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Electrospinning: Distribution of charges in liquid jets

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An analysis of the radial distribution of charges in liquid jets is presented. Two cases where considered: (1) when the charges are uniformly distributed through the jet cross-section but are allowed to concentrate at the jet surface with time; (2) when the charges reach a steady state where the Coulomb repulsion and Brownian mixing are counterbalanced keeping the charges inside the jet. Using the first model, we showed that the charge adsorption in nonpolar fluids occurs much faster than that in polar fluids. This provides the basis for the consideration of the second model applicable for polar liquids. We examined this case and found that a steady state does exist, but the concentration of charges is limited from above by a critical concentration inversely proportional to the square of the jet radius. It was shown that above this critical concentration, the charges should accumulate at the jet surface producing an infinitely large surface charge. Using this analysis, we suggest the classification of different regimes of electrospinning when the jets are mostly carrying the volume or surface charges. © *2011 American Institute of Physics*. [doi:10.1063/1.3671629]

I. INTRODUCTION

Recent progress in nanofiber formation by electrostatic spinning, known as electrospinning, has significantly advanced different fields of materials science and engineering. Electrospun nanofibers find applications as bio-materials for tissue engineering and scaffolds,[1–3] smart textiles,[4–6] and catalysts and many others.[7–10] Electrospinning significantly enriched the library of spinnable polymers including some polymers that cannot form fibers by conventional methods.[7–10]

In electrospinning, a polymer solution is electrically charged by high voltage to produce cone-like protuberances at the liquid-air interface. Increasing voltage further, one reaches a moment when the electrostatic force exceeds the surface tension, and a protuberance transforms into a spike emanating a jet.[7–11] This formation of tiny threads was discovered by George Mathias Bose in 1745. Since Boys' time, the effect was actively used to spin fine fibers.[12,13] Typically, the diameter of electrospun fibers is measured in hundreds of nanometers, and it is hard to reduce this number down to tenths of nanometers. The charge distribution in the jet is an important factor controlling the jet stability. In this paper, we analyze the mechanism of jet charging, leaving aside the hydrodynamic features of jet thinning that have been extensively discussed and reviewed recently.[8–14]

II. ORIGIN OF CHARGES IN ELECTRICALLY GENERATED JETS

The most popular model of charge carrying liquid is the Taylor–Melcher model of leaky dielectrics.[15,16] One calls the dielectric "leaky" because it permits some free charges to be present in the material when the field is turned on. In many cases, the origin of these charges is not specified: For example, if the liquid is placed between two electrodes, the charges of opposite sign can migrate from one electrode to the other generating a nonzero current. But there is no need to know the number of free charge carriers: Omh's law completely describes this current. One can find one more assumption in the model of leaky dielectrics: The total charge is often assumed zero.[15,16] This neutrality condition guarantees that the material stays non-charged if the field is turned off. The Taylor–Melcher phenomenological model is very convenient and explains many practically important flows, in particular, it suggests a scenario of electrohydrodynamic tip streaming and jetting.[17]

In electrospinning, depending on the electrode configuration, a jet of a polymer solution is formed either at a syringe needle or at the roller-electrode.[7,8,11] When a liquid is subject to a sufficiently strong electric field, the conditions at the liquid/electrode interface become favorable for the detachment of charges from the electrode. Depending on the electrode polarity, the liquid tends to strip off either metal ions or electrons. One can visually see that the produced nanofibers are charged: Even after few hours after spinning, the fibers can be easily manipulated by applying electric field.

These observations suggest that the free charges can be present in the jet and, because the jet surface does not touch any electrode, it is naturally to question where these charges go. There are two possible scenarios of charge distribution through the jet cross-section: The charges can sit at the jet surface or they can be present inside the jet being distributed through the jet cross-section. The first scenario of surface charged jets is most likely realized in non-polar solvents having a low dielectric constant. The second scenario of space charged jets is expected to occur in polar solvents having a high dielectric constant. In the following sections, we analyze these hypotheses based on the general model of liquid dielectrics carrying free charges.[18–20] We assume that the charge is initially distributed uniformly over the liquid volume and study how it decreases with time, provided that the charges are subject to the Coulomb repulsion. In this formulation, we restrict ourselves to the physical constraint that the charge

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density variation should follow the Gauss law of electrostatics. To examine the second scenario of space charged jets, we introduce the Brownian diffusion that opposes the Coulomb repulsion between charges and allows them to wonder randomly through the jet cross-section. Using this model, we obtain the conditions when the space charge through the jet cross-section is distributed almost uniformly.

