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Volume 1 Physical Process, Methods, and Models

Editor Abbas Hamrang, PhD





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Edited by Abbas Hamrang, PhD

Gennady E. Zaikov, DSc, and A. K. Haghi, PhD Reviewers and Advisory Board Members



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LIST OF ABBREVIATIONS

18C6	18-crown-6
ACAC	Acetylacetonate ion
AFM method	Atomic-Force Microscopy method
ARD	Acireductone ligand
ASA	Active Surface Area
ATNMRI	Advanced Technologies and New Materials Research Institute
BEM	Boundary Element Method
BGK	Bhatnagar-Gross-Krook
BSA	Bovine Serum Albumin
BSQ	Band Sequential Format
Bu	Butyl radical
CHCl ₃	Chloroform
CO	Carbon monoxide
CTAB	Cetyltrimethylammonium bromide (Me ₃ (n-C ₁₆ H ₃₃)NBr)
CZCS	Coastal Zone Color Scanner
DMF	Dimethylformamide
DSMC	Direct Monte Carlo Simulation
EEZ	Exclusive Economic Zone
Et	Ethyl radical
GA	Glycidyl Methacrylate
Hacac	Acetylacetone
HDF	Hierarchial Data Format
HMPA	Hexamethylphosphorotriamide
IMAC	Immobilized Metal-Ion Affinity Chromatography
KPS	Potassium Persulphate
LEDs	Light Emitting Diodes
MD	Molecular Dynamics
Me	Methyl radical
Мо	Molybdenum
MODIS	Moderate Resolution Imaging Spectroradiometer
MP	N-methylpirrolidon-2

MPC	Methylphenylcarbinol
MSP	Methionine Salvage Pathway
MSt	Stearates of alkaline metals (M= Li, Na, K)
Ni(Fe)ARD	Ni(Fe)AcireductoneDioxygenase
NIR	Near Infrared
NNG	Nuclear grade Natural Graphite
NO	nitrogen monoxide
NSG	Nuclear grade Synthetic Graphite
OAc	Acetate ion
ODEs	Ordinary Differential Equations
PDEs	Partial Differential Equations
PEDA	Phosphorus-Boron-Nitrogen-Containing Oligomer
PEH	Phenyl ethyl hydro peroxide
PFZ	Potential Fishing Zones
QX	Quaternary ammonium salt
RH	Ethyl benzene
RLA	Repeated Load Axial
RV	Rotational Viscometer
SEM	Scanning Electron Microscopy
SST	Sea Surface Temperature
TEG	Thermal Expanded Graphite
TGA	Thermogravimetric Analyzer
UV-spectrum	Ultra Violet-spectrum
ZnO	Nano Zinc Oxide

LIST OF SYMBOLS

t_n^e	axial viscous normal stress, N/m ²
t_t^e	pressure, N/m ²
Ī	mean segment length, m
χ	aspect ratio
σ	electric field
φ	fiber orientation angle
ν	jet velocity, m ³ /s
y(j,l)	length distribution
τ,,	dielectric constant of the jet, N/m^2
<qq></qq>	suspension configuration tensor, N/m ²
A	accumulation built up within the system
A(s), S	current density, m ²
С	consumption used in system volume
G	generation produced in system volume
h	distance from pendent drop to ground collector
Ι	input entering through the system surface
J	jet current
K	Boltzmann's constant
m	equivalent mass
0	output leaving through system boundary
P'	polarization
Р	spinning distance
Q	flow rate, m ³ /s
R'	jet axial position
R	radius of jet, m

R ₀	initial radius
U _e	normal electric force, V
v	kinematic viscosity
\mathbf{V}_{0}	applied voltage
W _e	tangential electric force, M
β	Galactosidase and Bovine Serum Albumin
γ	surface tension of the fluid
ε'	Lagrangian axial strain
З	slope of the jet surface, J
З	surface tension
ρ	density of the fluid
$\sigma_{_{ m V}}$	viscoelastic stress
τ	relaxation time of the polymer

PREFACE

This volume highlights the latest developments and trends in materials science and engineering. It presents the developments of advanced materials and respective tools to characterize and predict the material properties and behavior. This book has an important role in advancing materials science and engineering in macro and nanoscale. Its aim is to provide original, theoretical, and important experimental results that use non-routine methodologies often unfamiliar to the usual readers. It also includes chapters on novel applications of more familiar experimental techniques and analyses of composite problems that indicate the need for new experimental approaches.

The book is for professors and instructors of specific teaching courses, students and postgraduate students focusing on adhesive interaction improvement, and industry professionals working in materials science.

In chapter 1, a new approach in nanostructured materials is a computational-based material is developed. This is based on multiscale material and process modeling spanning on a large spectrum of time as well as on length scales. The cost of designing and producing novel multifunctional nanomaterials can be high and the risk of investment can be significant. Computational nanomaterials research that relies on multiscale modeling has the potential to significantly reduce development costs of new nanostructured materials for demanding applications by bringing physical and microstructural information into the realm of the design engineer.

Chapter 2 is focused on metals immobilization, and selected membranes with highest sulphonation degree were immobilized.

The study presented in chapter 3 was undertaken with the objective of evaluating the correlation of the chlorophyll a and sea surface temperature derived from the satellite MODIS.

Mechanisms of catalysis with binary and triple catalytic systems is investigated in chapter 4. Synthesis of synthetic mineral-based alloys liquation phenomena of differentiation is reviewed in chapter 5.

The aim of chapter 6 was to study structural changes in siminals, specifically raw hornblendite materials, under shock impact.

The purpose of chapter 7 was obtaining fire-retardant coatings based on perchlorovinyl resin with improved adhesive properties to protect fiberglass plastics. The chapter presents the results of studies on the influence of a modifier based on the phosphorus-boron-nitrogen-containing oligomer (PEDA) and filler, which is thermal-expanded graphite on physical, mechanical and fire retardant properties of the coatings.

The goal of chapter 8 is to evaluate the influence of nano ZnO on the engineering properties of bitumen and asphalt concrete mixtures. For this purpose, the authors performed penetration grade, softening point, ductility, and rotational viscometer (RV) tests on modified bitumen by four different content of nano ZnO and repeated load axial (RLA) test on asphalt concrete mixtures by three different content of nano ZnO. With the experimental results and the numerical analysis with Matlab Software, two experimental models were proposed for prediction of the creep behavior of both conventional and modified asphalt mixtures with optimum nano ZnO for different conditions depending on temperature and stress.

Microstructural complexity of natural and synthetic graphite particles is reviewed in chapter 9.

