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Physical Principles of Electrospinning

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Chapters:

1. **Introduction**:

The present study aims at bridging prospective nano-technology and theoretical physics, along with some relevant applications. The study was initiated with organising a treatise (Lukas *et. al.*, 2008) on the fundamentals of the subject of disintegration of liquid drops under electric field (Zeleny, 1914) that, strictly speaking, brought the area of 'electrohydrodynamics' under the purview of physical analysis during the early part of the 20th century. In order to enable a deeper understanding of the subject, care was taken to include as many references as possible for a monograph was the first of its kind. The subsequent part of the research involves extension of the existing theory for capillary electrospinners (Zeleny, 1914; Taylor, 1969) to that of free liquid surface electrospinners (Pokorny *et. al.*, 2008). Ultimately a grand theory is proposed to unify the present phenomenon with other known electrohydrodynamics to provide better understanding of the process (Sarkar *et. al.*, 2008). The theoretical formulations were carried out along with some allied instrumentations (Chugh *et. al.*, 2006; Goyal *et. al.*, 2006) to study the process comprehensively. Some related analytical results, like wetting phenomenon of fibres, were also used to draw analogy to the process of electrospinning (Pociute *et. al.,* 2008).

2. Electrospinning zone:

Structurally, electrospun polymeric jet almost resembles a tree, as is shown below (Lukas *et. al.*, 2008).

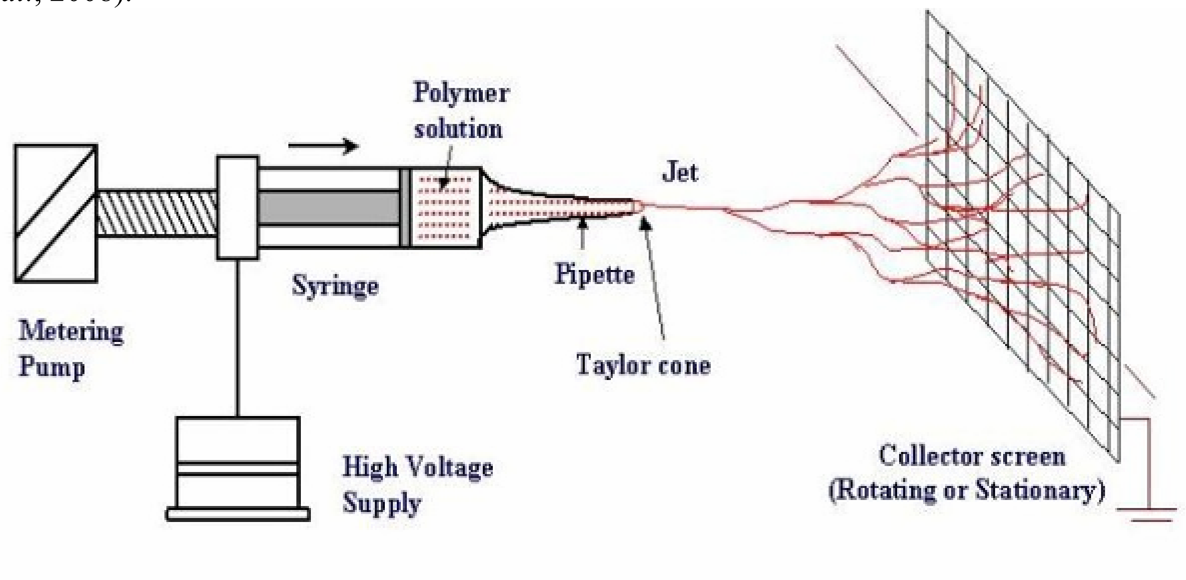

Fig. 2.1: Schematic diagram of an electrospinning set up

It has remarkable manifold external morphology, with its 'roots' evolving from an extremely thin surface layer of the polymer solution that serves as one of the electrodes. Tracing the jet further downstream, one finds stable part of the jet that looks like stem of the tree. Noticeably, the following whipping zone of the jet branches out like that of a tree. Eventually the nanofibres collected on the other electrode, connected to a high voltage source, may literally be thought of as the 'fruits' of the entire process. Physically, the phenomenon of electrospinning is a consequence of a tug of war between electrostatic and capillary forces. The first of them speaks of charged or polarized liquid bodies that disintegrate in external electrostatic fields while the last one causes liquid particles to flock together to minimize the liquid surface area. A liquid body disintegrates in two possible ways, depending on the internal molecular structure of it. Simple liquids, having relatively small molecules, spray in clouds of small charged droplets with a tendency to break down further until only a single elementary charge remains trapped in each of them (Grigor'ev and Shir'aeva, 1990). Liquids with higher viscosity, particularly, polymer solutions disintegrate in long tiny liquid columns while moving from one electrode to the other. The internal pressure, caused by an enormous concentration of charged particles of the similar nature, forces them to be stretched longitudinally. This stretching tendency, along with jet rheology, results in wild lateral jet motion and enormous elongation leading to quick decrease of the jet radius value. Narrowing down of the jet diameter results in an increased curvature of it that in turn brings about another phenomenon forcing the solvent to be very effectively driven out from the jet. Hence, the whipping jet operates as a significant operative dryer.