III. DISTRIBUTION OF FREE CHARGES IN LIQUID JETS

In this section, we analyze the characteristic features of uniformly charged fluids. The charged jet is modeled as a straight liquid cylinder of radius R subject to an external electric field $\mathbf{E_0}$ directed parallel to the jet axis. The fluid velocity is constant, and it does not change with time. In the first moment, the density of a unipolar charge in the jet is set Q_0. We assume that the charges are repelled from the jet core moving toward the jet surface. We consider only time-dependent variation of the charge density $Q(t)$. For the description of the charge distribution in the jet, one can use the continuum model of charged fluids.[18–20] Within this model, the charge transport is described by the continuity equation :[19,20]

$$\frac{\partial Q}{\partial t} + \nabla \cdot (Q\mathbf{J}) = 0, \tag{1}$$

with the flux $\mathbf{J}$ taken in the form

$$\mathbf{J} = \mathbf{v} + \xi\mathbf{E} - D\nabla \ln Q, \tag{2}$$

where $\mathbf{v}$ is the fluid velocity, $\mathbf{E}$ is the electrostatic field inside the jet, $D = k_B T\xi/e$, is the diffusion coefficient, k_B is the Boltzmann constant, T is the temperature, e is the charge of a free carrier, and ξ is its mobility. The first term in Eq. (2) describes the advection of free carriers; the second term describes the forced movement of free carriers in electric field. The third term corresponds to the Brownian diffusion of free charges caused by the gradient of the chemical potential. It is assumed that the concentration of charges is small so that the chemical potential takes on the form of the chemical potential of an ideal gas. The charge-to-charge interactions are accounted for through local electric filed $\mathbf{E}$, which is dependent on the charge density. The third term in Eq. (2) plays no role for uniformly charged jets, hence in this section, it can be omitted. Assuming that the liquid is incompressible,

$$\nabla \cdot \mathbf{v} = 0, \tag{3}$$

and taking into account the Poisson equation for the electric field

$$\nabla \cdot \mathbf{E} = Q/\varepsilon_0\varepsilon, \tag{4}$$

where ε_0 is the permittivity of vacuum, ε is the dielectric constant (relative permittivity) of the liquid, we obtain from Eqs. (1) to (4),

$$\frac{\partial Q}{\partial t} + \frac{\xi}{\varepsilon_0\varepsilon}Q^2 = 0. \tag{5}$$

Equation (5) has the solution

$$Q(t) = \frac{Q_0}{1 + \dfrac{\xi Q_0 t}{\varepsilon_0\varepsilon}}. \tag{6}$$

Here Q_0 is the initial charge density. To find the charge collected at the jet surface at each moment of time, we substitute Eq. (6) in the Poisson Eq. (4). Accounting for the boundary condition for the axial component of the field, $\mathbf{E}_{||} = \mathbf{E_0}$, we see that the axial component of electric field in the jet is constant. However, the radial component of the field is not constant. This 2D electric field is a solution to the Poisson equation, $(1/r)d(rE_\perp)/dr = Q(t)/(\varepsilon_0\varepsilon)$. Integrating this equation, one obtains the radial component of electric field inside the jet as

$$E_\perp = \frac{Q(t)r}{2\varepsilon_0\varepsilon} \ (r < R). \tag{7}$$

Due to the conservation of charges, the radial component of the field outside the jet is written as

$$E_\perp = \frac{Q_0 R^2}{2\varepsilon_0 r} \ (r > R). \tag{8}$$

These two equations [Eqs. (7) and (8)] allow one to find the charge accumulated at the jet surface at any moment of time:

$$\sum = \varepsilon_0 E_\perp|_{r=R+0} - \varepsilon\varepsilon_0 E_\perp|_{r=R-0} = Q_0 R/2 - Q(t)R/2$$
$$= \frac{\xi Q_0^2 R t}{2\varepsilon_0\varepsilon}\left[1 + \frac{\xi Q_0 t}{\varepsilon_0\varepsilon}\right]^{-1}. \tag{9}$$

Equation (9) suggests that at the first moments of time, $t \to 0$, the charge concentrates at the surface with almost constant rate, $d\Sigma/dt \approx \xi Q_0^2 R/(2\varepsilon_0\varepsilon)$. As time tends to infinity, the surface charge density approaches its maximum value, $\Sigma_\infty = Q_0 R/2$. This limiting case implies that the charge that was initially distributed within the jet of length L, will be completely adsorbed on the jet surface, $2\pi R L \Sigma_\infty = \pi R^2 L Q_0$.