-Abbas Hamrang, PhD

ADVANCES IN ELECTROSPUN NANOFIBERS MODELING: AN OVERVIEW

S. RAFIEI, S. MAGHSOODLOU, B. NOROOZI, and A. K. HAGHI

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1.1 AN INTRODUCTION TO NANOTECHNOLOGY

The nanostructure materials productions are most challenging and innovative processes, introducing, in the manufacturing, a new approaches such as self-assembly and self-replication. The fast growing of nanotechnology with modern computational/experimental methods gives the possibility to design multifunctional materials and products in human surroundings. Some of them are smart clothing, portable fuel cells, and medical devices are some of them. Research in nanotechnology began with applications outside of everyday life and is based on discoveries in physics and chemistry. The reason for that is needed to understand the physical and chemical properties of molecules and nanostructures in order to control them.

A new approach in nanostructured materials is a computational-based material development. It is based on multiscale material and process modeling spanning, on a large spectrum of time as well as on length scales. The cost of designing and producing novel multifunctional nanomaterials can be high and the risk of investment to be significant. Computational nanomaterials research that relies on multiscale modeling has the potential to significantly reduce development costs of new nanostructured materials for demanding applications by bringing physical and microstructural information into the realm of the design engineer.

One of the most significant types of these one-dimensional nanomaterials is nanofibers, which can be produced widely through electrospinning procedure. A drawback of this method, however, is the unstable behavior of the liquid jet, which causes the fibers to be collected randomly. So a critical concern in this process is to achieve desirable control. Studying the dynamics of electrospinning jet would be easier and faster if it can be modeled and simulated, rather than doing experiments. This chapter focuses on modeling and then simulating of electrospinning process in various views. In order to study the applicability of the electrospinning modeling equations, which discussed in detail in earlier parts of this approach, an existing mathematical model in which the jet was considered as a mechanical system was interconnected with viscoelastic elements and used to build a numeric method. The simulation features the possibility of predicting essential parameters of electrospinning process and the results have good agreement with other numeric studies of electrospinning, which modeled this process based on axial direction.

Understanding the nanoworld makes up one of the frontiers of modern science. One reason for this is that technology based on nanostructures promises to be hugely important economically [1–3]. Nanotechnology literally means any technology on a nanoscale that has applications in the real world. It includes the production and application of physical, chemical, and biological systems at scales ranging from individual atoms or molecules to submicron dimensions, as well as the integration of the resulting nanostructures into larger systems. Nanotechnology is likely to have a profound impact on our economy and society in the early twentyfirst century, comparable to that of semiconductor technology, information technology, or cellular and molecular biology. Science and technology research in nanotechnology promises breakthroughs in areas such as materials and manufacturing [4], nanoelectronics [5], medicine and healthcare [6], energy [7], biotechnology [8], information technology [9], and national security [10]. It is widely felt that nanotechnology will be the next Industrial Revolution [9].

As far as "nanostructures" are concerned, one can view this as objects or structures whereby at least one of its dimensions is within nano-scale. A "nanoparticle" can be considered as a zero dimensional nano-element, which is the simplest form of nanostructure. It follows that a "nanotube" or a nanorod" is a one-dimensional nano-element from which slightly more complex nanostructure can be constructed of [11-12].

Following this fact, a "nanoplatelet" or a "nanodisk" is a two-dimensional element, along with its one-dimensional counterpart, which is useful in the construction of nanodevices. The difference between a nanostructure and a nanodevice can be viewed upon as the analogy between a building and a machine (whether mechanical, electrical or both) [1]. It is important to know that as far as nanoscale is concerned; these nano-elements should not consider only as an element that form a structure while they can be used as a significant part of a device. For example, the use of carbon nanotube as the tip of an Atomic Force Microscope (AFM) would have it classified as a nanostructure. The same nanotube, however, can be used as a singlemolecule circuit, or as part of a miniaturized electronic component, thereby appearing as a nanodevice. Therefore the function, along with the structure, is essential in classifying which nanotechnology subarea it belongs to. This classification will be discussed in detail in further sections [11, 13].

As long as nanostructures clearly define the solids' overall dimensions, the same cannot be said so for nanomaterials. In some instances a nanomaterial refers to a nano-sized material while in other instances a nanomaterial is a bulk material with nano-scaled structures. Nanocrystals are other groups of nanostructured materials. It is understood that a crystal is highly structured and that the repetitive unit is indeed small enough. Hence a nanocrystal refers to the size of the entire crystal itself being nano-sized, but not of the repetitive unit [14].

Nanomagnetics are the other type of nanostructured materials, which are known as highly miniaturized magnetic data storage materials with very high memory. This can be attained by taking advantage of the electron spin for memory storage, hence the term "spin-electronics," which has since been more popularly and more conveniently known as "spintronics" [1, 9, 15]. In nanobioengineering, the novel properties of nano-scale are taken advantage of for bioengineering applications. The many naturally occurring nanofibrous and nanoporous structure in the human body further adds to the impetus for research and development in this subarea. Closely related to this is molecular functionalization whereby the surface of an object is modified by attaching certain molecules to enable desired functions to be carried out such as for sensing or filtering chemicals based on molecular affinity [16–17].

With the rapid growth of nanotechnology, nanomechanics are no longer the narrow field, which it used to be [13]. This field can be broadly categorized into the molecular mechanics and the continuum mechanics approaches which view objects as consisting of discrete many-body system and continuous media, respectively. As long as the former inherently includes the size effect, it is a requirement for the latter to factor in the influence of increasing surface-to-volume ratio, molecular reorientation and other novelties as the size shrinks. As with many other fields, nanotechnology includes nanoprocessing novel materials processing techniques by which nano-scale structures and devices are designed and constructed [18, 19].

Depending on the final size and shape, a nanostructure or nanodevice can be created from the top-down or the bottom-up approach. The former refers to the act of removal or cutting down a bulk to the desired size, while the latter takes on the philosophy of using the fundamental building blocks—such as, atoms and molecules, to build up nanostructures in the same manner. It is obvious that the top-down and the bottom-up nanoprocessing methodologies are suitable for the larger and two smaller ends, respectively, in the spectrum of nano-scale construction. The effort of nanopatterning—or patterning at the nanoscale would therefore fall into nanoprocessing [1, 12, 18].

1.2 NANOSTRUCTURED MATERIALS

Strictly speaking, a nanostructure is any structure with one or more dimensions measuring in the nanometer (10^{-9} m) range. Various definitions refine this further, stating that a nanostructure should have a characteristic dimension lying between 1 nm and 100 nm, putting nanostructures as intermediate in size between a molecule and a bacterium. Nanostructures are typically probed either optically (spectroscopy, photoluminescence, etc.) or in transport experiments. This field of investigation is often given the name mesoscopic transport, and the following considerations give an idea of the significance of this term [1, 2, 12, 20, 21].

