Textile Progress
Vol. 41, No. 2, 2009, 59–140

Physical principles of electrospinning (Electrospinning as a nano-scale technology of the twenty-first century)

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(*Received 3 March 2009; final version received 7 April 2009*)

The history of electrospinning is briefly introduced at the beginning of the article. The fundaments of the process are then analysed physically to be translated into a successful technology. Self-organisation of fluid in electrospinning is perceived as a consequence of various instabilities, based on electrohydrodynamics and, thus, highlighted as a key factor, theorising the subject successfully to elevate it to a highly productive technology to manufacture nano-scale materials. The main physical principle of the self-organisation is appearance of unstable tiny capillary waves on liquid surfaces, either on a free liquid surface or on that confined in a capillary, which is influenced by external fields. The jet path is described, as well as its possible control, by special collectors and spinning electrodes. Two electrospinning variants, i.e. melt and core–shell electrospinning, are discussed in detail. Two scarcely referred exceptional features of electrospinning, electric wind and accompanying irradiations, are introduced in in-depth detail. Lastly, care is taken over the quality of polymeric solutions for electrospinning from the standpoint of Hansen solubility parameters and entanglements among polymeric chains.

Keywords: electrospinning; electrospinning variants; nanofibres; liquid jet; self-organisation; dielectric diffusion; radiation; polymer solution

7. Exceptional features of electrospinning

Two exceptional features of electrospinning are covered by this section. The first of them is an ion-driven electric wind that influences a jet path in a spinning zone that, undoubtedly, assists in solution evaporation and jet discharge. The last exceptional features are various kinds of radiations accompanying jet creation and nanofibre formation.

7.1 Electric wind in electrospinning

Electrospinning is an enormously versatile process in which dynamics of both polymeric jets and the ambient atmospheric gas/air are involved. Inside a spinning zone, i.e. in the space between a spinning electrode and a collector, a strong electrostatic field acts whose strength reaches its local maxima in the vicinity of tiny charged bodies, e.g. needle electrodes, tiny liquid jets or droplets. Ionisation of ambient gas/air and ion acceleration appearing in the zones of high field strength results in gas fluxes with the power of a wind. So, this effect will now be referred to as 'electric wind' [91]. Since electrospinning jets and their whipping parts culminate in nanofibres with enormously low mass but immense surface area, the flux of the ambient gas in the spinner can significantly affect the jet path. The electric wind partially sways the assembling process of nanofibres on a collector, and hence is an important factor from a technological point of view. Surprisingly, the electric wind has being overlooked in works on electrospinning.

A vivid idea about real electric wind power can be presented through Brown's patent [92] introducing his invention of an electro-kinetic apparatus generating a reactive draught aroused by an electric field in an asymmetric capacitor. This phenomenon is also known as the Bielefeld–Brown effect and the Brown's apparatus is frequently entitled 'lifter'. The

Figure 40. Flying lifter.

lifter is in essence a reactive engine that works in the air of normal pressure and temperature and is strong enough to lift solid bodies against the Earth attraction, as shown in Figure 40. Lifters, as asymmetric condensers, are usually designed with one of two electrodes much more slender, compared to the last one, commonly made by a tiny wire, usually of a plate shape. The tiny wire electrode concentrates the electrostatic field that causes air ionisation in the vicinity of these slender bodies. Created ions depending on their charge sign are attracted either by the wire with which they immediately collide, or they drag along a long distance to the last plate-like electrode. During this long path, the ions are accelerated by the electric field, and hence they transmit their momentum to ambient gas molecules causing their organised wind-like motion. Electrospinners, particularly the needle ones, are also asymmetric capacitors with quite different surface areas of spinning electrodes and collectors, and hence the electric wind is generated by them too.