Unlike classic spinning technologies, the devices and equipments in this process are free of complex passive or rotating components. So the magnificence of mechanical engineering is replaced in the set up by diverse physical self-organising actions. Hence, a better understanding of its intrinsic physics is needed for technological developments

3. Historical Overview:

Investigation of physical phenomena, connected to electrospinning started with William Gilbert (1600) (Lukas *et. al.*, 2008), who the first person to discover that a spherical drop of water on a dry surface was drawn up in a conical shape when a piece of rubbed amber was brought within a suitable distance from it. In fact, such shape deformation of liquid bodies in an external electrostatic field governs this modern spinning technology. However, as Gilbert did not have sufficiently high voltage source to study the droplet motions in higher electrostatic fields, humankind had to wait nearly next three hundred years until Rayleigh calculated the limiting charge that an isolated drop of certain radius could hold before it became unstable. It was found that the instability led to creation of daughter droplets that were ten times smaller than the original one.

The principle of electrospinning originated through Zeleny's work (Lukas *et. al.*, 2008). He was aware of creation of very fine fibre-like jets in his apparatus (Lukas *et. al.*, 2008) but, unfortunately, it did not attract his attention.

Formhals (Lukas *et. al.*, 2008) is commonly recognized as the father of present day electrospinning technology for his patent, entitled as "Improvements in or relating to processes and apparatus for the production of artificial filaments".

Preliminary electrodynamic analysis near a wedge shaped conductor that has quite a remarkable characteristic similarity with electrospraying and electrospinning of conductive liquids, was carried out by Landau (Landau, 1960), where his predicted critical semi-vertical angle of the conical fluid shape at the onset of the phenomena was slightly different from that of Taylor (Lukas *et. al.*, 2008). It may be observed (Landau, 1960; Gray, 1953) that Landau arrived at a different mathematical structure than that of Taylor with some simplified assumption, thus resulting in that small variation of the resulting angle. However, officially, the first groundbreaking analysis of Zeleny's work was marked with Taylor's effort that subsequently led to his name being coined with the conical shape of the fluid drop in an electric field (Lukas *et. al.*, 2008) at critical stage just before disintegration. He observed that elongated spheroids quickly developed an apparently conical end due to electrical forces, and liquid jet appeared from vertex of the cone. Through a detailed analysis he obtained the characteristic value of the cone's semi-vertical vertex angle, α, as 49.3^o (Lukas *et. al.*, 2008). It is noteworthy that Taylor found the practical interest of the subject of his research in the area of meteorology and did not relate at all his effort to fibre spinning. He was convinced that the studied phenomenon had strong relevance in the production of thunderstorms.

Another meteorologist, Matthews (Matthews, 1967), was also attracted in the same field and studied mass loss and distortion of freely falling water drops in an electric field. Results of his experimental work were used by Taylor to prove his theoretical prediction of instability of uncharged liquid spheroids in external electrostatic fields. Unfortunately, further development and application of the said principle for electrospinning took quite a considerable period from the time of its origin. Research in the field of electrospinning revived recently, especially after Reneker and co-workers (Lukas *et. al.*, 2008) spun various kinds of polymers during the nineties. Some other contemporaneous works in this area were focussed on the role of chain entanglements on fibre formation during electrospinning of polymer solutions in good solvents (Lukas *et. al.*, 2008) and on enhancement of productivity and efficiency of the technology (Lukas *et. al.*, 2008) through experiments and modelling of multiple jets.

4. Disintegration of Liquid Bodies

The stability analysis of charged liquid bodies, as carried out by Rayleigh, frequently used in the technical literatures (Lukas *et. al.*, 2008):

$$\varphi\sqrt{\frac{\varepsilon}{r\gamma}} \geq 2 \quad \text{and} \quad Q^2 \geq 64\pi^2\varepsilon r^3\gamma \qquad (4.1)$$

As was showed by Taylor (Lukas *et. al.*, 2008) free charged liquid droplets are in principle unstable since they elongate to reach the shape of spheroids with the major and minor axes as a and b, respectively. As the ratio a/b increased, the critical values of both φ and Q decreased too. Consequently, it may be stated that charged spheroids are always unstable and therefore, disintegration proceeds. Accordingly, conditions in (4.1) represent qualitative explanation of procedures that lead to creation of still tinier droplets, made by charged liquid bodies.

Taylor also analysed the behaviour of uncharged liquid drops in an electric field and found, that an uncharged spherical drop, when placed in an electric field, slowly deformed to take the shape of a spheroid at lower values of electric field intensity. In that process, the ratio of its major and minor axes gradually increased. The drop remained intact until the ratio reached a value of 1.9 and thereafter disintegrated into daughter droplets.

In Zeleny's experiments study of the potential necessary for instability of a liquid meniscus involved a hydrostatic pressure, p, which was regulated in a way to maintain a definite height of the meniscus (Lukas *et. al.*, 2008). The meniscus became unsteady, when the electrostatic potential between the tube and the metal plate / collector went beyond a certain value. Considering the fluid as a conductor that wetted the top of the tube, the equation at the equilibrium condition of the meniscus was given as:

$$2\pi r\gamma\cos\alpha + W = F + \pi r^2 p \qquad (4.2)$$

where α was the angle between the fluid surface and the tube axis at the point on the rim of the top, where it left the tube, W was the weight of the fluid above the top, F was the attractive force between the tube and the plate and r , the radius of the tube. Zeleny, however, used a very small value of r to neglect the effect of W. The left hand side of the Equation (4.2) represents forces that pull the liquid back to the capillary. The first term represents force due to the surface tension that acts along the tube perimeter while the last one, W, arises due to the total gravitational force acting on the liquid volume above the tube's rim. The first term on the right hand side of the relation is composed of force, F, due to the coulomb interaction of the induced charge with the external electrostatic field. The last term of the right hand side accounts for the force due to the hydrostatic pressure.

On the other hand, van Dyke in Taylor's work (Taylor, 1969) calculated the attractive force, F, acting between a long cylinder of length L and radius r, and a perpendicular plane at a distance h, when a potential V was applied between them. He found the force F to lie between limiting values of $\frac{V^2}{4\ln(4h/r)}$, and $\frac{V^2}{4\ln(2h/r)}$.