What makes nanostructured materials very interesting and award them with their unique properties is that their size is smaller than critical lengths that characterize many physical phenomena. Generally, physical properties of materials can be characterized by some critical length, for example, a thermal diffusion length, or a scattering length. The electrical conductivity of a metal is strongly determined by the distance that the electrons travel between collisions with the vibrating atoms or impurities of the solid. This distance is called the mean free path or the scattering length. If the sizes of the particles are less than these characteristic lengths, it is possible that new physics or chemistry may occur [1, 9, 17].

Several computational techniques have been employed to simulate and model nanomaterials. Since the relaxation times can vary anywhere from picoseconds to hours, it becomes necessary to employ Langevin dynamics besides molecular dynamics in the calculations. Simulation of nanodevices through the optimization of various components and functions provides challenging and useful task [20, 22]. There are many examples where simulation and modeling have yielded impressive results, such as nanoscale lubrication [23]. Simulation of the molecular dynamics of DNA has been successful to some extent [24]. Quantum dots and nanotubes have been modeled satisfactorily [25, 26]. First principles calculations of nanomaterials can be problematic if the clusters are too large to be treated by Hartree–Fock methods and too small for density functional theory [1]. In the next section various classifications of these kinds of materials are considered in detail.

1.2.1 CLASSIFICATION OF NANOSTRUCTURED MATERIALS

Nanostructure materials as a subject of nanotechnology are low dimensional materials comprising of building units of a submicron or nanoscale size at least in one direction and exhibiting size effects. The first classification idea of NSMs was given by Gleiter in 1995 [3]. A modified classification scheme for these materials, in which 0D, 1D, 2D and 3D dimensions are included suggested in later researches [21]. These classifications are as follows:

1.2.1.1 0D NANOPARTICLES

A major feature that distinguishes various types of nanostructures is their dimensionality. In the past 10 years, significant progress has been made in the field of zero-dimension nanostructure materials. A rich variety of physical and chemical methods have been developed for fabricating these materials with well-controlled dimensions [3, 18]. Recently, 0D nanostructured materials such as uniform particles arrays (quantum dots), heterogeneous particles arrays, core–shell quantum dots, onions, hollow spheres and nanolenses have been synthesized by several research groups [21]. They have been extensively studied in light emitting diodes (LEDs), solar cells, single-electron transistors, and lasers.

1.2.1.2 1D NANOPARTICLES

In the last decade, 1D nanostructured materials have focused an increasing interest due to their importance in research and developments and have

a wide range of potential applications [27]. It is generally accepted that these materials are ideal systems for exploring a large number of novel phenomena at the nanoscale and investigating the size and dimensionality dependence of functional properties. They are also expected to play an important role as both interconnects and the key units in fabricating electronic, optoelectronic, and EEDs with nanoscale dimensions. The most important types of this group are nanowires, nanorods, nanotubes, nanobelts, nanoribbons, hierarchical nanostructures and nanofibers [1, 18, 28].

1.2.1.3 2D NANOPARTICLES

2D nanostructures have two dimensions outside of the nanometric size range. In recent years, synthesis of 2D nanomaterial has become a focal area in materials research, owing to their many low dimensional characteristics different from the bulk properties. Considerable research attention has been focused over the past few years on the development of them. 2D nanostructured materials with certain geometries exhibit unique shapedependent characteristics and subsequent utilization as building blocks for the key components of nanodevices [21]. In addition, these materials are particularly interesting not only for basic understanding of the mechanism of nanostructure growth, but also for investigation and developing novel applications in sensors, photocatalysts, nanocontainers, nanoreactors, and templates for 2D structures of other materials. Some of the three-dimension nanoparticles are junctions (continuous islands), branched structures, nanoprisms, nanoplates, nanosheets, nanowalls, and nanodisks [1].

1.2.1.4 3D NANOPARTICLES

Owing to the large specific surface area and other superior properties over their bulk counterparts' arising from quantum size effect, they have attracted considerable research interest and many of them have been synthesized in the past 10 years [1, 12]. It is well known that the behaviors of NSMs strongly depend on the sizes, shapes, dimensionality and morphologies, which are thus the key factors to their ultimate performance and applications. Therefore, it is of great interest to synthesize 3D NSMs with a controlled structure and morphology. In addition, 3D nanostructures are an important material due to its wide range of applications in the area of catalysis, magnetic material and electrode material for batteries [2]. Moreover, the 3D NSMs have recently attracted intensive research interests because the nanostructures have higher surface area and supply enough absorption sites for all involved molecules in a small space [58]. On the other hand, such materials with porosity in three dimensions could lead to a better transport of the molecules. Nanoballs (dendritic structures), nanocoils, nanocones, nanopillers and nanoflowers are in this group [1, 2, 18, 29].

1.2.2 SYNTHESIS METHODS OF NANOMATERIALS

The synthesis of nanomaterials includes control of size, shape, and structure. Assembling the nanostructures into ordered arrays often becomes necessary for rendering them functional and operational. In the last decade, nanoparticles (powders) of ceramic materials have been produced in large scales by employing both physical and chemical methods. There has been considerable progress in the preparation of nanocrystals of metals, semiconductors, and magnetic materials by employing colloid chemical methods [18, 30].

The construction of ordered arrays of nanostructures by employing techniques of organic self-assembly provides alternative strategies for nanodevices. Two and three-dimensional arrays of nanocrystals of semiconductors, metals, and magnetic materials have been assembled by using suitable organic reagents [1, 31]. Strain directed assembly of nanoparticle arrays (e.g., of semiconductors) provides the means to introduce functionality into the substrate that is coupled to that on the surface [32].

Preparation of nanoparticles is an important branch of the materials science and engineering. The study of nanoparticles relates various scientific fields, for example, chemistry, physics, optics, electronics, magnetism and mechanism of materials. Some nanoparticles have already reached practical stage. In order to meet the nanotechnology and nano-materials development in the next century, it is necessary to review the preparation techniques of nanoparticles. All particle synthesis techniques fall into one of the three categories: vapor-phase, solution precipitation, and solid-state processes. Although vapor-phase processes have been common during the early days of nanoparticles development, the last of the three processes mentioned above is the most widely used in the industry for production of micronsized particles, predominantly due to cost considerations [18, 33].

Methods for preparation of nanoparticles can be divided into physical and chemical methods based on whether there exist chemical reactions [33]. On the other hand, in general, these methods can be classified into the gas phase, liquid phase and solid phase methods based on the state of the reaction system. The gas phase method includes gas-phase evaporation method (resistance heating, high frequency induction heating, plasma heating, electron beam heating, laser heating, electric heating evaporation method, vacuum deposition on the surface of flowing oil and exploding wire method), chemical vapor reaction (heating heat pipe gas reaction, laser induced chemical vapor reaction, plasma enhanced chemical vapor reaction), chemical vapor condensation and sputtering method. Liquid phase method for synthesizing nanoparticles mainly includes precipitation, hydrolysis, spray, solvent thermal method (high temperature and high pressure), solvent evaporation pyrolysis, oxidation-reduction (room pressure), emulsion, radiation chemical synthesis and sol-gel processing. The solid phase method includes thermal decomposition, solid-state reaction, spark discharge, stripping, and milling method [30, 33].