Unfortunately, the Bielefeld–Brown effect is only sparsely referred to. One of the exceptions is Canning et al.'s work [93] in which the formula is derived for a lifter drag force F:

$$F = \frac{2dnmI}{e}, \tag{7.1}$$

where F is a total reactive force caused by the lifter wind, d is the distance between asymmetric electrodes, n is a number of collisions of one particle in unit time under normal pressure and temperature. In air at atmospheric pressure, there are 10^{10} collisions per second. Parameter m denotes an ion mass (the ions are mostly ionised nitrogen molecules, the most plentiful element in the air), commonly of the value 4.7×10^{-26} kg, and I represents electric current realised by the ionic flux. The ion charge e is supposed to be the elementary one, i.e. 1.6×10^{-19} C. Canning et al. evaluated the reactive force F for a lifter with the distance between electrodes $d = 7$ cm and the current $I = 3.5$ mA as $F = 1.44$ N.

Analogous relation to Equation (7.1) has been introduced by Primas [94]:

$$F = \frac{dI}{k}, \tag{7.2}$$

where parameter k is ion mobility. Ion mobility depends on a lot of parameters such as pressure, temperature, chemical nature of a gas, etc. For a positive ion, its mobility has the value $k = 2.1 \times 10^{-4}$ m^2 V^{-1} s^{-1}. Relation (7.2) provides an estimate of the lifter reactive force F slightly smaller than the Canning's formula for the same values of d and I, $F = 1.2$ N. Experimental measurements of the force value were carried out by Malik [95]. Undoubtedly, both estimates and also measurements give a sufficiently big force to significantly affect a path of an electrospinning jet in a spinning zone.

Using ion mobility, k, speed, v_{d}, of the electric wind can also be evaluated, since k is the proportionality constant between v_{d} and a field strength E. The field strength can be estimated from the rate of a voltage difference U between the electrodes and their mutual distance d. Hence, Equation (7.3) holds v_{d} introduced by Akopjan et al. [96]:

$$v_{\mathrm{d}} = k\frac{U}{d}. \tag{7.3}$$

The drift ion velocity in a spinner with the voltage difference 10 kV and the distance 7 cm between the spinning electrode and the collector is estimated using Equation (7.3) as a value $v_{\mathrm{d}} = 2.1 \times 10^{-4}[\mathrm{m}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}]\ 10^4[\mathrm{V}]/0.07[\mathrm{m}] = 30[\mathrm{m/s}]$. More details about the average ion velocity in external electrostatic field can also be found in Lysenko [97]. The velocity of the electric wind is hence quite comparable with the velocity of a jet motion, vide Reneker and Yarin [4].

The ionisation inside lifters as well as inside spinning zones of electrospinners is caused predominantly by collisions of accelerated ions with neutral gas particles, see Petrzilka and Šafrata [98] and Grigor'ev and Sinkevich [99]. The gas/air at vicinities of charged slender bodies in a spinning zone may be considered to be in a stage just before a massive electric discharge accompanying avalanches of newly created ions. However, the field strength $\vec{E}$ sizably decays in electrospinners with the increasing distance from sharp edges of needle tips or jets. Consequently, a self-employed discharge bridging the spinning electrode with the collector does not appear as a rule. Petrzilka claims that ionisation in air can be caused both by collisions of electrons and positive ions with electro-neutral gas molecules. Free electrons in the lower atmosphere are generated by natural Earths and cosmic radiations at a rate of 10 particles in cubic centimeter per second, see Stakhanov [100], and recombine in 10 ns with neutral air atoms and molecules to form negative ions. As a result, the natural voluminous particle density of negative ions near the Earth surface is from 500 to 800 particles per cubic centimeter, as introduced in Grigor'ev and Sinkevich [99]. This concentration is 7 to 12 times higher than that of the positive ions. Higher concentration of negative ions can be demonstrated using the following classic experiment.