In a retrospection of the evolution of the present day theory of 'electrically driven jets', one will find evidence of a two-plate apparatus that precedes the above formulation of van Dyke based on Zeleny's apparatus (Taylor, 1969; Lukas *et. al.*, 2008). Such an apparatus was constructed with an aim to eliminate the error due to the assumption that a very long cylinder was necessary to have the total force on it almost the same as on a semi-infinite needle. It consisted of two parallel plates, separated by distance, h, and kept at a potential difference of V volts. Through the middle of the lower plate arose the metallic hypodermic tube to a height L and the fluid was supplied either from a reservoir or, from a graduated syringe, connected to the tube by a pipe (Lukas *et. al.*, 2008).

For the two-plate apparatus, the value of force, F, exerted on cylinder of length L was given as (Taylor, 1965):

$$F = \frac{V^2 L^2}{4h^2} \frac{1}{\ln(2L/r) - \frac{3}{2}} \tag{4.3}$$

Taylor (Lukas *et. al.*, 2008) determined the lowest value of V at which a fairly conducting and viscous fluid was drawn from the tube, when the hydrostatic pressure, p, was made zero to make the top of the liquid like that of a plane mirror with gradual increment of the voltage. As the voltage was increased, the meniscus started to become convex and ultimately took a conical shape with a semi-vertical angle close to the equilibrium value 49.3^{o}. Thus, an approximate expression for predicting the critical potential at which jets or drops appeared at $p = 0$ could be put forward by setting $\alpha = 49.3^0$ (Lukas *et. al.*, 2008) in (4.2) and substituting for F from (4.3). Since, $2\cos 49.3^0 = 1.30$, the following relation came out:

$$V^2 = \frac{4H^2}{L^2}(\ln\frac{2L}{R} - \frac{3}{2})(1.30\pi RT)(0.09) \tag{4.4}$$

where, the factor 0.09 was inserted to predict the voltage in kilovolts.

5. Self Organisation of Jets in an Electric Field—Generalization of Taylor's Theory:

Electrospinning, a special case of electrojetting, may be analysed from the point of view of self organisation of liquid jets under electric field (Pokorny *et. al.*, 2008). This has been the main objective of the thesis. The relevant physical principle may be investigated both theoretically and experimentally using a cleft made from metallic plates (Pokorny *et. al.*, 2008). The cleft itself, then, serves as a field concentrator and resembles the simplest model (physical) of the process, where jets self-organize on a very narrow, nearly one-dimensional, free liquid surface, confined between the plates.

In this analysis it is supposed that electro-hydrodynamics of a liquid surface may conveniently be analysed with the waves running on an one-dimensional approximation of the fluid surface, confined in an extremely narrow and infinitely deep cleft between two infinitely long plates that are oriented along the horizontal axis (say, x-axis) of a three dimensional rectangular Cartesian system (Pokorny *et. al.*, 2008) The wave's vertical displacement along the z-axis is described using the periodic real part of a complex quantity ξ.

$$\xi = A\exp[i(kx - \omega t)] \tag{5.1}$$

The liquid in the cleft is subjected to fields of gravitation and electricity in addition to capillary effects, caused by nonzero curvature of its surface. The related dispersion law of liquid surface may be given as (Pokorny *et. al.*, 2008):

$$\omega^2 = \left(\rho g + \gamma k^2 - \varepsilon E_0{}^2 k\right)\frac{k}{\rho} \tag{5.2}$$

For a particular liquid, the critical parameter to initiate jetting is the field strength, E_0. When E_0 exceeds a critical value, E_c, the square of the angular frequency, ω^2, becomes negative and so, ω becomes purely imaginary. The imaginary angular frequency, defined as, $q = \mathrm{Im}\,(\omega)$, then abruptly changes the behaviour of the superficial waves that obey the following relation:

$$\xi = A e^{qt} \exp(ikx) \tag{5.3}$$

The critical field strength E_c for unstable waves may be derived as (Pokorny *et. al.*, 2008):

$$E_c = \sqrt[4]{4\gamma\rho g / \varepsilon^2} \tag{5.4}$$

From Equation (5.4) follows a threshold condition $\frac{1}{2}\varepsilon E_c^2 = \frac{\gamma}{a}$, where $a = \sqrt{\frac{\gamma}{\rho g}}$ is the capillary length, frequently used in colloid chemistry and wetting theory (Pokorny *et. al.*, 2008). Accordingly, the threshold condition may be interpreted as the equilibrium of the pressures due to electric forces $\frac{1}{2}\varepsilon E_c^2$ and that of the capillary forces, $\frac{\gamma}{a}$, following Young-Laplace equation, where the role of a mean surface curvature is played by $1/a$. The capillary length represents the hidden/latent characteristic length scale of needle-less electrospinning from free liquid surfaces. It is convenient to define a dimensionless electrospinning number Γ as $\frac{a\varepsilon E_0^2}{2\gamma}$, which differs from the one introduced by Shenoy *et. al.* (Shenoy *et. al.*, 2005). Using this definition, electrospinning is initiated only if $\Gamma \geq 1$, its critical value reaches $\Gamma_C = 1$. Minimal and negative square values of the angular frequency ω^2 correspond to the maximal growth factors, *q*'s, inherently connected with the self-organisation caused by the mechanism of the fastest forming instability. The minimal value of ω^2 with respect to *k* is obtained by solving $\frac{d\omega^2}{dk} = 0$, thus obtaining two solutions k_1 and k_2, that are expressed together as:

$$k_{1,2} = \frac{2\varepsilon E_0^2 \pm \sqrt{\left(2\varepsilon E_0^2\right)^2 - 12\gamma\rho g}}{6\gamma} \tag{5.5}$$