In other classification, there are two general approaches to the synthesis of nanomaterials and the fabrication of nanostructures, bottom–up and top–down approach. The first one includes the miniaturization of material components (up to atomic level) with further self-assembly process leading to the formation assembly of nanostructures. During self-assembly the physical forces operating at nanoscale are used to combine basic units into larger stable structures. Typical examples are quantum dot formation during epitaxial growth and formation of nanoparticles from colloidal dispersion. The latter uses larger (macroscopic) initial structures, which can be externally controlled in the processing of nanostructures. Typical examples are etching through the mask, ball milling, and application of severe plastic deformation [3, 13].

Some of the most common methods are described in following:

1.2.2.1 PLASMA BASED METHODS

Metallic, semiconductive and ceramic nanomaterials are widely synthesized by hot and cold plasma methods. A plasma is sometimes referred to as being "hot" if it is nearly fully ionized, or "cold" if only a small fraction, (for instance 1%), of the gas molecules are ionized, but other definitions of the terms "hot plasma" and "cold plasma" are common. Even in cold plasma, the electron temperature is still typically several thousand centigrades. Generally, the related equipment consists of an arc melting chamber and a collecting system. The thin films of alloys were prepared from highly pure metals by arc melting in an inert gas atmosphere. Each arc-melted ingot was flipped over and remelted three times. Then, the thin films of alloy were produced by arc melting a piece of bulk materials in a mixing gas atmosphere at a low pressure. Before the ultrafine particles were taken out from the arc-melting chamber, they were passivized with a mixture of inert gas and air to prevent the particles from burning up [34–35].

Cold plasma method is used for producing nanowires in large scale and bulk quantity. The general equipment of this method consists of a conventional horizontal quartz tube furnace and an inductively coupled coil driven by a 13.56 MHz radio-frequency (RF or radio-frequency) power supply. This method often is called as an RF plasma method. During RF plasma method, the starting metal is contained in a pestle in an evacuated chamber. The metal is heated above its evaporation point using high voltage RF coils wrapped around the evacuated system in the vicinity of the pestle. Helium gas is then allowed to enter the system, forming high temperature plasma in the region of the coils. The metal vapor nucleates on the He gas atoms and diffuses up to a colder collector rod where nanoparticles are formed. The particles are generally passivized by the introduction of some gas such as oxygen. In the case of aluminum nanoparticles the oxygen forms a layer of aluminum oxide about the particle [1, 36].

1.2.2.2 CHEMICAL METHODS

Chemical methods have played a major role in developing materials imparting technologically important properties through structuring the mate-

rials on the nanoscale. However, the primary advantage of chemical processing is its versatility in designing and synthesizing new materials that can be refined into the final end products. The secondary most advantage that the chemical processes offer over physical methods is a good chemical homogeneity, as a chemical method offers mixing at the molecular level. On the other hand, chemical methods frequently involve toxic reagents and solvents for the synthesis of nanostructured materials. Another disadvantage of the chemical methods is the unavoidable introduction of byproducts, which require subsequent purification steps after the synthesis, in other words, this process is time consuming. In spite of these facts, probably the most useful methods of synthesis in terms of their potential to be scaled up are chemical methods [33, 37]. There are a number of different chemical methods that can be used to make nanoparticles of metals, and we will give some examples. Several types of reducing agents can be used to produce nanoparticles such as NaBEt, H, LiBEt, H, and NaBH, where Et denotes the ethyl $(-C_2H_2)$ radical. For example, nanoparticles of molybdenum (Mo) can be reduced in toluene solution with NaBEt,H at room temperature, providing a high yield of Mo nanoparticles having dimensions of 1-5 nm [30].

1.2.2.3 THERMOLYSIS AND PYROLYSIS

Nanoparticles can be made by decomposing solids at high temperature having metal cations, and molecular anions or metal organic compounds. The process is called thermolysis. For example, small lithium particles can be made by decomposing lithium oxide, LiN_3 . The material is placed in an evacuated quartz tube and heated to 400°C in the apparatus. At about 370°C the LiN_3 decomposes, releasing N₂ gas, which is observed by an increase in the pressure on the vacuum gauge. In a few minutes the pressure drops back to its original low value, indicating that all the N₂ has been removed. The remaining lithium atoms coalesce to form small colloidal metal particles. Particles less than 5 nm can be made by this method. Passivation can be achieved by introducing an appropriate gas [1].

Pyrolysis is commonly a solution process in which nanoparticles are directly deposited by spraying a solution on a heated substrate surface, where the constituent reacts to form a chemical compound. The chemical reactants are selected such that the products other than the desired compound are volatile at the temperature of deposition. This method represents a very simple and relatively cost-effective processing method (particularly in regard to equipment costs) as compared to many other film deposition techniques [30].

The other pyrolysis-based method that can be applied in nanostructures production is a laser pyrolysis technique, which requires the presence in the reaction medium of a molecule absorbing the CO, laser radiation [38, 39]. In most cases, the atoms of a molecule are rapidly heated via vibrational excitation and are dissociated. But in some cases, a sensitizer gas such as SF₆ can be directly used. The heated gas molecules transfer their energy to the reaction medium by collisions leading to dissociation of the reactive medium without, in the ideal case, dissociation of this molecule. Rapid thermalization occurs after dissociation of the reactants due to transfer collision. Nucleation and growth of NSMs can take place in the as-formed supersaturated vapor. The nucleation and growth period is very short time (0.1-10 ms). Therefore, the growth is rapidly stopped as soon as the particles leave the reaction zone. The flame-excited luminescence is observed in the reaction region where the laser beam intersects the reactant gas stream. Since there is no interaction with any walls, the purity of the desired products is limited by the purity of the reactants. However, because of the very limited size of the reaction zone with a faster cooling rate, the powders obtained in this wellness reactor present a low degree of agglomeration. The particle size is small (~5-50 nm range) with a narrow size distribution. Moreover, the average size can be manipulated by optimizing the flow rate, and, therefore, the residence time in the reaction zone [39, 40].

