small) for fluids of sufficiently low conductivity. Since our experiments never observe a destabilization of the jet through a dramatic ballooning near the nozzle, our calculations imply that the charge distribution near the nozzle must be small enough so this cannot occur; hence we feel that \( \sigma(0) = 0 \) is a physically reliable approximation (when the fluid conductivity is sufficiently small). A reason for why this is so is that a basic assumption underlying the derivation of the equations for the jet shape is that the time scale for charge relaxation across the cross section of the jet is much faster than that for axial charge relaxation. This assumption clearly breaks down at the nozzle, where there has not been sufficient time for radial charge relaxation to occur. Without radial charge relaxation, the surface charge density has not had time to build up. (We thank Professor D. Saville for providing this argument to us.)

A typical comparison of the radius of the theoretical profile for the jet with experiments is shown in Fig. 6, for a glycerol jet in an electric field \( E_e = 5 \text{ kV/cm} \), with a volume flow rate \( Q = 1 \text{ ml/min} \). The agreement is terrible: the theoretical profile systematically decays too slowly away from
the nozzle. The reason for this disagreement is not the choice of the effective boundary condition. Extensive experimentation with different boundary conditions (e.g., varying the fraction of the current carried by surface advection) showed that the agreement shown in Fig. 6 is the best achievable. [And, as described earlier, if \( \sigma(0) \) is increased too much from zero, we could not even find steady solutions at the parameter values of the experiments.]

The problem instead is that we have computed this profile under the assumption that the applied field \( E_\infty \) is uniform in \( z \). However, in the experiment, the metal nozzle protrudes 7.2 mm from the top capacitor plate, which is a small fraction of the distance between the two capacitor plates. However, this causes fringe fields. Near this nozzle the local \( E_\infty \) will be higher than the average field between the two plates. Experimentally, there is strong evidence that these fringe fields are important in determining the shape and stability of the jet: when the nozzle is pushed out or retracted, there are significant changes in the stability characteristics. When the nozzle is pulled in, the initiation voltage for a steady jet increases, and vice versa. The fringe field of the nozzle is therefore crucial to determine the behavior of the jet near the

FIG. 9. Experimental pictures that were edge detected to produce the experimental profiles of Fig. 8.
nozzle, which sets the behavior for the rest of the jet downstream.

We therefore need to compute the fringe field. Using Matlab’s PDE Toolbox we computed the field in the vicinity of an experimental nozzle, and extracted from this solution the variation in \( E_z(z) \) away from the nozzle. The result of a typical finite element calculation is shown in Fig. 7. The calculation assumes that the nozzle is a perfectly conducting solid cylinder with the same protrusion and outer diameter as that in the experiment. An average of the cross-sectional electric field was extracted from the finite element calculation, as \( E_z(z) \).

When we include the effects of the fringe fields near the nozzle, agreement improves markedly. Figure 8 shows nine such comparisons at three different values of applied field (22, 26, and 30 kV over 6 cm) and at three different flow rates (1.0, 1.5, and 2.0 mL/min). The photographs from which the experimental curves in Fig. 8 were extracted are shown in Fig. 9. The improvement from Fig. 6 to Fig. 8(c) is considerable. Agreement between theory and experiment is best at low flow rates and high voltages. One reason for this is perhaps that in these limits, the electric field is greater at the nozzle while the rate of charge advection is less, so our assumption that all the current at the nozzle is carried in solid cylinder with the same protrusion and outer diameter as that in the experiment. An average of the cross-sectional electric field was extracted from the finite element calculation, as \( E_z(z) \).

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air interface at the axial position where the liquid is attached to the nozzle. This is mathematically similar (though physically different) to our method of fixing the charge density at the nozzle; their calculations appear to indicate that the charge density is very small near the nozzle, as we have found here. Another difference between the two calculations is that they treat a finite jet with an end, while our jet thins indefinitely. Finally, the experiments reported here have a different current voltage relationship than those reported by Hartmann et al.: whereas they present scaling laws stating the current is independent of the voltage, our experiments and simulations show a strong dependence. Presumably this is due to the differences in geometries of the two studies.

To conclude this section, we have demonstrated quantitative agreement between theory and experiments for jet shapes of low conductivity fluids. Such agreement required accurate computation of both the fringe fields of the nozzle and invention of an effective boundary condition on the surface charge density at the nozzle. Both of these features significantly influenced the shape and surface charge density on the jet. Since the surface charge strongly affects stability, it is clear that the properties of both electrosprays and electrospinning fibers will generically depend strongly on precise details of the nozzle configuration. The methods developed in this section for determining the jet shape do not work for higher conductivity fluids. We believe that the reason for this is that our understanding of the mechanisms for charge transport near the nozzle is inadequate.

The relationship between the surface charge and radius of the jet also implies scaling laws for the real and imaginary parts of the growth rate of the whipping instabilities as a function of experimental parameters. We have numerically calculated the maximum growth rate and oscillating frequency of the whipping mode as a function of external field, and fluid parameters. We find that the whipping frequency increases linearly with the applied field strength, increases like the square root of the conductivity, and decreases with the square root of the viscosity. Similarly the growth rate increases linearly with the electric field strength and conductivity, and decreases inversely with viscosity. The oscillatory frequency is numerically much larger than the growth rate, consistent with our experiments. The dominant forces determining these forces are the net force and torque exerted on the charged jet by the external electric field. In a future work...