Minimum of ω^2 occurs at that value of *k*, whichever is greater (Pokorny *et. al.*, 2008). Since, the average inter-jet distance is described in terms of the wavelength, $\lambda = 2\pi / k$, its dependency on E_0 is governed by the relation $\lambda = \frac{12\pi\gamma}{2\varepsilon E_0^2 + \sqrt{\left(2\varepsilon E_0^2\right)^2 - 12\gamma\rho g}}$ (Pokorny *et. al.*, 2008). This can be expressed more comprehensively using the capillary length, *a*, and the previously introduced electrospinning number Γ as $\lambda = \frac{3\pi\, a}{\Gamma + \sqrt{\Gamma^2 - 3/4}}$. Therefore, the critical wavelength, $\lambda_c = \frac{2\pi}{k_c} = 2\pi\, a$, may directly and easily be expressed with the capillary length, *a*. The relation between dimensionless intra-jet distance $\Lambda = \frac{\lambda}{a}$ and Γ given below:

$$\Lambda = \frac{3\pi}{\Gamma + \sqrt{\Gamma^2 - 3/4}} \tag{5.6}$$

is universal for needle-less electrospinning of all conductive liquids (Pokorny *et. al.*, 2008). The critical value of the dimensionless intra-jet distance is $\Lambda_C = 2\pi$.

The relaxation time, τ, and the electrospinning number, Γ. may be expressed through a dimensionless wave number $K = \frac{2\pi}{\Lambda} = ak$ that belongs to the fastest growing wave as $\tau = \frac{1}{\mathrm{Im}(\omega)} = \sqrt{\frac{a}{g}}\sqrt{\frac{3}{2K(K\Gamma - 1)}}$ (Pokorny *et. al.*, 2008). The quantity $\sqrt{\frac{a}{g}}$ represents a characteristic time-scale of the system and hence a relation between dimensionless relaxation time $T = \frac{\tau}{\sqrt{a/g}}$ and Γ can be related comprehensively as:

$$T = \sqrt{\frac{3}{2K(K\Gamma - 1)}} \tag{5.7}$$

The dependence of T on Γ is universal for all conductive liquids and holds for $\Gamma \geq 1$ (Pokorny *et. al.*, 2008). The characteristic time scale $\sqrt{a/g}$ is of the order of time during which a body travels through a distance, equivalent to the capillary length, a , after it is released and to have a free fall under gravity (Pokorny *et. al.*, 2008).

Experimental: Apparently, there exist two parallel theories explaining an onset of electrospinning: Taylor's for capillary spinners and the one framed here for electrospinning from free liquid surfaces. On the contrary, from the appropriate philosophical point of view of *Non-Dualism*, electrospinning as a phenomenon exists in its unity, independently on any theoretical tool used for its investigation and description (Wikipedia, 2008). Keeping this aspect in mind presently, the critical field strength for electrojetting (a limiting case of electrospinning) from free liquid surface (for distilled water), E_c, is firstly compared with E_c's for distilled water jets from capillaries of various radii *r*, measured by Zeleny (Pokorny *et. al.*, 2008). In his experiments, Zeleny applied no hydrostatic pressure to the liquid in the capillary, thus meeting a system of assumptions in the present analysis. It is assumed for this moment that electrospinning from a needle/capillary in conventional electrospinners may occur only under the condition that the needle diameter, *2r*, approaches the wavelength of the fastest growing wave, predicted by the newly introduced theory of free liquid surface electrospinning. Critical field strengths, according to Zeleny's observations are plotted for capillary radii, *r*, up to 2*r* = 1.086 mm. For greater capillary radii, Zeleny's extrapolation formula $E\sqrt{r} = 56.9 * 30000\ Vm^{-1/2}$ is used (Pokorny *et. al.*, 2008). The curves show that critical field strength, predicted by the present theory and Zeleny's experimental data set are quite comparable. Therefore, the theory in question and the above assumption that the critical field strength value, E_C, allows the creation of surface wave whose wavelength λ is quite comparable to the capillary diameter 2*r*, are positively confirmed (Pokorny *et. al.*, 2008).

Dimensionless wavelength, Λ, versus electrospinning number, Γ, is plotted with experimental data (Pokorny *et. al.*, 2008), obtained from linear clefts, with which very dilute aqueous solutions of polyvinyl-alcohol were spun. Fresh 8% solutions were prepared by dissolving the Poly-vinyl-alcohol in distilled water (Pokorny *et. al.*, 2008). For the stabilizing the solutions' surface tension, 2 % (v/v) Butyl-alcohol was added. Surface tension, *γ*, of the solution was 48 mN/m. The temperature during the observations was $21^{o}C \pm 2^{o}C$ and the relative moisture was $73\% \pm 2\%$. The solution density, ρ , was 879.5 kg $m^{-3} \pm 0.5$ kg m^{-3}.