1.2.2.4 LASER BASED METHODS

The most important laser based techniques in the synthesis of nanoparticles is pulsed laser ablation. As a physical gas-phase method for preparing nanosized particles, pulsed laser ablation has become a popular method to prepare high-purity and ultra-fine nanomaterials of any composition [41, 42]. In this method, the material is evaporated using pulsed laser in a chamber filled with a known amount of a reagent gas and by controlling condensation of nanoparticles onto the support. It's possible to prepare nanoparticles of mixed molecular composition such as mixed oxides/nitrides and carbides/nitrides or mixtures of oxides of various metals by this method. This method is capable of a high rate of production of 2–3 g/min [40].

Laser chemical vapor deposition method is the next laser-based technique in which photoinduced processes are used to initiate the chemical reaction. During this method, three kinds of activation should be considered. First, if the thermalization of the laser energy is faster than the chemical reaction, pyrolytic and/or photothermal activation is responsible for the activation. Secondly, if the first chemical reaction step is faster than the thermalization, photolytical (nonthermal) processes are responsible for the excitation energy. Thirdly, combinations of the different types of activation are often encountered. During this technique a high intensity laser beam is incident on a metal rod, causing evaporation of atoms from the surface of the metal. The atoms are then swept away by a burst of helium and passed through an orifice into a vacuum where the expansion of the gas causes cooling and formation of clusters of the metal atoms. These clusters are then ionized by UV radiation and passed into a mass spectrometer that measures their mass: charge ratio [1, 41–43].

Laser-produced nanoparticles have found many applications in medicine, bio-photonics, in the development of sensors, new materials and solar cells. Laser interactions provide a possibility of chemical clean synthesis, which is difficult to achieve under more conventional NP production conditions [42]. Moreover, a careful optimization of the experimental conditions can allow a control over size distributions of the produced nanoclusters. Therefore, many studies were focused on the investigation the laser nanofabrication. In particular, many experiments were performed to demonstrate nanoparticles formation in vacuum, in the presence of a gas or a liquid. Nevertheless, it is still difficult to control the properties of the produced particles. It is believed that numerical calculations can help to explain experimental results and to better understand the mechanisms involved [43]. Despite rapid development in laser physics, one of the fundamental questions still concern the definition of proper ablation mechanisms and the processes leading to the nano particles formation. Apparently, the progress in laser systems implies several important changes in these mechanisms, which depend on both laser parameters and material properties. Among the more studied ablation mechanisms there are thermal, photochemical and photomechanical ablation processes. Frequently, however, the mechanisms are mixed, so that the existing analytical equations are hardly applicable. Therefore, numerical simulation is needed to better understand and to optimize the ablation process [44].

So far, thermal models are commonly used to describe nanosecond (and longer) laser ablation. In these models, the laser-irradiated material experiences heating, melting, boiling and evaporation. In this way, three numerical approaches were used [29, 45]:

 Atomistic approach based on such methods as Molecular Dynamics (MD) and Direct Monte Carlo Simulation (DSMC). Typical calculation results provide detailed information about atomic positions, velocities, kinetic and potential energy;

- **Macroscopic approach** based hydrodynamic models. These models allow the investigations of the role of the laser-induced pressure gradient, which is particularly important for ultra-short laser pulses. The models are based on a one fluid two-temperature approximation and a set of additional models (equation of state) that determines thermal properties of the target;

- **Multi-scale approach** based on the combination of two approaches cited above was developed by several groups and was shown to be particularly suitable for laser applications.

1.3 NANOFIBER TECHNOLOGY

Nano fiber consists of two terms "Nano" and "fiber," as the latter term is looking more familiar. Anatomists observed fibers as any of the filament constituting the extracellular matrix of connective tissue, or any elongated cells or thread like structures, muscle fiber or nerve fiber. According to textile industry fiber is a natural or synthetic filament, such as cotton or

nylon, capable of being spun into simply as materials made of such filaments. Physiologists and biochemists use the term fiber for indigestible plant matter consisting of polysaccharides such as cellulose, that when eaten stimulates intestinal peristalsis. Historically, the term fiber or "Fiber" in British English comes from Latin "fibra." Fiber is a slender, elongated thread like structure. Nano is originated from Greek word "nanos" or "nannos" refer to "little old man" or "dwarf." The prefixes "nannos" or "nano" as nannoplanktons or nanoplanktons used for very small planktons measuring 2 to 20 micrometers. In modern "nano" is used for describing various physical quantities within the scale of a billionth as nanometer (length), nanosecond (time), nanogram (weight) and nanofarad (charge) [1, 4, 9, 46]. As it was mentioned before, nanotechnology refers to the science and engineering concerning materials, structures and devices which has at least one dimension is 100 nm or less. This term also refers for a fabrication technology, where molecules, specification and individual atoms, which have at least one dimension in nanometers or less is used to design or built objects. Nano fiber, as the name suggests the fiber having a diameter range in nanometer. Fibrous structure having at least one dimension in nanometer or less is defined as Nano fiber according to National Science Foundation (NSC). The term Nano describes the diameter of the fibrous shape at anything below one micron or 1000 nm [4, 18].

Nanofiber technology is a branch of nanotechnology whose primary objective is to create materials in the form of nanoscale fibers in order to achieve superior functions [1, 2, 4]. The unique combination of high specific surface area, flexibility, and superior directional strength makes such fibers a preferred material form for many applications ranging from clothing to reinforcements for aerospace structures. Indeed, while the primary classification of nanofibers is that of nanostructure or nanomaterial, other aspects of nanofibers such as its characteristics, modeling, application and processing would enable nanofibers to penetrate into many subfields of nanotechnology [4, 46, 47].

It is obvious that nanofibers would geometrically fall into the category of one dimensional nano-scale elements that includes nanotubes and nanorods. However, the flexible nature of nanofibers would align it along with other highly flexible nano-elements such as globular molecules (assumed as zero dimensional soft matter), as well as solid and liquid films of nanothickness (two dimensional). A nanofiber is a nanomaterial in view of its diameter, and can be considered a nanostructured material if filled with nanoparticles to form composite nanofibers [1, 48].

The study of the nanofiber mechanical properties as a result of manufacturing techniques, constituent materials, processing parameters and other factors would fall into the category of nanomechanics. Indeed, while the primary classification of nanofibers is that of nanostructure or nanomaterial, other aspects of nanofibers such as its characteristics, modeling, application and processing would enable nanofibers to penetrate into many subfields of nanotechnology [1, 18].

Although, the effect of fiber diameter on the performance and processibility of fibrous structures has long been recognized, the practical generation of fibers at the nanometer scale was not realized until the rediscovery and popularization of the electrospinning technology by Professor Darrell Reneker almost a decade ago [49, 50]. The ability to create nanoscale fibers from a broad range of polymeric materials in a relatively simple manner using the electrospinning process, coupled with the rapid growth of nanotechnology in recent years have greatly accelerated the growth of nanofiber technology. Although, there are several alternative methods for generating fibers in a nanometer scale, none matches the popularity of the electrospinning technology due largely to the simplicity of the electrospinning process [18]. These methods will be discussed in following sections.