FIG. 12. (a) Close to the nozzle, the centerline of the jet is straight. Small axisymmetric distortions can be seen on the axis of the jet. (b) Further down the jet from the nozzle, the axisymmetric disturbances have grown into large blobs which propagate down the centerline. The two video frames show the jet at two different times (separated by a fraction of a second) at the same spatial location. (c) Further downstream, the centerline itself starts to whip. The two frames show the jet at two different times at the same spatial location.
we plan on testing these relations with systematic experiments.

IV. COMPARISON OF STABILITY CHARACTERISTICS WITH EXPERIMENTS

Combining knowledge of the jet shape and surface charge density along the jet from Sec. III with the stability characteristics yields predictions for the behavior of the jet as a function of experimental parameters.

We will start with one such comparison, to give a flavor for how the techniques developed in this article can be applied. We have taken a close up high speed 1000 frames/second movie of a PEO/water jet with viscosity $\nu = 16.7 \text{ cm}^2/\text{s}$, conductivity $K = 11 \mu \text{S/cm}$, $Q = 5 \text{ ml/min}$, a voltage drop of 9 kV over 15 cm, and a measured current of 0.9 $\mu\text{A}$. Viewed on large scales far from the nozzle, the jet looks like a whipping rope (Fig. 11).

Figure 12 shows a succession of frames from the movie at different times and at different spatial locations along the jet. The first frame shows a segment of the jet very close to the nozzle with a slight axisymmetric excitation. The second set of frames shows two different pictures of the same jet a few nozzle diameters downstream, taken at the same spatial location, separated in time by a fraction of a second. The axisymmetric disturbances have grown into large axisymmetric blobs that travel downstream. The third set of images is even farther from the nozzle; here the centerline of the jet begins to whip back and forth. The axisymmetric blobs continue to propagate down the axis of the whipping jet.

Now we want to demonstrate how these results can be explained using the formalism developed in this article. Figure 13 shows the stability diagram described in Sec. II for the parameters of this PEO/water jet. The black region in the figure denotes parameter values where an axisymmetric instability dominates, and the white region denotes where the whipping mode dominates. The solid line denotes the asymptotic law $s = I/Qh$, where we have used the measured value of the current to place the offset. Before reaching this asymptotic regime, the jet most likely curves upwards towards $s = 0$ at large $h$, for the reasons discussed in the previous section.

It is easy to rationalize qualitatively the sequence of instabilities observed in the video frame from this stability diagram: initially, the jet starts at a large radius with a small surface charge. In this regime, the jet is predominantly unstable to axisymmetric disturbances. However, in order to reach the asymptotic regime the path of the jet moves into the region of the diagram where whipping instabilities dominate. (Note that if the current were much smaller, the asymptotic regime would not overlap the whipping region of the stability diagram and the jet would not whip.)
We should remark that it is clear from the dynamics of Fig. 12 that nonlinear effects are also of paramount importance. The fact that the axisymmetric blobs saturate and do not cause the jet to fragment is a nonlinear effect, as is the interaction of these blobs with the whipping motion.

V. OPERATING DIAGRAMS

Theoretical operating diagrams are calculated by combining the stability analysis of an electrically forced jet with our experimental observation that the instabilities leading to electrospinning are convective in nature. Denote $A(t)$ the amplitude of a perturbation (of a given mode) to the jet and $\omega$ its corresponding growth rate. Then

$$\frac{\dot{A}}{A} = U \frac{d}{dz} \log (A) = \omega,$$

so that

$$A(z) = A(0) \exp \left( \int_0^z \frac{dz'}{U(z')} \frac{\omega(h(z'), E(z'), \sigma(z'))}{U(z')} \right),$$

where $U(z) = Q/(\pi h^2)$ is the advection velocity of the perturbation. (In general the advection velocity also includes the group velocity of the perturbation, which we neglect in these illustrative calculations.) Given the shape and charge density of a jet, this formula predicts both when and how the jet will become unstable. If the distance between the nozzle and the grounded plate is $d$, then the maximum amplitude of a perturbation as it is advected away from the nozzle is given by the amplification factor.
\[ \Gamma = \frac{A(d)}{A(0)} = \exp \left( \int_0^d dz' \pi \frac{h(z')^2 \omega(h(z'), E(z'), \sigma(z'))}{Q} \right). \quad (13) \]

Evaluating the integral requires using the properties of the jet (radius, charge density, etc.) as it thins from the nozzle.

An operating diagram summarizes how the amplification factor \( \Gamma \) depends on the external electric field and volume flow rate \( Q \) at a fixed set of fluid parameters. Such operating diagrams are given in Fig. 14 for glycerol jets, and Fig. 15 for PEO electrospraying jets. (These figures are reproduced from Ref. 14.) The diagrams show the contours of \( \Gamma \) for both the axisymmetric and whipping modes. The general shape of the operating diagram is insensitive to the precise contour chosen over the range of reasonable amplification factors. We generally choose \( \Gamma = 2\pi \) as a representative contour.