Electrospinning of free liquid surface was carried out with stainless steel linear cleft, having outer length, $L = 70.46 \pm 0.07$ mm, inner length 60.03 ± 0.03, height, $H = 20.08 \pm 0.02$ mm, breadth, $b = 0.30 \pm 0.2$ mm, and outer width $w = 2.87 \pm 0.02$ mm. Upper edges of both the plates were serrated. The serrations hindered spilling of the polymeric solution from the cleft to a certain extent. Distance between neighbouring teeth was 1.68 ± 0.02 mm and their height was $2.03 \pm .003$ mm. The clefts, emitting polymeric (polyvinyl alcohol) jets at the voltage 32kV and 43 kV (as a gross observation on inhomogeneous medium), are portrayed below:

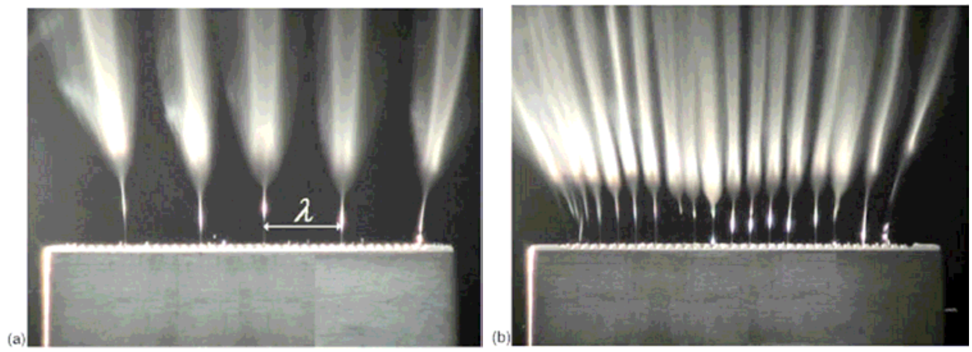

Fig. 5.1. Linear clefts emit polymeric jets. Clefts in (a) and (b) emit polymeric polyvinyl alcohol jets at the voltages, 32 and 43 kV, respectively. The interjet distance/wavelength is λ.

The circular metallic collector had diameter of $149{,}9 \pm 0{,}1$ mm. The distance between the cleft and the collector was kept at distances of 70-90 mm. The distance was constant for each series of experiments (Pokorny *et. al.*, 2008). Linear clefts were supplied with polymeric solution at volume rate of 6 - 15 ml/hour using linear pump or with hydrostatic pressures corresponding to 15 - 55 cm of water column. Field strengths (Pokorny *et. al.*, 2008) were calculated from voltage values assuming a linear relationship between them for particular spinner geometry representing particular distance between the cleft and the collector. The proportionality constant was determined from the critical voltage, i.e. the lowest voltage for which jets appear, and from the critical field strength value predicted by Equation (5.4). The dependence of Λ on the electrospinning number, Γ, from the theoretical prediction is qualitatively similar to that obtained from experiments (Pokorny *et. al.*, 2008). Standard deviations of experimental data, i.e of Λ, are, however, large as compared to corresponding average values since, the system is enormously sensitive to a large number of parameters, like, surface tension and concentration fluctuations, mutual adjustment of the position of the cleft and collector, feeding rate of the cleft with the polymer solution and curvature of the liquid surface in the cleft.

6. Electrospinning as an Application of the Physical Law of Dielectric Diffusion:

In an effort to overcome the physical shortcoming of the wave theory (Pokorny *et. al.*, 2008), based on mostly a mathematical approach to explain electrohydrodynamics, an even more generalized and robust physical approach is adopted **(**Sarkar *et. al.,* 2008). Changing the strandpoint in describing the systém from minimisation of superficial energy, characterised by the asscoiated wave's angular frequency, to the one considering minimisation of energy stored inside a 'condenser' by a medium of a certain permittivity seems to have ability not only to describe the detailed dynamics in that zone, but even able to unify all electrohydrodynamic phenomena, like, electrospinning, electrospinning, electrocapillarity, and electrophoresis (Sarkar *et. al.,* 2008).

The phenomenon of *Dielectric Diffusion* was firstly reported by Breuer and Robinson (Breuer and Robinson, 1969) as,'*When an electric field interacts with a medium of inhomogeneous dielectric constant, there is a flow of matter in the direction of increasing dielectric constant*'. The stated phenomenon, however may appropriately through 'minimization of energy in a capacitor' (Sarkar *et. al.,* 2008).

Minimization of energy in a capacitor: The actual permittivity of a material in an electric field is a product of permittivity of vacuum and relative permittivity of the medium (Feynman, 1971) that indicates how the material behaves in an external electric field, i.e., ability to get polarized under external electrostatic field. The resultant electric field intensity decreases due to higher polarisation of the more conductive medium, and as it depends non-linearly on electric field intensity, the overall energy of the system decreases eventually. Accordingly, when an electric field interacts with an inhomogeneous medium having different dielectric constants, matter with lowest dielectric constant tends to fill the entire inter-collector space. The energy stored in a capacitor in a way reflects the energy stored between the two poles of the power supply to it. Thus, ideally (neglecting internal resistance of the supply and the wire), the two plates of the capacitor have a tendency towards arriving equipotential condition by reducing the energy stored between them. In other words, the mass of the dielectric in the capacitor required to minimize the energy depends indirectly on its permittivity, determining its conductivity. In all practical cases there is a potential drop across the inter-plate gap due to resistance and therefore, a competition between the dielectrics when an inhomogeneous medium fills the charged capacitor.