Imagine an experimental apparatus that consits of sharp needles, each of which is connected with one of two poles of a high-voltage source. Massive air ionisation will appear in the needle tip vicinity due to high field strength in this area. The positive polarisation of the needle is assumed initially. Negative ions collide immediately with the positive needle as they are attracted by Coulombic forces. In this way, ions transmit most of their momentum to the needle, and only a small percentage of it is transferred to air molecules. As has been described previously, the negative ions recombine with positive charges on the target. However, positive ions are repelled from the positively charged needle and accelerated on a relatively long distance to high velocity and momentum. This momentum is transmitted to the surrounding gas molecules via collisions, thus causing their flux. By analogy, similar events proceed in the vicinity of a negatively charged needle. So, this is the mechanism by which the electric wind is initialised. Since the initial concentration of negative ions in lower atmosphere of Earth is higher than the concentration of negative ones, the electric wind is stronger close to the negatively charged needle. The mechanism of this wind creation is graphically described in Figure 41. Details can be found in Kozlov and Solovyov's [101] work.

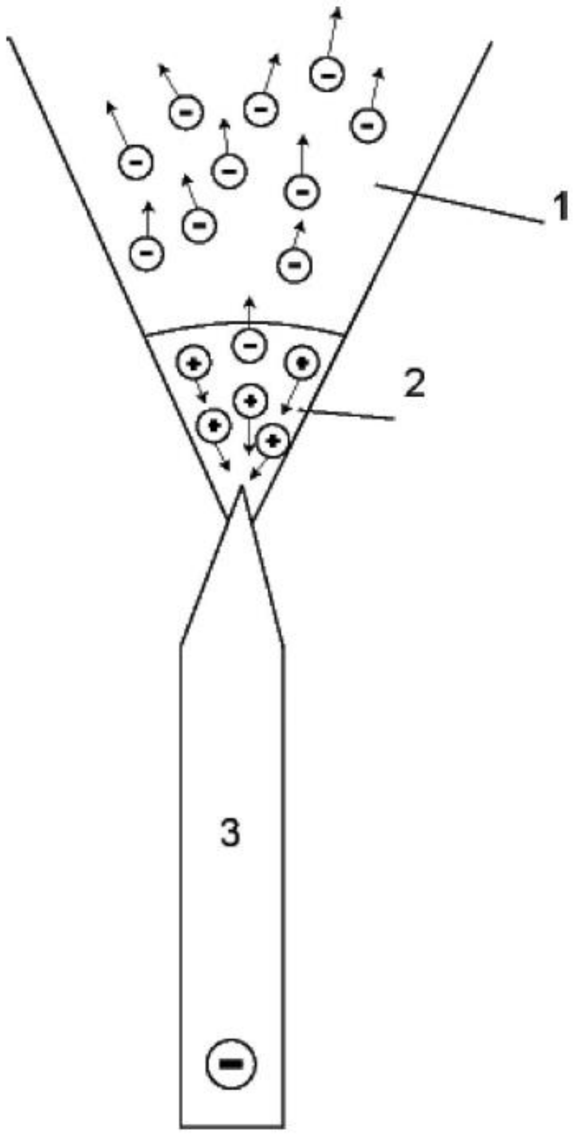

Figure 41. Emergence of the electric wind: in the vicinity of a point electrode (3), positive as well as negative ions are created inside the so-called bipolar area (2). The ions with charge of opposite nature to that of the point recombine with it. Remaining ions are repelled by the point and accelerated away, as shown by (1), called unipolar area.