For the practical applications of Eqs. (6) and (9), it is convenient to express time t in terms of the jet flow rate, q, say measured in g/s. We take a piece of jet with fluid density ρ and radius R. The time needed for a particle entering the chosen piece of the jet to exit at the position $x = L$ is estimated as $t = L(\rho\pi R^2)/q$. Measuring length L in the jet radii, $L = aR$, we rewrite Eq. (6) as

$$Q_{exit} = \frac{Q_0}{1 + \dfrac{\xi Q_0 \rho}{\varepsilon_0\varepsilon}\dfrac{\pi a R^3}{q}}. \tag{10}$$

As follows from Eq. (10), the greater the flow rate, the longer the jet maintains its initial charge density Q_0. Decreasing the flow rate, one increases the probability for the charges to concentrate at the jet surface. Hence the volumetric charge density drops faster as the flow rate slows down. As a characteristic of the rate of charge adsorption at the jet surface, it is
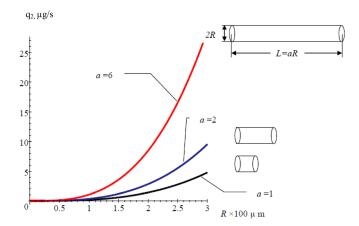
q_2, μg/s

FIG. 1. (Color online) The critical flow rate measured in micrograms per second as a function of the jet radius measured in hundreds of micromeers. The lines separate the regions where the charge density reduces twice at the jet length $L = aR$.

convenient to introduce flow rate q_2 at which the charge density reduces in two times, $Q_2 = Q_0/2$ when the given slice travels the distance $L = aR$. As follows from Eq. (1), this criterion reads:

$$q_2 = \frac{\pi \xi Q_0 \rho}{\varepsilon_0 \varepsilon} a R^3. \tag{11}$$

For example, taking the following parameters as the typical for electrospinning: $Q_0 = 1$ C m^{-3}, $\xi = 10^{-6}$ m^{2}V^{-1}s^{-1}, $\rho = 1000$ kg m^{-3}, $\varepsilon = 2$, we have for the factor

$$\frac{\pi \xi Q_0 \rho}{\varepsilon_0 \varepsilon} = 1.774 \cdot 10^8 \frac{kg}{s}. \tag{12}$$

In Fig. 1, we plot q_2 as a function of the jet radius measured in hundreds of micrometers. If the experimental flow rate corresponds to a region above any particular curve in Fig. 1, the charge density at the jet exit is expected to be smaller than Q_0 but greater than $Q_0/2$. Below these curves, the charge density is always smaller than $Q_0/2$.

As follows from Eq. (9), the rate of charge adsorption on the jet surface significantly depends on the dielectric constant of the liquid: the greater the dielectric constant, the smaller the adsorption rate is. In nonpolar liquids, where the dielectric constant is of the order of one, the repulsion of charges is strong, hence their rate of adsorption on the surface is fast. In polar liquids, where the dielectric constant is ten or hundred times greater than that of vacuum, the electric field is significantly screened by the solvent. Hence the charges weaker repel each other thus significantly decreasing their rate of adsorption on the jet surface.

IV. LIMITING BROWNIAN MIXING OF CHARGES IN LIQUID JETS

In the previous section, we ignored the effect of the Brownian diffusion assuming that the charges are distributed uniformly through the jet. On the other hand, the Brownian diffusion stabilizes the space charges preventing them to escape from the jet core to the surface. Therefore, it is instructive to examine the case when the charges are not uniformly distributed through the jet cross-section and the Brownian diffusion is important. In applications to nanofiber electrospinning where the liquid jets are very long, it is important to understand whether the space charge can reach a steady state when the Coulomb repulsion of charges is counterbalanced by the Brownian mixing.

In a steady state flow, the conservation of charges reads $\nabla \cdot (Q\mathbf{J}) = 0$. Assume that at the spatial scale comparable with the jet diameter, neither the jet diameter nor the charge change appreciably along the jet axis. Therefore, we can say that the axial component of the flux is constant, $\mathbf{J}_{\|} = \mathbf{v}_{\|} + \xi\mathbf{E}_{\|} = const$. The radial component of the flux is zero, $\mathbf{J}_r = 0 = \xi\mathbf{E}_r - Dd(\ln Q)/dr$. Introducing the field potential as $\mathbf{E}_r = -d\phi_-/dr$, one can integrate the resulting equation $[\xi d\phi_- + Dd(\ln Q)]/dr = 0$ to obtain the Boltzmann distribution for the charge density:

$$Q_V = ce\exp(-e\phi_-/kT), \tag{13}$$

where ϕ_- is the potential inside the liquid column, c is the charge concentration at the column axis, and e is the charge of the charge carrier. Substituting Eq. (13) into the Poisson Eq. (4), we obtain the Poisson-Boltzmann equation as

$$-\frac{1}{r}\frac{d}{dr}\left(r\frac{d\phi_-}{dr}\right) = \frac{ce}{\varepsilon_0 \varepsilon}\exp(-e\phi_-/kT). \tag{14}$$