Force acting on a solid dielectric in an electric field: According to Feynman, the force, *F*, acting on a *solid dielectric slab*, partially inserted in a parallel plate capacitor (Fig. 6.1), of width *W* tries to push the material into the inter-plate region to fill it, and is quantitatively derived using conservation of energy as (Feynman, 1971):

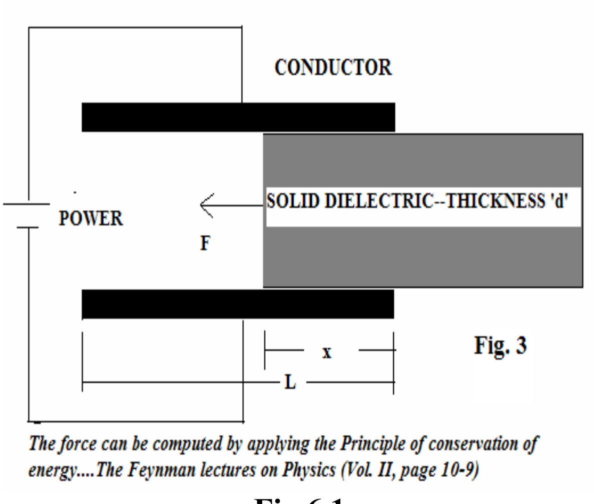

Fig 6.1

$$F_x = -\frac{\partial U}{\partial x} = -\frac{Q^2}{2}\frac{\partial}{\partial x}\left(\frac{1}{C}\right) = \frac{V^2}{2}\frac{\varepsilon_0 W}{d}(\kappa - 1) \qquad (6.1)$$

Where the symbols *U, Q, C,* ε_0, and κ stand for the energy stored in the condenser, the charge on the condenser , capacitance, permittivity of vacuum and dielectric constant of the material, respectively.

7. Solvent Evaporation:

One of the most fascinating features of electrospinning is the ability of the spun fibre to oust small solvent molecules during extremely short period of time when the jet travels from the electrode to the collector. The principle of the phenomenon leading to the evaporation of more than 80% of the solution from the jet during a fraction of second has its explanation in the realm of thermodynamics (Lukas *et. al.*, 2008).

One can distinguish two components of the energy, U , of each thermodynamic system that are particularly involved in a liquid. One of them is called the free, or Helmholtz energy, *F*, representing the part of the liquid energy U that is used to do a work that is sometimes connected with voluminous changes. The other part of the liquid energy is connected with entropy part of the total energy U that can never be obtained from the system by exploiting it at a constant temperature. This "hidden" part of the system energy is expressed as the product of entropy S and temperature T. From the foregoing follows

$$F = U - ST \qquad (7.1)$$

Then the differential free energy, dF, has the shape

Since entropy is supposed to be a function of energy U, the number of particles N, and volume V, thus $S = S(U, N, V)$, its differential has the following structure (Lukas *et. al.*, 2008)

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV \qquad (7.2)$$

where indices V, N, and U denote constant quantities for the particular differentiation. The three particular derivatives in (14) have well-known meanings[62] that are:

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T}, \qquad \left(\frac{\partial S}{\partial N}\right)_{U,V} = -\frac{\mu}{T}, \qquad \left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{p}{T} \qquad (7.3)$$

where μ is chemical potential and p denotes pressure. Thus, one obtains:

$$dF = \mu dN - pdV - SdT \qquad (7.4)$$

Equation (16) is the thermodynamic relation to which behaviour of liquids with curved surfaces may be associated. The introductory step is the assumption of a constant temperature during processes when the surface curvature changes. It means the last term on the right side of (16) is considered null. The next step is to introduce into the equation in question only measurable quantities. Hence, instead of the free energy differential dF, the free energy density $f = dF / dV$ is considered further to obtain the following relation.

$$f = \left(\frac{dF}{dV}\right)_T = \mu c - p \qquad (7.5)$$

where particle volume concentration c has been defined as, $c = dN / dV$. Changing the liquid surface curvature, the pressure, p, varies according to the Laplace's law while free energy density, f , as well as concentration, c , are supposed to remain unchanged. So, from the free energy density conservation, one obtains:

$$\mu_f c - p_f = \mu_c c - p_c \qquad (7.6)$$

Hence, the pressure increment, $\Delta p = p_c - p_f$, between a curved liquid, indexed with c, and a flat one, indexed with f, has to be balanced by the adequate increase of chemical potential $\Delta\mu = \mu_c - \mu_f$ that is naturally multiplied by the concentration c. Indices of μ are similar to those of p. The general form of Laplace/capillary pressure for a curved surface is expressed as $p = \gamma\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$ where $1/r_1$ and $1/r_2$ are two main curvatures belonging to main radii r_1 and

r_2. A nearly cylindrical liquid jet, related to electrospinning, has one of the radii of infinite value while the last one is equal to the jet radius r at a chosen distance z along its path from the Taylor cone. Therefore, (7.6) may be written as:

$$\Delta\mu = \frac{1}{c}\frac{\gamma}{r} \tag{7.7}$$

The last relation particularly expresses the Thomson-Kelvin law (Lukas *et. al*., 2008). Thompson-Kelvin law is based on condition of thermodynamic equilibrium. Though apparently it may be seem that the resultant relationship does not lead to any equality of chemical potentials since constant temperature, pressure, and chemical potentials are necessary conditions for thermodynamic equilibriums, yet one may consider the ambient air to act as an enormously huge thermodynamic reservoir where chemical potential remains nearly unchanged during jet evaporation. Then particles will flow from areas at higher chemical potential to the areas with lower chemical potential. Since all the quantities of right hand side of (7.6) are positive, $\Delta\mu$ is positive. Thus, $\mu_c > \mu_f$ and accordingly particles will flow from the jet to the ambient air. The difference in chemical potentials increases with elongation and evaporation of the jet/fibre. Both these processes lead to the accelerated evaporation. Due to the polymeric nature, the solution of the jet evaporates selectively. Solvent molecules escape to the ambient air while polymeric chains remain in the jet to form solid fibre. In this way, electrospinning works as a very effective dryer.