1.3.1 VARIOUS NANOFIBERS PRODUCTION METHODS

As it was discussed in detail, nanofiber is defined as the fiber having at least one dimension in nanometer range which can be used for a wide range of medical applications for drug delivery systems, scaffold formation, wound healing and widely used in tissue engineering, skeletal tissue, bone tissue, cartilage tissue, ligament tissue, blood vessel tissue, neural tissue, etc. It is also used in dental and orthopedic implants [4, 51, 52]. Nano fiber can be formed using different techniques including: drawing, template synthesis, phases separation, self-assembly and electrospinning.

1.3.1.1 DRAWING

In 1998, nanofibers were fabricated with citrate molecules through the process of drawing for the first time [53]. During drawing process, the fibers are fabricated by contacting a previously deposited polymer solution droplet with a sharp tip and drawing it as a liquid fiber, which is then solidified by rapid evaporation of the solvent due to the high surface area. The drawn fiber can be connected to another previously deposited polymer solution of droplets significantly limits the ability to extend this technique, especially in three-dimensional configurations and hard to access spatial geometries. Furthermore, there is a specific time in which the fibers can be pulled. The viscosity of the droplet continuously increases with time due to solvent evaporation from the deposited droplet. The continual shrinkage in the volume of the polymer solution droplet affects the diameter of the fiber drawn and limits the continuous drawing of fibers [54].

To overcome the above-mentioned limitation is appropriate to use hollow glass micropipettes with a continuous polymer dosage. It provides greater flexibility in drawing continuous fibers in any configuration. Moreover, this method offers increased flexibility in the control of key parameters of drawing such as waiting time before drawing (due to the required viscosity of the polymer edge drops), the drawing speed or viscosity, thus enabling repeatability and control on the dimensions of the fabricated fibers. Thus, drawing process requires a viscoelastic material that can undergo strong deformations while being cohesive enough to support the stresses developed during pulling [54–55].

1.3.1.2 TEMPLATE SYNTHESIS

Template synthesis implies the use of a template or mold to obtain a desired material or structure. Hence the casting method and DNA replication can be considered as template-based synthesis. In the case of nanofiber creation by [56], the template refers to a metal oxide membrane with through-thickness pores of nano-scale diameter. Under the application of water pressure on one side and restrain from the porous membrane causes extrusion of the polymer which, upon coming into contact with a solidifying solution, gives rise to nanofibers whose diameters are determined by the pores [1, 57].

This method is an effective route to synthesize nanofibrils and nanotubes of various polymers. The advantage of the template synthesis method is that the length and diameter of the polymer fibers and tubes can be controlled by the selected porous membrane, which results in more regular nanostructures. General feature of the conventional template method is that the membrane should be soluble so that it can be removed after synthesis in order to obtain single fibers or tubes. This restricts practical application of this method and gives rise to a need for other techniques [1, 56, 57].

1.3.1.3 PHASE SEPARATION METHOD

This method consists of five basic steps: polymer dissolution, gelation, solvent extraction, freezing and freeze-drying. In this process, it is observed that gelatin is the most difficult step to control the porous morphology of nano fiber. Duration of gelation varied with polymer concentration and gelation temperature. At low gelation temperature, nano-scale fiber network is formed, whereas, high gelation temperature led to the formation of platelet-like structure. Uniform nano fiber can be produced as the cooling rate is increased, polymer concentration affects the properties of nano fiber, as polymer concentration is increased porosity of fiber decreased and mechanical properties of fiber are increased [1, 58].

1.3.1.4 SELF-ASSEMBLY

Self–assembly refers to the build-up of nano scale fibers using smaller molecules. In this technique, a small molecule is arranged in a concentric manner so that they can form bonds among the concentrically arranged small molecules, which upon extension in the plane's normal gives the longitudinal axis of a nano fiber. The main mechanism for a generic selfassembly is the inter-molecular forces that bring the smaller unit together. A hydrophobic core of alkyl residues and a hydrophilic exterior lined by peptide residues was found in obtained fiber. It is observed that the nano fibers produced with this technique have diameter range 5–8 mm approximately and several microns in length [1, 59].

Although there are a number of techniques used for the synthesis of nanofiber but electrospinning represents an attractive technique to fabricate polymeric biomaterial into nanofibers. Electrospinning is one of the most commonly used methods for the production of nanofiber. It has a wide advantage over the previously available fiber formation techniques because here electrostatic force is used instead of conventionally used mechanical force for the formation of fibers. This method will be debated comprehensively in the following sub-sections.

1.3.1.5 ELECTROSPINNING OF NANOFIBERS

Electrospinning is a straightforward and cost-effective method to produce novel fibers with diameters in the range of from less than 3 nm to over 1 mm, which overlaps contemporary textile fiber technology. During this process, an electrostatic force is applied to a polymeric solution to produce nanofiber [60, 61] with diameter ranging from 50 nm to 1000 nm or greater [49, 62, 63]; Due to surface tension the solution is held at the tip of syringe. Polymer solution is charged due to applied electric force. In the polymer solution, a force is induced due to mutual charge repulsion that is directly opposite to the surface tension of the polymer solution. Further increases in the electrical potential led to the elongation of the hemispherical surface of the solution at the tip of the syringe to form a conical shape known as "Taylor cone" [50, 64]. The electric potential is increased to overcome the surface tension forces to cause the formation of a jet, ejects from the tip of the Taylor cone. Due to elongation and solvent evaporation, charged jet instable and gradually thins in air primarily [62, 65–67]. The charged jet forms randomly oriented nanofibers that can be collected on a stationary or rotating grounded metallic collector [50]. Electrospinning provides a good method and a practical way to produce polymer fibers with diameters ranging from 40-2000 nm [49-50].

1.3.1.5.1 THE HISTORY OF ELECTROSPINNING METHODOLOGY

William Gilbert discovered the first record of the electrostatic attraction of a liquid in 1600 [68]. The first electrospinning patent was submitted by John Francis Cooley in 1900 [69]. After that in 1914 John Zeleny studied on the behavior of fluid droplets at the end of metal capillaries, which caused the beginning of the mathematical model the behavior of fluids under electrostatic forces [65]. Between 1931 and 1944 Anton Formhals took out at least 22 patents on electrospinning [69]. In 1938, N.D. Rozenblum and I.V. Petryanov-Sokolov generated electrospun fibers, which they developed into filter materials [70]. Between 1964 and 1969 Sir Geoffrey Ingram Taylor produced the beginnings of a theoretical foundation of electrospinning by mathematically modeling the shape of the (Taylor) cone formed by the fluid droplet under the effect of an electric field [71, 72]. In the early 1990s several research groups (such as Reneker) demonstrated electrospinning has been increasing exponentially every year [69].