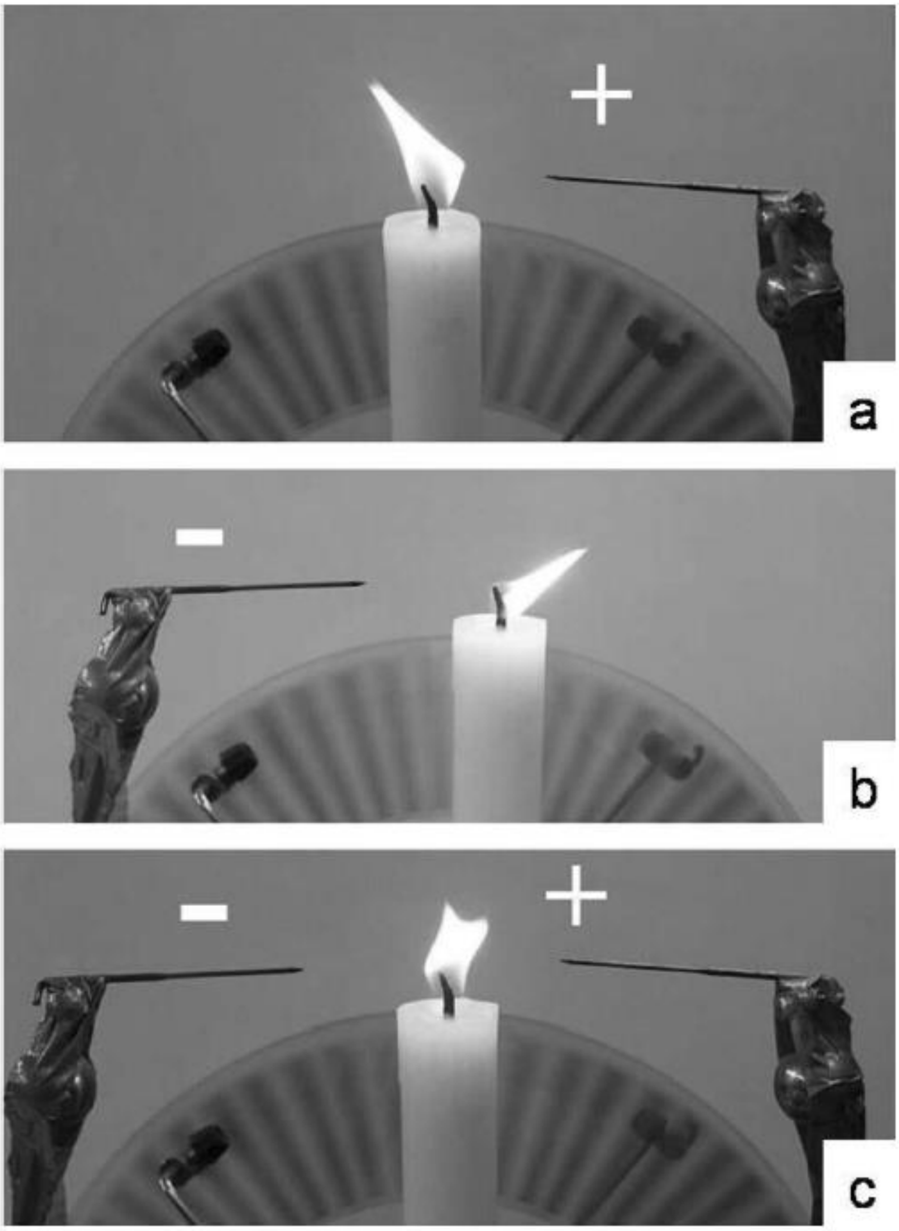

Figure 42. An inflection of a candle flame caused by electric wind: wind direction depends on its polarity: (a) Electric wind generated by a positively charged point electrode, (b) electric wind caused by a negatively charged point, and (c) the flame inflection proves that the negatively charged wind prevails the positive one at the same distance from point electrodes.

A classic experiment can demonstrate the power of the just-described electric winds caused by ions of different signs. As a high-voltage source for the experiment, the Wimshurst electrostatic machine [102] was used, ensuring nearly the same absolute potential values on both negatively and positively charged needles. A flame of a candle was employed as a detector of the electric wind strength. The experiment is shown in Figure 42 in three parts. The first of them, i.e. Figure 42a, depicts the flame inflection caused by the electric wind flowing from the negative needle electrode. The next figure, Figure 42b, depicts the effect of the wind from the positive needle, while Figure 42c depicts the simultaneous action of electric winds caused by both the needle electrodes. It is obvious from the last figure part that the negative wind prevails the same distance from both needles, as supposed to the previously introduced arguments.