Assuming that the air outside the jet is not charged, the external electric potential must satisfy the equation

$$\frac{1}{r}\frac{d}{dr}\left(r\frac{d\phi_+}{dr}\right) = 0. \tag{15}$$

The boundary conditions for Eqs. (14) and (15) are (i) the continuity of the potential and the normal component of displacement vector at the jet surface, $r = R$:

$$\phi_+ = \phi_-, \frac{d\phi_+}{dr} = \varepsilon\frac{d\phi_-}{dr}, \tag{16}$$

(ii) the boundary condition for the potentials at the jet axis, and (iii) at infinity. Because the reference potential can be arbitrarily chosen, we set the zero potential at the jet axis,

$$\phi_-(0) = 0. \tag{17}$$

The potential at infinity must behave logarithmically as follows from the Gauss law,

$$\phi_+(r) \rightarrow \ln r, \quad r \rightarrow \infty. \tag{18}$$

Thus, Eqs. (14) to (18) constitute the mathematical model of charge distribution in the jet. It is convenient to introduce the dimensionless potential and spatial variable as

$$-\phi_\pm \rightarrow \Phi_\pm kT/e, \quad r = \sqrt{kT\varepsilon\varepsilon_0/ce^2}X = l_D X. \tag{19}$$

In other words, we measure the distances in the Debye lengths, l_D. With the new unknown and variable, the equation for the internal field takes the form

$$\frac{1}{X}\frac{d}{dX}\left(X\frac{d\Phi_-}{dX}\right) = \exp(\Phi_-). \tag{20}$$

The outside field is described by the Laplace Eq. (15). As shown in the Appendix, the potential inside the jet takes the form

$$\Phi_- = -\ln\left(\left(r/l_D\sqrt{8}\right)^2 - 1\right)^2.$$ (21)

The external potential is described as

$$\Phi_+ = D\ln(r/R) + const.$$

$$D = -4\varepsilon\left(\frac{R}{l_D\sqrt{8}}\right)^2 \bigg/ \left[\left(\frac{R}{l_D\sqrt{8}}\right)^2 - 1\right].$$ (22)

And finally, the charge density distribution takes the following form[21]

$$Q_V = ce\left(1 - \frac{r^2}{8l_D^2}\right)^{-2}.$$ (23)

Concentration of the charges at the column axis is still unknown. We can express it through the average charge density Q (number of charges per unit volume) as

$$Q = \frac{2}{R^2}\int_0^R rQ_V(r)dr = \frac{ce}{1 - R^2/8l_D^2}, \quad \text{or}$$

$$c = \frac{(Q/e)}{1 + R^2eQ/(8kT\varepsilon\varepsilon_0)}.$$ (24)

In Fig. 2, we plot the concentration of charges as a function of jet radius and the distribution of charges in the jet. As seen, the density profile is flattened as the jet radius decreases. If the jet radius is smaller than the Debye length (submicrometer jets in the example shown in Fig. 2), the density is almost uniform over the jet cross-section. This uniformity is a manifestation of intensive interactions between the surface and core charges and rigorous Brownian mixing. As the radius increases and becomes comparable and greater than the Debye length, the screening effect starts to play a

role leading to the weakened interactions between the core and surface charges. The charges are pushed to the surface and concentrate there.

An analysis of Eqs.(23) and (24) reveals very interesting criterion of the applicability of the model with spatially distributed charges: to make this model work the Debye length cannot be smaller than

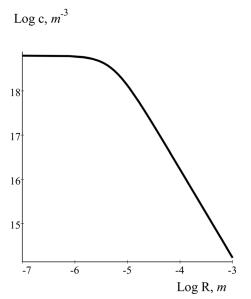$$l_D = \sqrt{kT\varepsilon\varepsilon_0/ce^2} > \sqrt{8}R.$$ (25)