1.3.1.5.2 ELECTROSPINNING PROCESS

Electrospinning process can be explained in five significant steps including [48, 73–75]:

a) Charging of the polymer fluid

The syringe is filled with a polymer solution, the polymer solution is charged with a very high potential around 10–30 kV. The nature of the fluid and polarity of the applied potential free electrons, ions or ion-pairs are generated as the charge carriers form an electrical double layer. This charging induction is suitable for conducting fluid, but for nonconducting fluid charge directly injected into the fluid by the application of electrostatic field.

b) Formation of the cone jet (Taylor cone)

The polarity of the fluid depends upon the voltage generator. The repulsion between the similar charges at the free electrical double layer works against the surface tension and fluid elasticity in the polymer solution to deform the droplet into a conical shaped structure i.e. known as a Taylor cone. Beyond a critical charge density Taylor-cone becomes unstable and a jet of fluid is ejected from the tip of the cone.

c) Thinning of the jet in the presence of an electric field

The jet travels a path to the ground; this fluid jet forms a slender continuous liquid filament. The charged fluid is accelerated in the presence of an electrical field. This region of fluid is generally linear and thin.

d) Instability of the jet

Fluid elements accelerated under electric field and thus stretched and succumbed to one or more fluid instabilities, which distort as they grow following many spiral and distort the path before collected on the collector electrode. This region of instability is also known as whipping region.

e) Collection of the jet

Charged electro spun fibers travel downfield until its impact with a lower potential collector plate. The orientation of the collector affects the alignment of the fibers. Different type of collector also affects the morphology and the properties of producing nanofiber. Different type of collectors are used: Rotating drum collector, moving belt collector, rotating wheel with beveled edge, multifilament thread, parallel bars, simple mesh collector, etc.

1.3.1.5.3 ELECTROSPINNING SET-UPS

Electrospinning is conducted at room temperature with atmospheric conditions. The typical set up of electrospinning apparatus is shown in Fig. 1.1. Basically, an electrospinning system consists of three major components: 1) a high voltage power supply, 2) a spinneret (such as a pipette tip) and 3) a grounded collecting plate (usually a metal screen, plate, or rotating mandrel); and uses a high voltage source to inject charge of a certain polarity into a polymer solution or melt, which is then accelerated towards a collector of opposite polarity [73, 76, 77]. Most of the polymers are dissolved in some solvents before electrospinning, and when it completely dissolves, forms polymer solution. The polymer fluid is then introduced into the capillary tube for electrospinning. However, some polymers may emit unpleasant or even harmful smells, so the processes should be conducted within chambers having a ventilation system. In the electrospinning process, a polymer solution held by its surface tension at the end of a capillary tube is subjected to an electric field and an electric charge is induced on the liquid surface due to this electric field. When the electric field applied reaches a critical value, the repulsive electrical forces overcome the surface tension forces. Eventually, a charged jet of the solution is ejected from the tip of the Taylor cone and an unstable and a rapid whipping of the jet occurs in the space between the capillary tip and collector which leads to evaporation of the solvent, leaving a polymer behind. The jet is only stable at the tip of the spinneret and after that instability starts. Thus, the electrospinning process offers a simplified technique for fiber formation [50, 73, 78, 79].



FIGURE 1.1 Scheme of a conventional electrospinning set-up.

1.3.1.5.4 THE EFFECTIVE PARAMETERS ON ELECTROSPINNING

The electrospinning process is generally governed by many parameters, which can be classified broadly into solution parameters, process param-

eters, and ambient parameters. Each of these parameters significantly affects the fiber morphology obtained as a result of electrospinning, and by proper manipulation of these parameters we can get nanofibers of desired morphology and diameters. These effective parameters are sorted as below [63, 67, 73, 76]:

- a) Polymer solution parameters, which includes molecular weight and solution viscosity, surface tension, solution conductivity and dielectric effect of solvent.
- **b) Processing parameters,** which include voltage, feed rate, temperature, effect of collector, the diameter of the orifice of the needle.
- a) Polymer solution parameters

1) Molecular weight and solution viscosity

Higher the molecular weight of the polymer, increases molecular entanglement in the solution, hence there is an increase in viscosity. The electro spun jet eject with high viscosity during it is stretched to a collector electrode leading to formation of continuous fiber with higher diameter, but very high viscosity makes difficult to pump the solution and also lead to the drying of the solution at the needle tip. As a very low viscosity lead in bead formation in the resultant electro spun fiber, so the molecular weight and viscosity should be acceptable to form nanofiber [48, 80].

2) Surface tension

Lower viscosity leads to decrease in surface tension resulting bead formation along the fiber length because the surface area is decreased, but at the higher viscosity effect of surface tension is nullified because of the uniform distribution of the polymer solution over the entangled polymer molecules. So, lower surface tension is required to obtain smooth fiber and lower surface tension can be achieved by adding of surfactants in polymer solution [80, 81].

3) Solution conductivity

Higher conductivity of the solution followed a higher charge distribution on the electrospinning jet, which leads to increase in stretching of the solution during fiber formation. Increased conductivity of the polymer solution lowers the critical voltage for the electro spinning. Increased charge leads to the higher bending instability leading to the higher deposition area of the fiber being formed, as a result jet path is increased and finer fiber is formed. Solution conductivity can be increased by the addition of salt or polyelectrolyte or increased by the addition of drugs and proteins, which dissociate into ions when dissolved in the solvent formation of smaller diameter fiber [67, 80].

4) Dielectric effect of solvent

Higher the dielectric property of the solution lesser is the chance of bead formation and smaller is the diameter of electro-spun fiber. As the dielectric property is increased, there is increase in the bending instability of the jet and the deposition area of the fiber is increased. As jet path length is increased fine fiber deposit on the collector [67, 80].

b) Processing condition parameters

1) Voltage

Taylor cone stability depends on the applied voltage, at the higher voltage greater amount of charge causes the jet to accelerate faster leading to smaller and unstable Taylor cone. Higher voltage leads to greater stretching of the solution due to fiber with small diameter formed. At lower voltage the flight time of the fiber to a collector plate increases that led to the formation of fine fibers. There is greater tendency to bead formation at high voltage because of increased instability of the Taylor cone, and theses beads join to form thick diameter fibers. It is observed that the better crystallinity in the fiber obtained at higher voltage, because with very high voltage acceleration of fiber increased that reduced flight time and polymer molecules do not have much time to align them and fiber with less crystallinity formed. Instead of DC if AC voltage is provided for electro spinning it forms thicker fibers [48, 80].

