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ELECTROHYDRODYNAMIC SPRAYING FUNCTIONING MODES: A CRITICAL REVIEW

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Abstract—The multiplicity of electrohydrodynamic spraying functioning modes has been and still continues to be, a cause of misunderstanding. The modes observed in air (and observable also in vacuum) are reviewed and several results are compared with those of earlier work. For regimes other than dripping, a terminology is proposed, the main modes being designated: cone-jet, multijet, microdripping, simple jet, ramified jet (including fan configuration) and spindle (including harmonic spraying).

1. INTRODUCTION

The terms "electrospray" or "electrostatic spraying" are ambiguous because they are currently used to designate at least two types of phenomena:

— the cases in which a liquid is sprayed by pneumatic or other means and in which the application of an electric field has only the effect of charging the drops (Law, 1983) and decreasing slightly their average size (Savage and Hieftje, 1978),
— the cases in which the electric field itself is the cause of the spraying of a liquid in fine droplets (Zeleny, 1915, 1917).

The present article concerns the latter cases. For this reason, the designation "electrohydrodynamic" (EHD) is used in the title, despite the fact that we have ourselves used the term "electrostatic" in other publications and that it is not always possible to make a very clear distinction between the two types of phenomena mentioned above.

In the ambient air, the continuous production of droplets by the EHD process is generally observed by applying a potential difference of several thousand volts between a plate and the end of a capillary supplied with liquid. The droplets emitted are charged. They may be neutralized if necessary by different methods (Cloupeau, 1994). Their size varies, depending on the conditions, from the millimeter to the submicron range.

In vacuum the electric field is not limited by the appearance of corona discharges. Consequently, liquid metals, which have a very high surface tension, can be atomized. With such liquids of very high conducivity, it is possible to obtain electric currents higher than in air and to produce extremely fine droplets or even atomic ions. This latter phenomenon will not be considered here.

In the course of his outstanding pioneering work, Zeleny (1915, 1917) had already observed several functioning modes leading to the production of aerosols with very different characteristics. Since the rediscovery of these phenomena by Vonnegut and Neubauer in 1952, considerable theoretical and experimental work have been accomplished (cf. Bailey, 1988) and other modes have been revealed. They have however not always been identified as such.

The multiplicity of these modes has been and still continues to be the source of misunderstandings in the interpretation and comparison of certain results. It is thus useful to review the characteristics of the main modes and their variants. The present article summarizes and updates the observations presented in earlier publications (Cloupeau and Prunet-Foch, 1989, 1990) in which we proposed a classification of modes that we have ourselves observed in air at atmospheric pressure.

As an example, various works of other authors are cited with regard to each of these modes. Some correspond to tests conducted in vacuum, because all the modes obtained in ambient air can also be obtained in vacuum with liquids at high boiling temperature.

2. EXPERIMENTAL

Our experiments were conducted in air at atmospheric pressure and at a temperature of about 20°C. In addition, several tests were carried out with the dielectric strength of the ambient air increased by the addition of CO_2 or freon 12, or lowered by the addition of a rare gas.

The spraying phenomena remain the same whatever the polarity of the spray head, as long as there is no corona discharge. Like many other authors, we have observed that spraying is less easily disturbed by corona discharges when the polarity of the spray head is positive; our experiments have thus been carried out with this polarity.

Most of the tests were conducted with stainless steel capillaries shown in Fig. 1, placed vertically to spray downward. This arrangement is preferable to the horizontal position for the study of the different modes, because it prevents excessive wetting effects at low voltages. The external surface of the capillaries was, in some cases, covered with a non-wetting product such as teflon. In every case, the liquid wetted the entire outlet section.

A potential difference U, varying from 0 to 20 kV, was applied between the capillary and a counterelectrode which could be of any form.

The capillaries were connected either to a special syringe pump, imposing known, perfectly constant volume flow rates, or to a tank supplying liquid under constant pressure.

The supply at constant pressure sometimes favours the stability of the spray. However, the flow rate depends on the applied pressure and pressure losses between the tank and the end of the capillary, which themselves are dependent on the liquid chosen and on its temperature. This volume flow rate may also depend on the applied voltage, since the electrostatic pressure on the meniscus produces a suction effect. The flow rate consequently must be measured with each test; in addition, precise measurements of low flow rates by conventional means require much time. In most of our tests, the supply of liquid was thus provided at a constant volume flow rate.

Water and various organic products were used in the pure state or in mixtures.

The variation limits of the other main parameters were the following:

— conductivity of liquids, K: 10^{-9}–10^{-1} S m^{-1} (i.e. resistivity of 10^{11}–10^{3} Ω cm);
— surface tension, γ: 0.022–0.073 N m^{-1};
— viscosity, μ: about 0.4–1500 mPa s;
— flow rate, $\dot{v}$: 10^{-3}–10 mm^3 s^{-1}.

These limits indicate what are considered here to be "low" and "high" values of K, γ, μ and $\dot{v}$.

The phenomena were observed by means of microscopes characterized by a large working distance and a maximum magnification of 1000. Lighting was either continuous or pulsed.

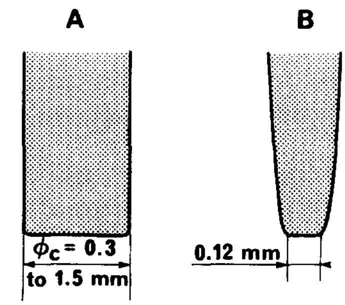


Fig. 1. Types of capillary.

Separate instant photographs were taken with an illumination time shorter than or equal to about 20 ns.

For the study of pulsating modes, the growth of the meniscus at the beginning of the cycle generated a photoelectric signal by interrupting a laser beam. The flashes were triggered with an adjustable delay in relation to this signal. This made it possible to reconstitute a complete cycle of the emission process with a series of snapshots taken over a long period.

Droplets sizes were determined by direct measurements or obtained from the distribution of the scattered light of a laser beam.