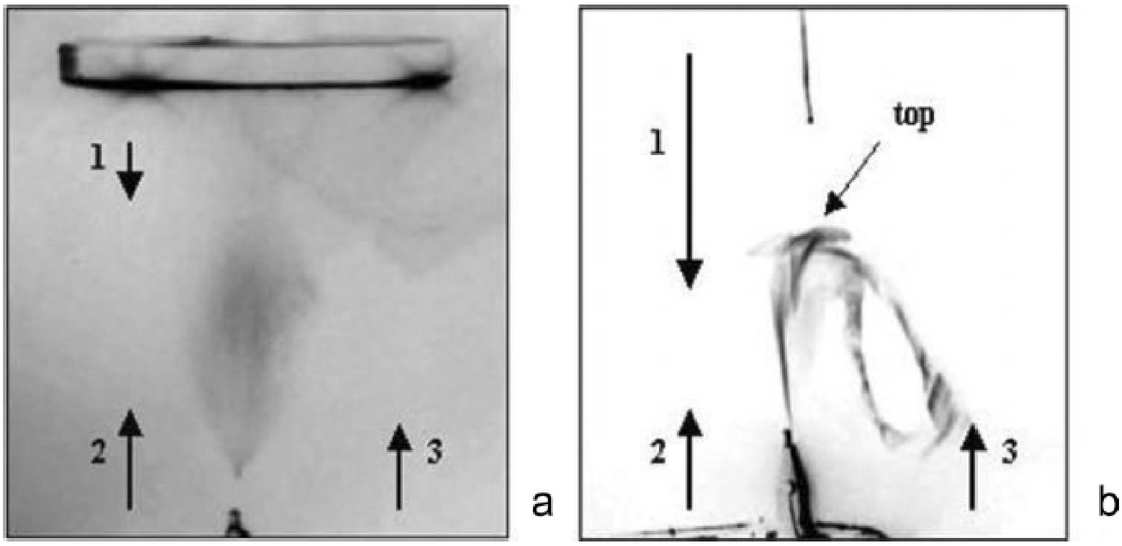

Figure 43. Comparison of jet path in two needle-spinners of various designs. (a) Electrospinner with a plate collector, (b) electrospinner with a needle-shaped collector. Spinning electrodes in both the cases are positively charged, while collectors are negative. The distance between the needle and collector are in both cases the same. Electric wind (1) caused by collectors is much stronger from the point collector than from the plate one. Electric winds (1) and (2) and electrostatic forces (3), in this case, compensate each other close to the middle of the spinning zone, where downward oriented wind (1) prevails and carries the jet back towards the spinning electrode.

Figure 43 illustrates electrospinning in two needle spinners that have collectors of different shapes. The first electrospinner, Figure 43a, is equipped with a plate collector, while the last one, Figure 43b, has a point/needle-shaped collector. In both the cases, the spinning needle electrodes are positively charged. The jet path is quite different inside the spinning zones of these two apparatuses. In the electrospinner with plate collector, the straight direction of the wind from the positive needle to the negative collector simply predominates. The negative wind does not prevail because the plate-like collector does not create sufficiently high field strength in its vicinity to create new ion pairs. The fibres are laid onto the collector since the wind does not have sufficient power to vanquish the Coulombic attraction between the jet and collector.

On the other hand, the jet in the spinner layout with needle-against-point collector shows a parabolic path during its flight. In the upward journey of the parabolic trajectory, the charge of the jet is high enough, and attractive Coulombic forces predominate over the electric wind. This is true for the first part of the jet in Figure 43b, where the jet is nearly mono-filamentous. The counter-current of the negative electric wind starts to balance electrostatic forces wherever the jet starts to whip/coil since its specific surface area increases accompanied by the appearance of the jet's discharge.