In principle, determining \( \Gamma \) requires solving for the steady-state jet profile and surface charge density for each external condition \((E, Q)\). As a first approximation in calculating all of these shapes, we have assumed that the surface charge density and the jet radius are related by the asymptotic formula \( \sigma = l h/Q \), and taken several types of approximations for the jet radius, such as (1) taking the jet radius as a constant and (2) taking the jet radius predicted by the asymptotic formulas of Eq. (6). Both procedures led to operating diagrams qualitatively and quantitatively similar to those shown in Fig. 15. We believe that the quantitative discrepancies between the theory and experiment are due to these approximations. In obtaining such good agreement with theory and experiment, we have further assumed the relations \( I \sim E \) and \( I \sim K \) found experimentally.

It is also of interest to understand how the operating diagrams change as a function of fluid parameters. Figure 16 shows operating diagrams at the same conditions as those in Fig. 15 except with viscosity ten times higher and lower respectively. Changing the viscosity leaves the onset threshold for the whipping instability unchanged, but substantially changes the onset for the varicose instability. The reason for this is that the viscous Rayleigh instability has a growth rate of order \( r_0 \sqrt{\rho/\eta} \) smaller than the inviscid Rayleigh instability. Most of the varicose instability occurs when the jet diameter is large enough that the growth rate is larger. For the less viscous jet we plot the contour \( \Gamma = e^{3\pi} \) for the varicose instability, because the \( \Gamma = e^{2\pi} \) contour is unstable throughout this parameter regime. Since our calculation of \( \Gamma \) depends on the distance between the plates like \( e^d \), this means that the jet will break up before it hits the bottom plate. The change in \( \Gamma \) implies the jet will break up about half-way between the plates (\( \sim 7 \text{ cm} \) from the top plate).

We can also study the effect of the conductivity of the fluid on the operating diagrams (Fig. 17). To do this, we assume (as the earlier experiments indicate) that the current through the jet is proportional to the conductivity (so that the surface charge on the jet increases linearly with the conductivity). Changing the conductivity of the fluid moves the onset thresholds for both instabilities. Higher conductivity leads to the suppression of the Rayleigh mode at lower field strengths and enhancement of the whipping instability. Lower conductivity enhances the varicose instability and suppresses the whipping instability. The mechanisms for these effects are that (as described in detail in part I) surface charge enhances the whipping mode and suppresses the varicose instability. Higher conductivity implies more surface charge on the jet.

These results have implications for the operating diagrams of electrospraying: Cloupeau and Prunet-Foch\textsuperscript{10,31} have measured the operating regimes for an electrospray (corresponding to low viscosity and high conductivity). Although quantitative comparisons with their results are not possible (because not all the parameters for the fluids used in their study are given), the operating diagram for a less viscous, highly conducting fluid bears resemblance to their measurements of where the “cone jet” mode of electrospraying exists. They identify the lower threshold of their stability diagram with the onset of the “cone jet” (i.e., the cessation of varicose instability), and the upper threshold as the point at which “multiple jets” appear. If we identify this latter threshold as the onset of whipping, the shape of our operating diagram is very similar to that reported by Cloupeau and Prunet-Foch. They also measure the dependence of their operating diagrams on liquid conductivity, and demonstrate that with increasing conductivity the critical flow rate at which the cone-jet mode sets in decreases. This is consistent with our findings here: higher conductivity fluids have a higher surface charge density. This stabilizes the Rayleigh mode, and allows a stable jet at a lower flow rate than otherwise possible. All of these qualitative relations merit further study.

VI. CONCLUSIONS
The research described in this article was conducted to develop a quantitative description of the mechanisms of electrospraying. Our experiments have demonstrated clear evidence that the essence of this phenomena is a whipping jet. The theory demonstrates the mechanism of the whipping: the charge density on the jet interacts with the external field to produce an instability. High surface charge densities tend to suppress the varicose instability, and enhance the whipping instability. It is the competition of these two factors that set the operating regime where electrospraying can occur. The quantitative agreement of the predicted operating diagrams with that observed experimentally indicates that the whipping mode predicted by linear stability analysis corresponds quantitatively with the bending of the jet observed experimentally, and which appears to be the primary mechanism underlying submicron fiber formation during electrospraying.

Since the surface charge (or the current passing through the jet) is the most important parameter for determining stability, it was necessary to understand how this charge is determined in experiments. The dependence of the current on the external field and conductivity differs from that typically observed in electrospraying experiments,\textsuperscript{17} where the current is independent of the voltage.

Eventually we hope that it will be possible to use ideas similar to those developed here to predict and correlate the
properties of the materials produced by electrospinning. For example, electrospinning produces a batch of uniform fibers whose diameter depends on the nozzle configuration and the fluid used. It would be extremely useful to extend the theoretical framework to predict the final fiber morphology as a function of experimental conditions.

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