The frequency f of droplet (or droplet train) production was determined by illuminating the droplets with a laser beam downstream of their point of formation; the diffused light was received by a photomultiplier and the resulting pulses were recorded on a storage oscilloscope.

Other observation and measurement devices have been described in an earlier article (Cloupeau and Prunet-Foch, 1989).

3. DRIPPING MODE

If, in the absence of an electric field, the liquid flows drop by drop at the outlet of the capillary, the application of a d.c. voltage between the capillary and the plate causes a rise in the emission frequency and a reduction in drop size (Fig. 2). This has a twofold cause:

(1) attraction of liquid towards plate due to the action of electric field on the charges located at the end of the hanging drop (Ogata *et al.*, 1976; Takamatsu *et al.*, 1981)

(2) apparent reduction in the surface tension of the liquid due to the fact that electric charges on the surface create an electrostatic pressure opposite to the capillary pressure.* This electrostatic pressure is at its maximum at the end of the pendent drop but it is also exerted in the drop detachment zone. It would appear that in several theoretical studies this has not been taken into account in the calculation of the force retaining the drop on the capillary, whereas it is obviously taken into account for calculating the profile of the electrified pendent drops (Borzabadi and Bailey, 1978).

In the dripping mode (or field enhanced dripping), the emission of drops may occur at regular time intervals, without the creation of satellites, so that all the drops have the same size. Such is the case in the example of Fig. 2 relating to diethyl sebacate flowing from a capillary type B. This figure also gives, for the two points A and B of the curve, the forms observed:

— when the meniscus is in its highest position;
— when the drop detaches.

In general, drop diameter remains greater than that of the capillary, thus leading to the emission of large drops at low frequencies. For a given flow rate, the maximum emission frequency may increase (and the minimum drop diameter decrease) significantly if the diameter of the capillary is reduced. Thus, for water and a flow of 4 $mm^3\,s^{-1}$, the maximum frequency observed with a type-A capillary, with $\phi_c = 0.5$ mm, is only about 10 drops s^{-1}, corresponding to the results of Raghupathy and Sample (1970); it is greater than 1000 for a non-wettable slender type-B capillary. Using a capillary with an outer diameter of 27 μm and a high-voltage pulse generator, Sato (1984) was able to produce distilled water droplets of 28 μm at the rate of 2700 s^{-1}. The use of such fine capillaries, easily subject to clogging, is however delicate and the production of such small droplets is unusual in this functioning mode.

Contrary to the preceding case each main drop may be accompanied by the formation of one or several satellite droplets. In Fig. 3, relating to a somewhat viscous liquid, it is seen that

* The apparent reduction in the surface tension due to the electrostatic pressure should not be confused with the true, but low, variation in surface tension that may result through a modification of the orientation of certain molecules on the surface of the liquid under the action of the field (Schmid *et al.*, 1962). This distinction is unfortunately not made in Michelson's book (1990).

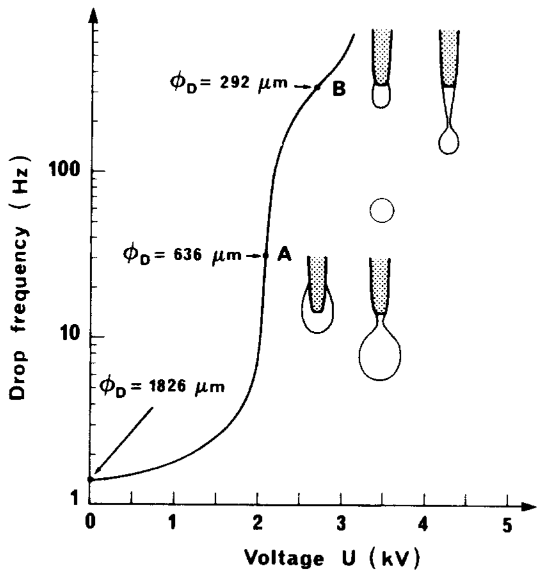


Fig. 2. Dripping mode; drop frequency versus applied voltage. Capillary type B; liquid, diethyl sebacate; $K=2\times10^{-8}$ Sm^{-1}; $\mu=7$ mPa s; $\dot{v}=4.3$ mm^{3}s^{-1}.

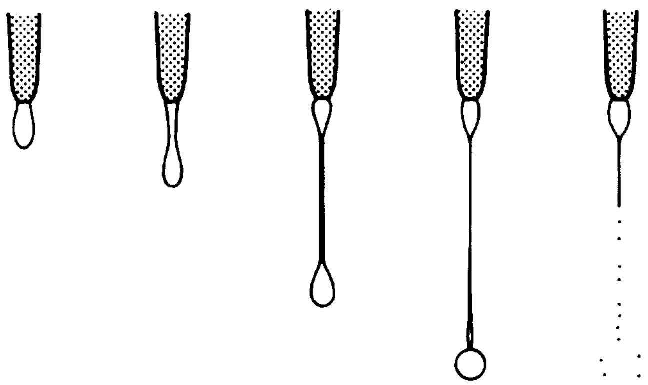


Fig. 3. Dripping mode; different stages of drop formation. Non-wetting capillary type B; liquid, cyclohexanol; $K=2.1\times10^{-6}$ Sm^{-1}; $\mu=68$ mPa s; $\dot{v}=1.25$ mm^{3}s^{-1}; $f=160$ main drops s^{-1}.

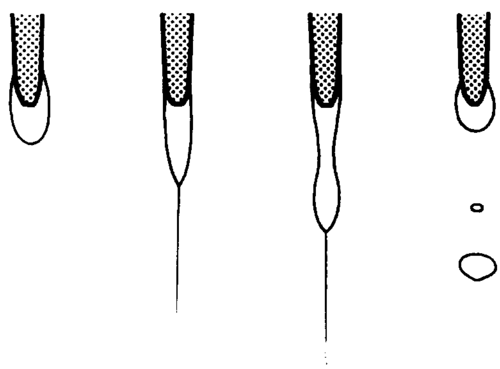


Fig. 4. Dripping mode with emission of a jet; different stages of drop formation. Capillary type B; liquid, ethyl alcohol; $K=10^{-5}$ Sm^{-1}; $\dot{v}=1.1$ mm^{3}s^{-1}; $f=70$ main drops s^{-1}.

the linking filament is long and thin when the main drop detaches; it breaks up into a large number of small droplets.