The jet discharge can be evaluated by several considerations and experimental evidences. The first of them is based on the observation of a solvent evaporation. Polymeric nanofibres, electrospun from polymeric solutions generally reach a collector in an almost perfectly dried state. More than 90% of a solvent evaporates from a jet during its path from a spinning electrode to a collector. One can assume the same fraction of an original net-charge, as the fraction of evaporated solvent, escapes from the jet too. The reason for the solvent evaporation due to the Kelvin law has been discussed in sub-section 4.2, while an experimental evidence of the charge decrease in the jet is introduced here.

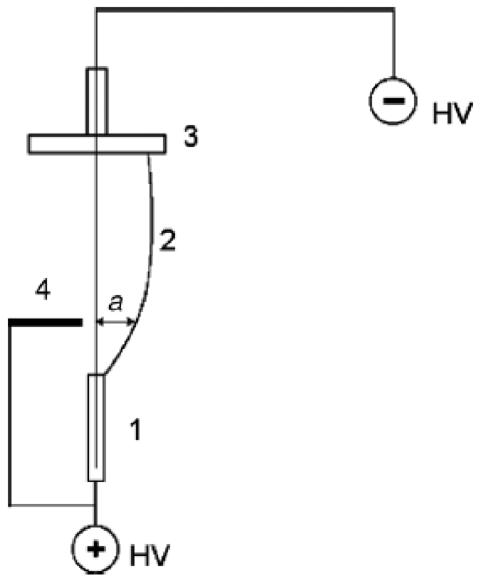

Figure 44. Diagram of the device with the auxiliary electrode, which measured the deflection of the jet path, as sketched in 45: (1) denotes a needle spinning electrode, (2) is a jet, (3) a collector, (4) auxiliary electrode, and parameter a is the deflection of the jet.

The discharge from the jet was also experimentally investigated using equipment designed by Chvojka [103] and depicted in Figure 44. The principle of the experiment consists in observation of the influence of the auxiliary electrode on the jet path. The auxiliary electrode has a shape of a small sphere movable along the jet path. As the spinning electrode was used, a hypodermic needle directly connected to a syringe. The jet path was recorded using the movie camera PANASONIC NV-CS120. The deviations of the jet from its straightforward path were evaluated from individual pictures of the record using the image analyses system LUCIA, see Figure 45. It is evident from the diagram that jet deviation varies along its path to the collector. It is obvious, therefore, that the repulsive force between the liquid jet and the ball-shaped auxiliary electrode are much stronger in the initial jet path than later in the area close to the collector.

Returning to the experiment with the spinner layout with needle-against-point, the equilibrium between electric wind and Coulombic forces sets in the summit of the parabolic jet trajectory (Figure 43b). During the subsequent part of the jet's journey, the electric charge in the jet is minimal since it escaped with evaporating solvent, and also neutralised by the oppositely charged ions of the electric wind. The strong attraction of oppositely charged particles by electrospinning jets will also be discussed in sub-section 7.2 while dealing with Radon daughter isotopes. The coiling jet creates a sort of 'sail' as a consequence of its elongation and the increment of its specific surface area. Accordingly, the jet creates sufficiently large surface area to which the electric wind can transfer its momentum. Therefore, the dry fibres in Figure 43b are carried down by the electric wind without any chance to be trapped by the point collector. From the given experiment, it is possible to enunciate an empirical rule for the design of any electrospinner: the ratio of minimum dimensions of spinning electrode to collector must not be lower than 1:7–1:12, see Chvojka [103], to avoid many difficulties affecting fibre collection onto a collector. On the other hand, this effect can be utilised in some efforts to extricate the electrospinning jets and nanofibres from a spinning zone and to manipulate them by forces that are not electrostatic in nature. This method can find some application, especially in medicine.