8. Phenomenon of Wetting of Cylindrical Fibre:

The concept of energy minimisation in a condenser (Pokorny *et. al*., 2008 and Sarkar *et. al*., 2008) used to describe and simulate Rayleigh Plateau instability of liquid film on a cylindrical fibre, axially oriented along gravity (Pociute *et. al*., 2008). The classic theory of Rayleigh-Plateau instability, expressed through a suitable dispersion law (Pociute *et. al*., 2008), based on a hyper geometric, modified Bessel function, for wetting phenomenon of cylindrical fibre, gave very close similarity with that of 'electrohydrodynamics' as involved in electrospinning earlier. The only slight difference between the two phenomena is that in electrospinning, as the electric field intensity can be varied without any limit, the square of the angular frequency, ω^2, from the dispersion equation, does not have any lower limit beyond zero. In wetting phenomenon, however, the value of ω^2 is limited due to fixed value of gravity (Pociute *et. al*., 2008). This also indirectly indicates a dependency of the relative nature of the electric and gravity fields on the process of electrohydrodynamics. The computer simulation for the phenomenon is carried out successfully on the principle of energy minimisation (Pociute *et. al*., 2008), and, thus, bridging the wetting pheomenon with the theory of 'Dielectric Diffusion' and the wave theory.

9. Some Physical Applications and their Underlying Principles:

9.1. Grid Collector: For an electrostatically charged grid of wires, wherein the wires are placed parallel to each other, the electric field intensity, above and below the wires are identical (Feynman, 1971). It may be analysed and verified through experiment (Goyal *et. al*., 2006) that the electrostatic field decreases exponentially with a characteristic length scale as one moves away from the array of conducting wires. Within a distance from the lattice that is not greater than several lattice constant, the field is nearly homogeneous because the oscillation is negligible (Goyal *et. al*., 2006). In spite of their whipping and gyration of their path, nanofibres can be strongly attracted by inhomogeneous electrostatic field in the close vicinity of a collector. Nanofibre layer could be collected on a printed circuit board with long, thin parallel arrays of conducting strip of metals, separated from each other by a certain gap, (Goyal *et. al*., 2006).

9.2. Bilateral Electrospinner: Knowing the basic behaviour of liquid drops in an electric field (Chugh *et. al*., 2006), a 'bilateral electrospinner' was designed to hold an elongated drop of liquid, like that of conductive rain water in air with the help of two hypodermic needles, oriented horizontally with each of the orifices facing their corresponding collectors. One of the collectors was grounded while the other was supplied a negative high D.C potential. The hypodermic needles were connected to a vertically placed burette for desired supply of liquid. It is notable that the liquid level in it contributed to an additional hydrostatic pressure / linear pump to the liquid drop. The polymer flow was manipulated using a stop valve. The insulating material of the burette enabled it to be conveniently clamped to a metallic stand. Construction of the spinner is sketched in Fig. 9.3. Considering theoretical aspect of the bilateral electrospinner, an analysis of surface charge density on a thin conductive cylinder, placed in an electric field becomes somewhat indispensable.

If $\tau(\acute{z})$ is the linear charge density of the rod of a radius *a*, where $\acute{z}$ is any point on the length, *l*, of the rod (Fig.9.1), then it may be derived (Chugh, *et. al*. 2006) that $\tau(z) = \frac{Ez}{\ln\left(\frac{4(l^2 - z^2)}{a^2}\right) - 2}$. Plotting for ($\tau(z)/E$) v/s *z*, *ta*king a=1 mm and l/a = 100, Fig. 9.2 is obtained.

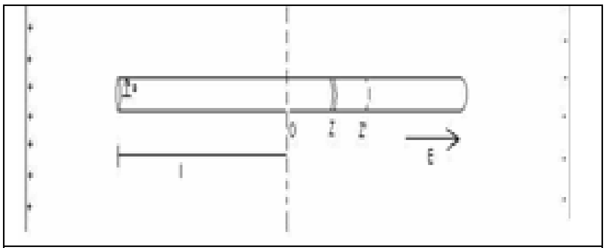

Figure 9.1: *Conductive rod in electric field*

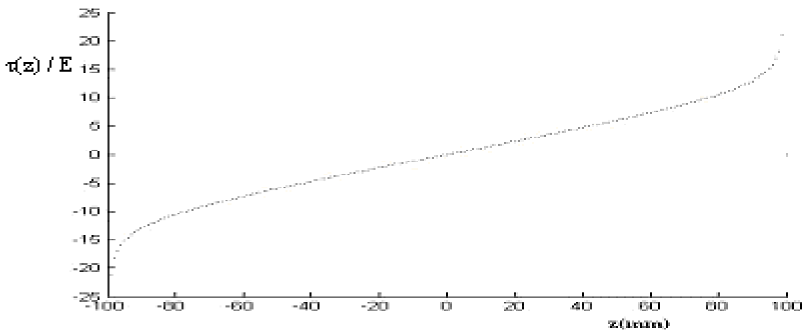

Figure 9.2:*Graph for* ($\tau(z)/E$) v/s *z*

Experimental Results

Fig.9.3 shows the experimental setup. The main objective was to observe critical voltages required for the spinning of nano-fibers with varying parameters.