It should also be pointed out that the electric field at the end of the pendent drop is sometimes sufficient to create a jet following the same process as for the cone-jet mode described below. A multitude of small droplets are then emitted during the formation cycle of each main drop (Fig. 4).

These examples show that, even in the case of the dripping mode, the emission of drops, far from always occurring in the same manner, exhibits a number of very different aspects.

4. CONE-JET MODE

4.1. *General*

One of the most interesting functioning modes is the one in which the meniscus takes on the form of a cone extended at its apex by a permanent jet whose breakup gives rise to the droplets. This mode was observed for the first time by Zeleny. It has been investigated since by many authors and has been given various names. In the absence of a consensus, we use the compound word "cone-jet" which simply denotes the form taken on by the liquid at the outlet of the capillary without prejudging the manner in which this configuration is maintained.

This mode may be obtained with liquids of highly varied conductivities. It allows the production of aerosols within a very large range of average drop sizes, including the submicron range, and the aerosols are sometimes monodispersed (i.e., σ_g is smaller than about 1.2).

This explains why a large part of the research in recent years on EHD spraying in air involves this mode, whether for a new important application (Fenn *et al.*, 1989), experimental work (Gomez and Tang, 1994) or theoretical work (Fernandez de la Mora and Loscertales, 1994).

4.2. *Origin of cone-jet configuration*

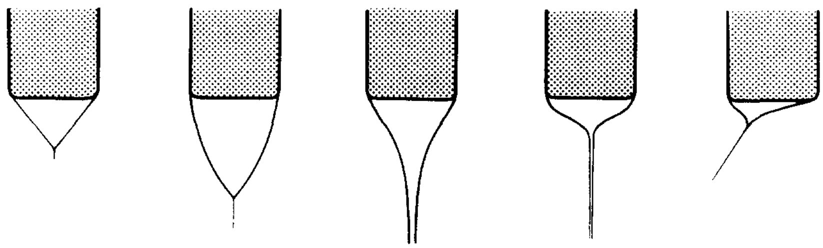
Taylor (1964) was the first to demonstrate that electrostatic pressure and capillary pressure can be balanced at any point on the surface of a liquid cone. Considering the ideal case of a cone with a straight generatrix, in which the hydrostatic pressure is zero, he showed that this equilibrium is obtained only for a single value of the applied potential, when the half-angle at the apex of the cone is equal to 49.3°.

Experience shows however that there are stable conical menisci for a certain range of variation in the hydrostatic pressure and applied potential; in addition, the value of the angle at the apex is variable and the generatrix of the cone may be either concave or convex. In their numerical analysis, Joffre *et al.* (1982, 1984, 1986) have taken into account the regulating effect exerted by the release of charges (due, for example, to a corona discharge) on the electric field in the vicinity of the apex; in this manner they have obtained all the above-mentioned characteristics in the case of a perfectly conducting liquid.

The creation of a permanent jet, for its part, requires a penetration of the field lines in the liquid, so that the liquid must not be a perfect conductor. Only this penetration will allow the appearance of a component of the electric field tangent to the surface, which, by acting on the surface charges, creates a force driving the liquid and an acceleration of the jet downstream (Horning and Hendricks, 1979; Smith, 1986; Hayati *et al.*, 1987; Fernandez de la Mora and Loscertales, 1994).

For liquids with relatively high conductivities, the jet formation zone is limited to the apex of the meniscus. The remaining surface is practically equipotential and an almost static equilibrium of forces exists at each point. The cone may then have a straight generatrix (Fig. 5a) or a curved one (Fig. 5b).

For decreasing conductivities, the acceleration zone extends further toward the base of the cone. In the limit, it begins at the outlet of the capillary. In this case, the expression "convergent jet" used by Mutoh *et al.* (1979) would be more appropriate. However, the



a b c d e

Fig. 5. Different forms of meniscus in cone-jet mode.

profile of the liquid at the capillary outlet often remains similar to that of a more or less open cone (Fig. 5c and d). Furthermore, let us consider a capillary of diameter ϕ_c at the end of which is formed a "Taylor cone" extended by a jet. If the jet formation and acceleration zone is considered to begin at the level of a section of the meniscus of diameter φ ($\varphi \ll \phi_c$), the same jet may be obtained with a capillary of diameter φ. In this case, the same spraying mode remains, although the part of the meniscus surface in which the equilibrium of forces is purely static has disappeared. Therefore, we shall use the term "cone-jet", whether the meniscus has a form corresponding essentially to a "Taylor cone" or to a "convergent jet".

In the mode thus defined, the cone-jet system may be asymmetrical (Fig. 5e). In the limit, the skewed cone-jet may be located at the periphery of the capillary's end.

4.3. *Length and diameter of jets*

The length of the jets increases with the viscosity, the resistivity and the flow rate of the liquid. In our experiments, it varied from about 10^{-5}–10^{-1} m. The large length of jets obtained for highly viscous liquids allows the production of fibres, for example, through solidification by cooling of an initially hot jet (Larrondo and Manley, 1981). Apart from this particular case, the jet ultimately breaks up into drops whose average size depends to a great extent on the diameter ϕ_J of the jet (measured downstream of the acceleration zone). This diameter depends mainly on the conductivity K and on the flow rate $\dot{v}$ of the liquid.

For a liquid of a given K, the cone-jet mode appears only within a limited range of values of $\dot{v}$ whose extent varies with the geometry of the emitter; within this range, ϕ_J decreases as $\dot{v}$ decreases.

As K increases, the boundaries of the range move towards lower flow rates $\dot{v}$; this is accompanied by a reduction of ϕ_J.