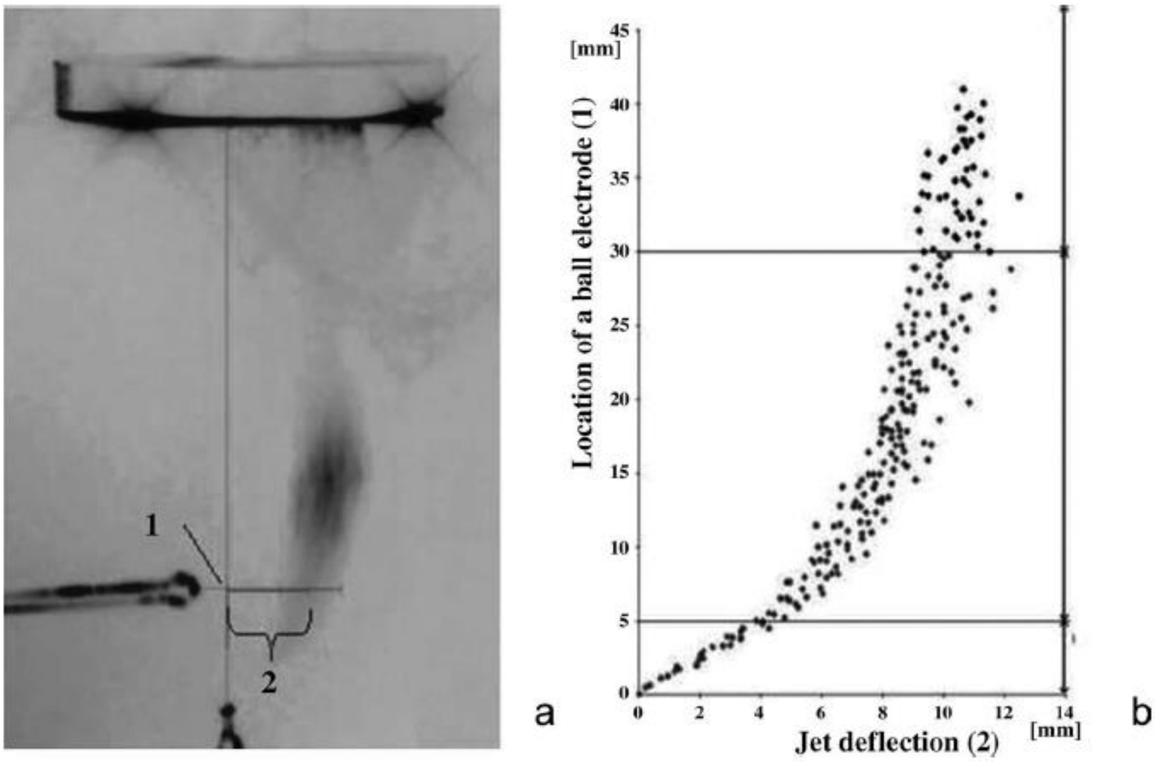

Figure 45. (a) Deflection of a jet path (2), caused by an auxiliary electrode (1). (b) The deflection depends on the position of the auxiliary electrode in the spinning zone.

In fact, it is both worthwhile and noteworthy to underline that the studies of electric wind strongly supported the idea of dielectric diffusion, as has been dealt with before in sub-section 3.7. The thorough and quite intriguing comprehensive study of electric wind does not only consolidate the concept of dielectric diffusion strongly, but also, remarkably, helps to reconcile and confirm the strong influence of influencing factors, like symmetry and relative orientation of the capacitor plates, as proposed by Sarkar [104] in his doctoral thesis on 'Physical Principles of Electrospinning'. The change of the electrode geometry in electrospinners can heavily influence a local distribution of field strength, E, and consequently it affects the electric wind and the jet path. However, the experimental procedure to study the diffusion by observing electric wind and radiation, as presented below, could help in effective understanding of the phenomenon from the standpoint of quantum physics, thus enabling more efficient, accurate and sophisticated instrumentation to handle the technology.