As this criterion fails, the charge density at the jet surface will tend to infinity. The Poisson-Boltzmann model cannot predict what will happen with the jet in this limiting case. One can propose at least two scenarios: the Coulomb explosion and run-off charge from the jet surface into surrounding gas. The analysis of these cases is beyond the scope of this paper.
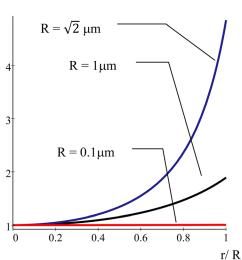
Thus two models lead to the same conclusion: the jets formed from polar and non-polar liquids will tend to accumulate the charges at the jet surface. If the jet radius is greater than $R > \sqrt{kT\varepsilon\varepsilon_0/8ce^2}$, one can say that the jet will carry the charge mostly at its surface. Writing criterion (25) in terms of the charge density,

$$ce < kT\varepsilon\varepsilon_0/\left(8R^2e\right),$$ (26)

we can consider this condition as a criterion for the formation of jets with spatially distributed charges. For example, for an oil-based jet ($\varepsilon = 2$) that is formed at room temperature T = 300 K, criterion (26) suggests that the jet with the radius R = 1 μm will carry charges inside the jet core if the charge density will be smaller than 0.06 C/m^3 corresponding to the charge concentration smaller than $c = 3.5 \cdot 10^{17}$ m^{-3}. If the charge concentration is greater than this value, the jet can be considered surface charged.

One expects that the charge will be distributed almost uniformly over the jet cross-section if the jet radius is much smaller than the Debye length.

FIG. 2. (Color online) (a) Concentration of univalent charges at the jet axis as a function of the jet radius for the average charge density Q = 1 C/m^3 and the jet dielectric constant $\varepsilon = 2$; (b) the charge distribution in jets with different radii.

V. CONCLUSION

In this paper, we analyze the radial distribution of charges in jets supported by an external electric field. The field is directed along the jet axis, but the charges in the jet are allowed to move in the cross-section plane. Two cases where considered: (1) in the first case, the charges are uniformly distributed through the jet cross-section but move to the jet surface and concentrate there with time; (2) in the second case, the charge distribution is assumed time independent. We showed that the charge adsorption on the surfaces of nonpolar jets occurs much faster than that in polar jets. This effect is explained by significant charge screening in polar liquids leading to a weakened repulsion of charges. This weakening effect poses a natural question on whether the charge distribution could reach a steady state when the Brownian mixing of charges will be sufficient to keep the charges inside the jet. We examined this second model and found that a steady state does exist, but the concentration of charges is limited from above by the critical value $c_{cr} = kT\varepsilon\varepsilon_0/(8R^2 e^2)$. Above this critical concentration, the charges move to the jet surface. Thus the critical charge density separates two different regimes of jet formation. If $c < c_{cr}$, one expects to have the jets carrying the charges in the core. If $c > c_{cr}$, the charges will be mostly concentrated at the jet surface. The Poisson-Boltzmann model cannot predict what will happen with the jet when the surface charge tends to infinity. One can propose at least two scenarios: the Coulomb explosion and run-off charge from the jet surface into surrounding gas. The analysis of these cases deserves a special attention.

We believe that these notes provide new insight on the charging process of liquid jets and will be useful for the analysis of electrospinning process.

APPENDIX

To find the solution to Eq. (17), we put the substitution

$$u = \Phi_- + 2\ln X, \varsigma = \ln X.$$

Then Eq. (17) is rewritten as

$$\frac{d^2 u}{d\varsigma^2} = e^u. \tag{A1}$$

Rewriting Eq. (A1) as a dynamic system

$$\frac{du}{d\varsigma} = v \tag{A2}$$

$$\frac{dv}{d\varsigma} = e^u \tag{A3}$$

we find the first integral as

$$v^2/2 = e^u + C. \tag{A4}$$

Demanding the finiteness of the field at the column axis, $x = 0$, we obtain the constant C as

$$C = 2. \tag{A5}$$

Another integration gives the solution in the form (which was obtained by a different method by Weymann[21])

$$\Phi_- = \ln\frac{8G^2}{(G^2 X^2 - 1)^2}, \tag{A6}$$

with a constant G. The outside field can be found by solving the Laplace equation to give

$$\Phi_+ = D\ln(X/X_0) + C_1. \tag{A7}$$

Here $X_0 = R/l_D$ is the column radius measured in the Debye lengths. The continuity of the displacement vector gives the relation between the constants D and G as

$$\varepsilon\frac{d\Phi_-}{dX} = \frac{D}{X} \quad \text{as } X = X_0, \tag{A8}$$

or, substituting (A6), one obtains

$$D = -\frac{4\varepsilon X_0^2 G^2}{X_0^2 G^2 - 1}. \tag{A9}$$

In each potential, the integration constants G and c can be specified by choosing the reference potentials. Requiring that the internal potential is equal to zero at the jet axis, one has from Eq. (A6): $G^2 = 1/8$. The second continuity condition for the potential at $X = X_0$ gives

$$C_1 = -2\ln\left(\left(X_0/\sqrt{8}\right)^2 - 1\right). \tag{A10}$$

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