The result of these observations is that:

— for liquids with high conductivity, only fine jets and low flow rates can be obtained in the cone-jet mode,

— for liquids with low conductivity, it is not possible to obtain spontaneously fine jets and thus fine droplets. However, special methods of charge injection allow the atomization of insulating liquids (Kim and Turnbull, 1976; Kelly, 1984); these special conditions are not considered here.

Under our experimental conditions, ϕ_J varies from a few hundred to a few tens of microns. A jet with a much smaller diameter (estimated at 0.015 μm) was obtained with sulphuric acid by Fernandez de la Mora (1992).

4.4. *Breakup of jets into droplets*

4.4.1. *Varicose instabilities.* As long as the charge of the jet is not too high, the breakup into drops takes place in the same manner as for a neutral jet (Fig. 6a). If the distance λ between two consecutive breakups of a jet is equal to k times the diameter ϕ_J, the resulting

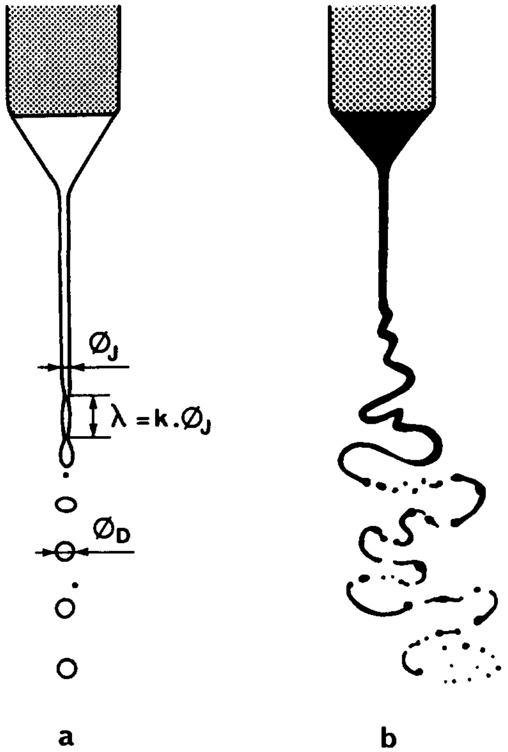


Fig. 6. Cone-jet mode: (a) varicose instabilities; (b) kink instabilities.

droplet has a diameter ϕ_D such that

$$\phi_D/\phi_J = (3k/2)^{1/3}. \tag{1}$$

For low viscosity liquids, the most probable value of k is about 4.5, leading to a ratio, ϕ_D/ϕ_J, of about 1.89. The theoretical results (Neukermans, 1973) and experimental results (Mutoh *et al.*, 1979; Cloupeau and Prunet-Foch, 1989; Tang and Gomez, 1994) show that the value of k varies little with the charge of the jet. On the other hand, k increases with the viscosity of the liquid (Weber, 1931).

The distance λ varies each time and satellite droplets may be created at the moment of the breakups. Depending on conditions, the aerosols produced are monodispersed or polydispersed.

The smaller droplets move away, faster than the larger ones, from the axis of the jet. This segregation phenomenon, investigated by Tang and Gomez (1994), could be used to improve the monodispersion of the aerosols. However, to obtain essentially uniform-sized droplets, it is necessary, as for uncharged jets, to cause the breakup of the jet at regular intervals by disturbances whose frequency is close to the average spontaneous break-up frequency (Cloupeau, 1994).

The fine aerosols produced spontaneously with liquids of relatively high conductivity sometimes exhibit, when they are illuminated with a white light, the characteristic colours of the High-Order Tyndall Spectra (HOTS) (Kerker, 1969). The term "rainbow mode" has recently been used to designate such a spraying regime. Let us note that, strictly speaking, this term does not characterize a mode as such. The HOTS, which disappear when the size of the drops produced in the cone-jet mode departs from the micron range, may also be observed for aerosols produced in the microdripping mode (cf. Section 5).

4.4.2. *Kink instabilities.* When the electrostatic pressure on the jet approaches the capillary pressure, the largest droplets just after their separation have a charge* which

* On a spherical drop formed from a jet segment with a length equal to $4.5\phi_J$, the Rayleigh limit charge is reached when the electrostatic pressure on the jet is equal to about 0.82 times the capillary pressure.

exceeds the Rayleigh limit charge (Rayleigh, 1879). They then emit a jet which resolves in turn into very fine droplets.

For slightly higher voltages, lateral kink-type instabilities appear. They increase as the voltage increases. The jet stretches out into disordered winding threads and is thinned out very irregularly (Fig. 6b). It breaks up into fine droplets of very different sizes. Our experiments show that, for a given conductivity of the liquid, these whipping motions are observed only above a certain flow rate.

4.5. *Droplet charge*

Assuming that the emitted droplets all have the same size and applying the energy minimization principle, Vonnegut and Neubauer (1952) established the following relationship between the charge-to-volume ratio q/v of a droplet and its diameter ϕ_D:

$$q/v = 6(2\varepsilon\gamma\phi_D^{-3})^{1/2}, \tag{2}$$

where ε is the permittivity of air.

The "Vonnegut charge" q_V deduced from this expression is equal to half the Rayleigh limit charge.

This theory was subsequently developed by adding considerations of statistical mechanics to account for the distributions of sizes and charges in droplets obtained under different conditions (Pfeifer and Hendricks, 1967). However, several experimental results show that the drop charge level depends greatly on production conditions and that the use of energy minimization principle is not justified (Krohn, 1973; Cloupeau and Prunet-Foch, 1989; Gomez and Tang, 1994).