Firstly, with three different PVA concentrations and the distance, d, between the orifice of the needle and the plate as 36mm, the diameter of the needle was varied. Critical voltages for the jets were observed (Figure 9.4). It was found that critical voltages varied

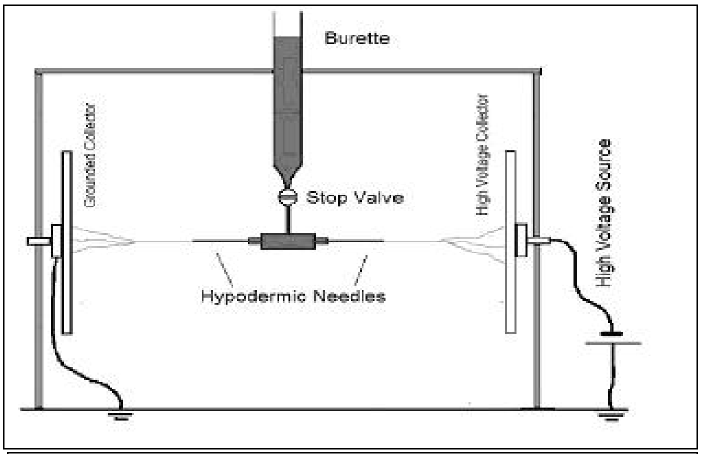

Figure 9.3: *Bilateral Electrospinner. (Courtesy Sandra Torres)*

inversely with PVA conc. and the critical voltages for the needle directed towards the grounded collector was higher. Secondly, experiments were carried out for distilled water and 12% PVA solution by varying the lengths of the needle and keeping the other parameters same (Table 9.1& 9.2). Needle plate distance was 34 mm.

Table 9.1:Critical Voltages for 0.7x2.5 mm needles

Plate \ Fluid	Distilled water	12% PVA
Negative	11 KV	8 KV
Grounded	19 KV	14 KV

Table 9.2:Critical Voltages for 0.7x25mm needles

Plate \ Fluid	Distilled water	12% PVA
Negative	8 KV	7 KV
Grounded	14 KV	13 KV

It can be seen that critical voltages required for smaller length needle is greater as compared to longer needles. This is probably due to less energy stored in the 'condenser zone' for shorter needles that has lesser surface area to accommodate charge.

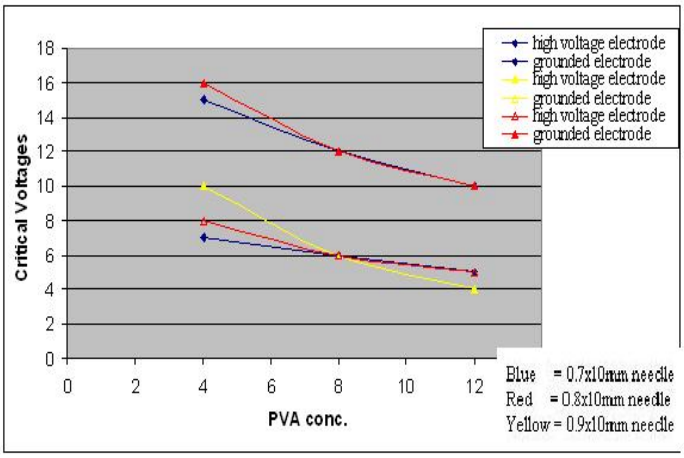

Figure 9.4 *Variation of critical voltages with varying PVA conc.*

Conclusion: The one-dimensional electrohydrodynamic theory of electrospinning from free surfaces of conductive liquids seems to complement the existing Taylor's analysis of capillary electrospinning (Taylor, 1969). While Taylor mainly concerned geometry of a liquid cone and critical voltage in the context of electric and capillary pressures acting there at equilibrium, this one adds a more generalized approach towards studying dynamics of surface waves. This approach leads to the discovery of the pair of electrospinning fundamental parameters, like, capillary length, *a*, and characteristic time scale, $\sqrt{\frac{a}{g}}$. Also, a set of three inherent dimensionless quantities is defined. These are electrospinning number, Γ, dimensionless wavelength, Λ, and dimensionless relaxation time, *T*, which efficiently characterize the process (Pokorny *et. al.*, 2008). The criticality appears for universal value of the electrospinning number, $\Gamma_c = 1$. The dimensionless wavelength in criticality is also universal for all conductive liquids, $\Lambda_c = 2\pi$. The theory is able to describe the dimensionless inter-jet distance Λ, even for electrospinning numbers Γ above the critical value, Γ_c, by the universal relationship (5.6). Moreover this approach reveals the universal relationship between the dimensionless relaxation time, *T*, and electrospinning number, Γ, viz. equation (5.7).

In an attempt to further generalize the phenomena of electro-hydrodynamics to describe the phenomena through ‘Energy minimisation‘ in a condenser, the theory of ‘*Dielectric Diffusion*‘ has been proposed, *which is presently under the process of further development* to explain them in detail. In this regard, it is worthwhile to remark that the theory for Bilateral electrospinner, as derived by Landau, also indicates that the, capacitance of the systém greatly influences the perofrmance of the dynamics and /or the technology of, electrospinning‘ itself, thus, indirectly supporting the concept of *Dielectric Diffusion* as the more fundamental reason behind behaviour of liquids in an electric field. Moreover, success of the same concept in explaining wetting phenomenon‘ (Pociute *et. al*., 2008) unfies the three theories completely.

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6. Chugh V., Sarkar A., Pokorný P., and Lukáš D. :”Disintegration of Liquid Drops and Bilateral Electrospinner”, *13th STRUTEX*, Liberec, November 2006;
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Summary: In an effort to realise the *physical principle(s) of electrospinning*, effort has been made to understand the pioneering experimental works of Zeleny (Lukas *et. al.,* 2008) along with theoretical foundation (Lukas *et. al.,* 2008) and its evolution (Landau, 1960; Gray, 1953). Subsequently the main effort has been generalization of the theory, starting from Zeleny's observation (Lukas *et. al.,* 2008) to the most fundamental phenomenon of Dielectric Diffusion by widening *the scope of analysis* within the limits of contmeporaneous scientific progress. However, the theory is under the process of further development. Allied instrumentation, to explore possibility of newer instrumentation, supported the formulated theories. The theory also remarkably fit into the phenomenon of wetting of fibres, axially oriented along gravity.

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