Let us however note the practical value of the Vonnegut formula. In the absence of corona discharge, the current i measured in the high-voltage circuit is equal to the current transported by the drops. Under these conditions, the ratio $i/\dot{v}$ of the current to the flow rate is equal to the ratio q/v in equation (2). The diameter ϕ_D given by this equation is then

$$\phi_D = [6(2\varepsilon\gamma)^{1/2}\dot{v}/i)]^{2/3}. \tag{3}$$

This diameter, calculated from easily measurable values of the current and of the flow rate, gives (in the absence of corona discharge) a correct order of magnitude for the average size of the droplets emitted, owing to the fact that the droplets generally have a high charge level (about 20–100% of the Rayleigh limit charge under our experimental conditions).

4.6. *Effects of corona discharges*

When spontaneous corona discharges are initiated at the outlet of the capillary, they reduce the electric field and generally constitute a spurious phenomenon. In fact,

(a) if they occur before the critical field, initiating the cone-jet regime, is reached, they prevent the establishment of this mode; this phenomenon occurs especially with liquids having a high surface tension and requiring high fields to offset the capillary pressure;

(b) if they occur once the regime has been established, fluctuations in the discharge current often prevent the conservation of steady-state conditions. However, if the voltage is increased, the discharge current can become regular and the stable cone-jet mode can reappear as a result of the reduction of the field due to the space charges.

Apparently, Meesters *et al.* (1992) attribute very special effects to the corona discharge that they have observed at the apex of Taylor cones with a device in which the droplets are neutralized by a secondary corona discharge of opposite polarity. According to these authors, the droplets are emitted directly at the apex of the cone and their sizes are much smaller than those obtained usually for the same liquids with the same flow rates. Experiments conducted under similar conditions to those of Meesters *et al.* show that the spraying regime obtained by these authors, in fact, corresponds to the classical cone-jet mode and that the average droplet size is not at all as small as indicated in their measurements (Cloupeau, 1994).

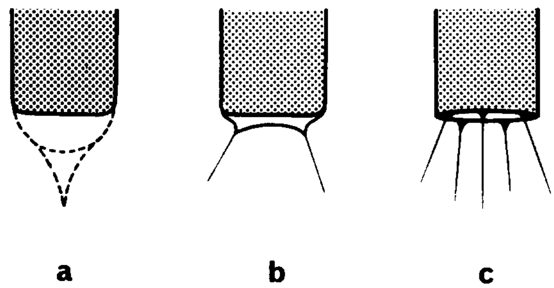


Fig. 7. Variants of the cone-jet mode: (a) pulsed cone-jet; (b) and (c) multijet.

4.7. *Variants*

Intermittent or pulsed cone-jet. When the voltage is slightly lower than that for which a single permanent jet is obtained, the jet may be emitted only intermittently, the apex of the meniscus alternately taking on a pointed or rounded form (Fig. 7a). In this pulsed cone-jet mode, emission phases may occur at perfectly regular time intervals. However, the diameter of the jet varies during these emission phases, so that the distribution of droplet sizes is never very narrow.

This mode corresponds to a transition regime of no practical interest.

Multijet or multicone-jet. When the voltage is gradually increased, the jet may split (Fig. 7b) with the meniscus forming two emissive cusps. Several emitting sites are then established around the end of the capillary (Fig. 7c). Their number increases with the applied voltage. This multijet mode makes it possible to obtain simultaneously a large number of jets on long circular or linear edges and, consequently, relatively high flow rates (Hines, 1966; Hughes and Pavey, 1981; Wilson, 1982).

An other advantage of the multijet mode should be pointed out. It stems from the fact that in the cone-jet mode a reduction in flow rate results in a reduction in the average size of the droplets and an increase in their emission frequency. For the same total flow rate, the sharing of the flow rate between multiple jets thus yields both finer drops and much higher emission frequencies than in the single cone-jet mode.

Cone-ramified jet. This configuration, which appears more rarely than the preceding ones, will be dealt with further below (cf. Section 6).

5. MICRODRIPPING MODE

By studying the spraying of dibutyl phthalate, pure or mixed with ethyl alcohol, Kozhenkov *et al.* (1974) and Kozhenkov and Fuks (1976) have obtained aerosols with a "high degree of particle monodispersity" sometimes exhibiting the HOTS phenomenon. Their observations using a pulsed laser giving an illumination time of 30 ns have demonstrated that the formation of the aerosol resulted "from the emission of single droplets from a liquid apex" and not from the breakup of a liquid thread. They have concluded that the authors who had observed the production of monodispersed aerosols at low flow rate by the stretching out and rupture of a liquid jet had been victims of an optical illusion: their observations had been carried out with flashes of excessively long duration and the fast succession of droplets gave the appearance of a continuous jet.

In fact, Kozhenkov *et al.* have observed a spraying mode, different from the cone-jet mode, which we call "microdripping" because the emission takes place drop by drop as in the conventional dripping mode, and the droplets have a much smaller diameter than the capillary outlet section.

An example of droplet emission in the microdripping mode is given in Fig. 8.

In general, at the apex of a rounded or conical meniscus there appears a jet which is more or less long and at the end of which there is an accumulation of liquid; this leads to the formation of a single droplet. After the separation of the droplet, the incipient jet retracts to a greater or lesser extent and the cycle begins again.

According to Figs 30 and 31 of the Cohen (1963) report, Hendricks and his co-workers have clearly obtained microdripping with 2-ethylhexyl phthalate (Octoil). For this same product, the series of snapshots given in Fig. 5 of the article by Carson and Hendricks (1965) is typical of microdripping (whereas Fig. 4 relative to glycerine is typical of the pulsed cone-jet mode).

We have observed the microdripping mode with diethyl sebacate, dioxane, ethyl benzoate, ethyl acetate, when these liquids, pure or mixed with other products, had a conductivity lower than 10^{-6} S m^{-1}. Unlike Kozhenkov *et al.*, we have not observed it with pure ethyl alcohol (whose conductivity is higher).

The microdripping mode and the cone-jet mode can appear under identical experimental conditions as shown in Fig. 9. In the transition zone, one spraying mode may replace the other, each being maintained for a rather long period. The diversity of the conditions under which microdripping appears is however much smaller than that of the cone-jet mode. The establishment of microdripping is observed only for low flow rates and depends, even more so than for other modes, on the experimental details such as the form and degree of wettability of the end of the capillary. In the experiments of Kozhenkov *et al.*, the capillaries were supplied with liquid under a slightly negative constant pressure, whereas we used a

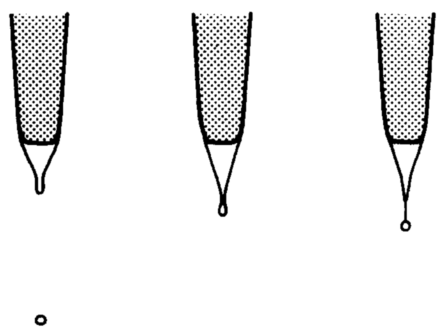


Fig. 8. Microdripping mode; different stages of drop formation. Capillary type B; liquid, dibutyl phtalate doped with triethylene glycol; $K = 1.8 \times 10^{-7}$ Sm^{-1}; $\dot{v} = 0.2$ mm^{3}s^{-1}; $f = 2700$ droplets s^{-1}.

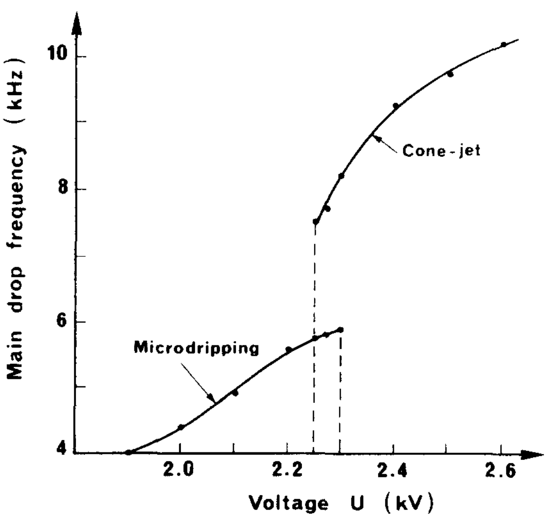


Fig. 9. Example of transition from microdripping to cone-jet mode: droplet frequency versus applied voltage. Capillary type B; liquid, dibutyl phtalate doped with triethylene glycol; $K = 1.5 \times 10^{-7}$ Sm^{-1}; $\mu = 7$ mPa s; $\dot{v} = 0.1$ mm^{3}s^{-1}.

constant flow supply, $\dot{v}$ being $>0.01\ \mathrm{mm^3\,s^{-1}}$; this explains perhaps why we did not observe microdripping for liquids with a conductivity higher than $10^{-6}\ \mathrm{S\,m^{-1}}$.

In our experiments, droplet diameters ranged from about 100 μm to a few micrometers and production frequencies ranged from a few tens of droplets to several tens of thousands of droplets per second.

An interesting characteristic of microdripping is that emission sometimes takes place at very regular time intervals, giving droplets of essentially uniform size. The spraying of partially evaporable solutions, combined with a neutralization device to prevent disintegration of the droplets, makes it possible to obtain monodispersed aerosols of micronic or submicronic droplets in which the distribution of sizes is narrower than for the droplets produced in the cone-jet mode.

To our knowledge, the microdripping mode has not formed the subject of any detailed study or of any application attempt during recent years. However, the "nipple shape" pointed out by Harris and Basaran (1993) in their detailed theoretical analysis of electrified pendent drops is most probably the key to an explanation of this mode.

Variants. The microdripping mode sometimes occurs intermittently and one or several departure sites may be set up along the periphery of the capillary.

6. SIMPLE JET AND RAMIFIED JET

In the absence of an electric field, the liquid forms a permanent jet if the flow rate is sufficiently high. This critical rate is reached when the kinetic energy of the liquid at the outlet of the capillary is greater than the surface energy required to create the surface of the jet (Lindblad and Schneider, 1965). In this case, the application of an even low voltage has the effect of charging and accelerating the jet already established.

A jet may also be obtained at flow rates substantially lower than the critical rate if the applied voltage exceeds a certain minimum value.

In every case, when the voltage is gradually increased, the behaviour of the jet is first similar to what is observed in the cone-jet mode; then more or less numerous ramifications occur.

Figure 10 gives some aspects observed with ethyl alcohol for a flow rate of $4\ \mathrm{mm^3\,s^{-1}}$ (lower than the critical rate, which is $6\ \mathrm{mm^3\,s^{-1}}$ for the slender capillary used).

In Fig. 10a, the jet breaks up into large drops possibly accompanied by satellite drops. In Fig. 10b, drops already detached sometimes emit one or two fine jets which will then break up into fine droplets. In Fig. 10c, the jet forms whipping thread before breaking up. In Fig. 10d, the jet forms a succession of thickened regions from which one or more fine jets emerge.

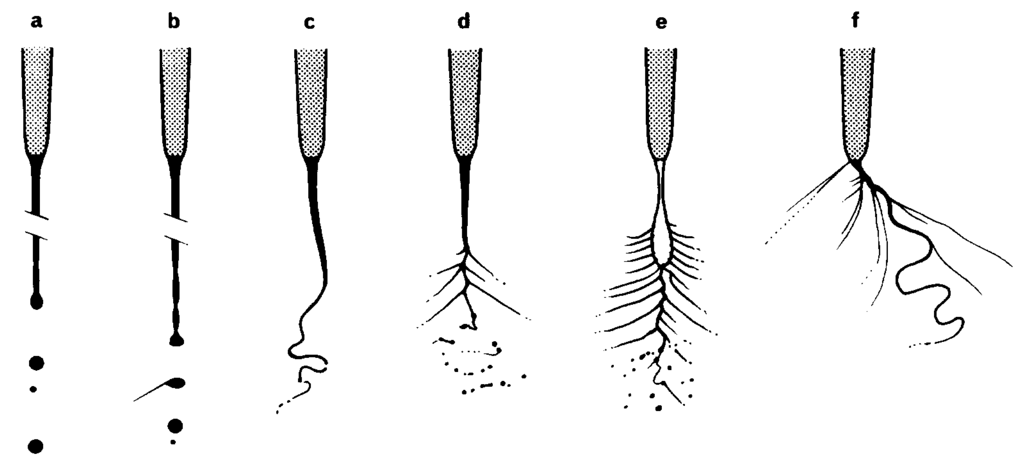


Fig. 10. Simple jet (a, b, c); ramified jet (d, e); random spraying (f). Capillary type B; liquid, ethyl alcohol; $K=10^{-5}\ \mathrm{S\,m^{-1}}$; $\dot{v}=4\ \mathrm{mm^3 s^{-1}}$; jet forms observed with increasing voltage.

In Fig. 10e, the jet shortly after leaving the capillary widens and many fine jets are emitted all around.

For higher voltages (Fig. 10f), the permanent part of the jet disappears and the aspect of the spraying changes constantly. Such random spraying may also be observed at low flow rates.*

Whipping motions of the type observed in Fig. 10c occur at very low flow rates with a cone-jet functioning mode (Fig. 6b) as well as at rates of a few tens or hundreds of $mm^3 s^{-1}$ (Magarvey and Outhouse, 1962; Taylor, 1969; Ogata *et al.*, 1981). For these very high rates the functioning mode represented in Fig. 10e was obtained with 2-propanol by Huebner (1970) who called it a "fan configuration". This mode does not occur with water in ambient air because corona discharges prevent reaching the required field. One need only increase the dielectric strength of the air to obtain it.

Ramified jets are rarely observed in the cone-jet mode because, when the voltage increases, the multijet mode appears before the electric field on the single jet reaches a sufficiently high value. The fan configuration has however been obtained with a spray head geometry preventing the appearance of the multijet. For example, a metal cylinder (diameter of 6 mm) pierced along its axis was slipped over the capillary ($\phi_c = 1$ mm) whose end projected by only a few tenths of a millimeter beyond the flat base of the cylinder.

7. SPINDLE MODE

In the preceding modes, the production of droplets stems from the breakup of a jet or directly from the detachment of part of the liquid volume accumulating in the meniscus. A special case of the dripping mode has however been pointed out (Fig. 4) in which these two types of droplet creation exist together. This coexistence is found almost every time in the mode which we shall call the "spindle" mode.

This mode is illustrated in Fig. 11 which shows different stages in a droplet formation cycle. The rounded meniscus (1) stretches out (2) and a fine jet emerges from its apex and breaks up into droplets (3). The elongation of the meniscus is accentuated (4, 5) and throttling occurs at the base of the tapered part (6). A spindle-shaped liquid volume finally detaches (7). It contracts to form a main drop (8), while the remaining jet continues to break up into fine droplets (9, 10).

Under other conditions, a filament subsists between the meniscus and the volume which is being detached, giving rise to one or more satellite drops; the volume which is detached can also have various forms and can itself resolve into several drops.

In our experiments, the spindle mode was observed for liquid conductivities greater than $10^{-7}\,Sm^{-1}$. The values of the frequencies and diameters of the main drops varied, respectively, from 50 to 10,000 drops s^{-1} and from 450 μm to less than 30 μm.

This mode was already investigated by Zeleny (1917, Figs 1 and 2). Vonnegut *et al.* (1962) also described it under the name "multistream regime" in the case where the drops are formed in an excessively irregular manner. Under other conditions, the main drop formation cycle is repeated so regularly that Johnson (1963) was able to observe it by stroboscopy. The same method was used by Sample and Bollini (1972) to determine the conditions under which drops of uniform size are obtained. The mode thus investigated, which they called "harmonic spraying", must be regarded as a special case of the spindle mode. The fact that they did not note the presence of jets, but only of satellite drops, is probably due to their observation technique and to the liquid used: for pure water, the jet is very fine and exhibits significant lateral instabilities; it is thus visible only if it is observed under high magnification and with very short illumination times.

The mode investigated by Tomita *et al.* (1986) under the name of "small drops" is certainly the spindle mode. The liquids used (water doped by KCl, possibly mixed with ethyl alcohol

* A theory has been developed by Kelly (1976) for a "high-voltage spraying" mode involving the spraying of metals in vacuum, and extended subsequently to aerosols produced with the "spray triode" device (Kelly, 1984). According to Kelly's (1976) description, this mode corresponds to electric fields much higher than those for which the cone-jet (Fig. 5a), the multijet (Fig. 7c) and even the random spraying of Fig. 10f appear. This special mode does not appear to have any equivalent in those we have observed in air.

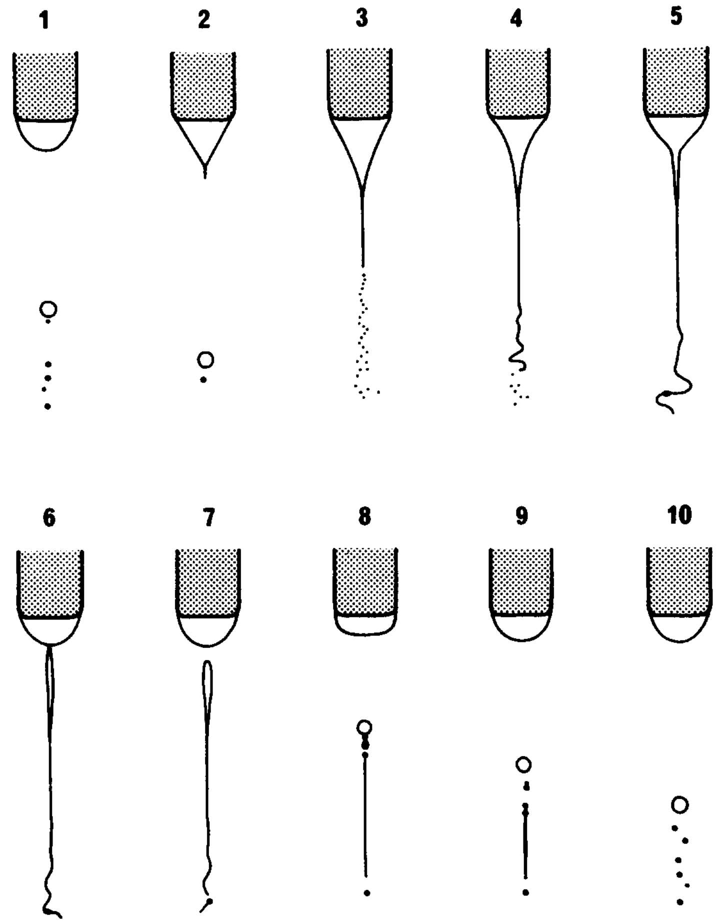


Fig. 11. Spindle mode; different stages of drop formation. Nonwettable capillary type A with $\phi_c = 0.5$ mm; liquid, ethyl alcohol; $K = 10^{-4}$ S m^{-1}; $\dot{v} = 1.1$ mm^3 s^{-1}; $f = 950$ main drops s^{-1}.

and glycerine) have conductivities of about 0.1–1 S m^{-1}, i.e. higher than in our experiments. Under these conditions, the jets, if they still exist, can produce only extremely fine droplets, so that the microdroplet emission phenomenon would be altogether marginal.

Concerning the production of the main drops, Sample and Bollini (1972) working with pure water observed that when the applied voltage increases, two harmonic spraying regions, I and II, appear. They are separated by a zone in which the spraying is irregular. This phenomenon can be attributed to the corona discharge effects (Cloupeau and Prunet-Foch, 1990).

It should be noted that the regularity of the frequency of liquid emissions does not necessarily mean that the main drops have a uniform size. In particular, for the high voltages in region II, the liquid volume which detaches has irregular shapes and often resolves into several drops of different size.

The harmonic spraying mode has also been investigated in vacuum with liquid metals (Bollini *et al.*, 1975) and glycerine (Bailey and Borzabadi, 1978).

It is also this mode that Grigor'ev *et al.* (1991) have adopted as the spraying model in their theory based on the Onsager principle of minimum energy dissipation. Let us note that these authors assume the liquid to be perfectly conducting and inviscid; in this ideal case, there would be no jet emission downstream of the drops.

8. PASSAGE FROM ONE MODE TO ANOTHER

Different atypical aspects of EHD spraying can be observed; in particular, during the transition from one mode to another, or when irregular corona discharges disturb the spraying. In the functioning modes we have described (except the random spraying mentioned in Section 6), the meniscus exhibits a certain permanency and/or the formation of drops exhibits a certain regularity.

These modes may be classified according to the manner in which the drops are formed: direct production at the end of the capillary or the meniscus; production by breakup of a jet; and cases in which these two types of production occur together.

They may also be divided into two categories. In the cone-jet, multijet, simple jet and ramified jet modes, the liquid flows from the meniscus in a continuous manner. On the other hand, in the dripping, microdripping, spindle and pulsed cone-jet modes, the emission of the liquid from the meniscus takes place discontinuously; all the latter modes may be said to be pulsating. This generic term has sometimes been used (Bailey and Borzabadi, 1978; Smith, 1986; Hayati *et al.*, 1987) to designate either of the two modes which we distinguish under the names of spindle and pulsed cone-jet modes. Although these two modes may have the same appearance upon observation under continuous illumination and the passage from one mode to the other may take place gradually, the distinction must be maintained because they lead to very different particle-size distributions of the drops for a given liquid:

— in the spindle mode, a significant part of the liquid flow is used for the formation of the main drops of relatively large size (this part increasing with the liquid conductivity);
— in the pulsed cone-jet mode, the entire flow resolves into a multitude of fine droplets.

The passage from one mode to another when one of the parameters of the experiment is modified may be sudden or gradual (Cloupeau and Prunet-Foch, 1990). For instance,

— the passage from dripping to spindle when the voltage is increased can be sudden for liquids of low viscosity (Sample and Bollini, 1972; Ogata *et al.*, 1976), and gradual for glycerine;
— the passage from the cone-jet to the simple jet when the flow rate is increased is not marked by any sudden variation in the frequency of production or the size of the drops if the liquid has a very low conductivity and the capillary is very fine. On the other hand, this transition does not exist if the liquid has a high conductivity.

The order of succession of the modes depends on the variable parameter chosen and the different conditions. For example, when the voltage is gradually increased, this order varies in particular with the conductivity K of the liquid and the type of liquid supply (at constant flow rate $\dot{v}$ or at constant pressure):

— for low K and a capillary supply at low constant $\dot{v}$, the following order is sometimes observed: dripping, spindle, microdripping, cone-jet, multijet, with the cone-jet mode possibly reappearing at high voltage when the spraying is accompanied by a strong corona discharge current;
— for a high K and a capillary supply at constant pressure near zero, the first mode to appear may be the cone-jet mode.

In general, too many parameters interact and it is not always possible to know beforehand the mode obtained when the values of the main parameters are given; tiny differences in experimental details such as the shape or wettability of the capillary end may lead to the initiation of one mode rather than another and considerably change the characteristics of the emitted aerosols. The uncertainty is further heightened by hysteresis phenomena. Different investigations can consequently be usefully complemented only if the modes to which their results correspond have been identified.

9. CONCLUSION

The main functioning modes of EHD spraying observed in air (but also observable in vacuum) have been described, and various results have been compared with those of earlier studies.

The absence of agreement on the terminology to be used and the need for a more specific or, quite the contrary, a more general term, leads us to propose new designations for the modes other than dripping. They are designated as follows. Cone-jet (with or without whipping motions) and its variants: pulsed cone-jet and multijet; microdripping; simple jet; ramified jet (including fan configuration); spindle (including harmonic spraying).

Perhaps this critical review and this attempt at unification of technical terms may help to understand better the meaning of past and future results on EHD spraying.

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