2) Feed rate

As the feed rate is increased, there is an increase in the fiber diameter because greater volume of solution is drawn from the needle tip [80].

3) Temperature

At high temperature, the viscosity of the solution is decreased and there is increase in higher evaporation rate, which allows greater stretching of the solution and a uniform fiber is formed [82].

4) Effect of collector

In electro spinning, collector material should be conductive. The collector is grounded to create stable potential difference between needle and collector. A nonconducting material collector reduces the amount of fiber being deposited with lower packing density. But in case of conducting collector there is accumulation of closely packed fibers with higher packing density. Porous collector yields fibers with lower packing density as compared to nonporous collector plate. In porous collector plate the surface area is increased so residual solvent molecules gets evaporated fast as compared to nonporous. Rotating collector is useful in getting dry fibers as it provides more time to the solvents to evaporate. It also increases fiber morphology [83]. The specific hat target with proper parameters has a uniform surface electric field distribution, the target can collect the fiber mats of uniform thickness and thinner diameters with even size distribution [80].

5) Diameter of pipette orifice

Orifice with small diameter reduces the clogging effect due to less exposure of the solution to the atmosphere and leads to the formation of fibers with smaller diameter. However, very small orifice has the disadvantage that it creates problems in extruding droplets of solution from the tip of the orifice [80].

1.4 INTRODUCTION TO THEORETICAL STUDY OF ELECTROSPINNING PROCESS

Electrospinning is a procedure in which an electrical charge to draw very fine (typically on the micro or nano scale) fibers from polymer solution or molten. Electrospinning shares characteristics of both electrospraying and conventional solution dry spinning of fibers. The process does not require

the use of coagulation chemistry or high temperatures to produce solid threads from solution. This makes the process more efficient to produce the fibers using large and complex molecules. Recently, various polymers have been successfully electrospun into ultrafine fibers mostly in solvent solution and some in melt form [79, 84]. Optimization of the alignment and morphology of the fibers is produced by fitting the composition of the solution and the configuration of the electrospinning apparatus such as voltage, flow rate, etc. As a result, the efficiency of this method can be improved [85]. Mathematical and theoretical modeling and simulating procedure will assist to offer an in-depth insight into the physical understanding of complex phenomena during electrospinning and might be very useful to manage contributing factors toward increasing production rate [75, 86].

Despite the simplicity of the electrospinning technology, industrial applications of it are still relatively rare, mainly due to the notable problems with very low fiber production rate and difficulties in controlling the process [67].

Modeling and simulation (M&S) give information about how something will act without actually testing it in real. The model is a representation of a real object or system of objects for purposes of visualizing its appearance or analyzing its behavior. Simulation is a transition from a mathematical or computational model for description of the system behavior based on sets of input parameters [87, 88]. Simulation is of ten the only means for accurately predicting the performance of the modeled system [89]. Using simulation is generally cheaper and safer than conducting experiments with a prototype of the final product. Also simulation can often be even more realistic than traditional experiments, as they allow the free configuration of environmental and operational parameters and can often be run faster than in real time. In a situation with different alternatives analysis, simulation can improve the efficiency, in particular when the necessary data to initialize can easily be obtained from operational data. Applying simulation adds decision support systems to the toolbox of traditional decision support systems [90].

Simulation permits set up a coherent synthetic environment that allows for integration of systems in the early analysis phase for a virtual test environment in the final system. If managed correctly, the environment can be migrated from the development and test domain to the training and education domain in real systems under realistic constraints [91]. A collection of experimental data and their confrontation with simple physical models appears as an effective approach towards the development of practical tools for controlling and optimizing the electrospinning process. On the other hand, it is necessary to develop theoretical and numerical models of electrospinning because of demanding a different optimization procedure for each material [92]. Utilizing a model to express the effect of electrospinning parameters will assist researchers to make an easy and systematic way of presenting the influence of variables and by means of that, the process can be controlled. Additionally, it causes to predict the results under a new combination of parameters. Therefore, without conducting any experiments, one can easily estimate features of the product under unknown conditions [93].

1.5 STUDY OF ELECTROSPINNING JET PATH

To yield individual fibers, most, if not all of the solvents must be evaporated by the time the electrospinning jet reaches the collection plate. As a result, volatile solvents are often used to dissolve the polymer. However, clogging of the polymer may occur when the solvent evaporates before the formation of the Taylor cone during the extrusion of the solution from several needles. In order to maintain a stable jet while still using a volatile solvent, an effective method is to use a gas jacket around the Taylor cone through two coaxial capillary tubes. The outer tube, which surrounds the inner tube will provide a controlled flow of inert gas, which is saturated with the solvent used to dissolve the polymer. The inner tube is then used to deliver the polymer solution. For 10-wt% poly (L-lactic acid) (PLLA) solution in dichloromethane, electrospinning was not possible due to clogging of the needle. However, when N2 gas was used to create a flowing gas jacket, a stable Taylor cone was formed and electrospinning was carried out smoothly.

1.5.1 THE THINNING JET (JET INSTABILITY)

The conical meniscus eventually gives rise to a slender jet that emerges from the apex of the meniscus and propagates downstream. Hohman et al.

[60] first reported this approach for the relatively simple case of Newtonian fluids. This suggests that the shape of the thinning jet depends significantly on the evolution of the surface charge density and the local electric field. As the jet thins down and the charges relax to the surface of the jet, the charge density and local field quickly pass through a maximum, and the current due to advection of surface charge begins to dominate over that due to bulk conduction.

The crossover occurs on the length scale given by [6]:

$$L_{N} = \left(K^{4}Q^{7}\rho^{3}(\ln X)^{2} / 8\pi^{2}E_{\infty}l^{5}\varepsilon^{-2}\right)^{1/5}$$
(1)

This length scale defines the "nozzle regime" over which the transition from the meniscus to the steady jet occurs. Sufficiently far from the nozzle regime, the jet thins less rapidly and finally enters the asymptotic regime, where all forces except inertial and electrostatic forces ceases to influence the jet. In this regime, the radius of the jet decreases as follows:

$$h = \left(\frac{Q^{3}\rho}{2\pi^{2}E_{\infty}l}\right)^{1/4} z^{-1/4}$$
(2)

Here z is the distance along the centerline of the jet. Between the "nozzle regime" and the "asymptotic regime," the evolution of the diameter of the thinning jet can be affected by the viscous response of the fluid. Indeed by balancing the viscous and the electrostatic terms in the force balance equation it can be shown that the diameter of the jet decreases as:

$$h = \left(\frac{6\mu Q^2}{\pi E_{\infty} I}\right)^{1/2} z^{-1} \tag{3}$$

In fact, the straight jet section has been studied extensively to understand the influence of viscoelastic behavior on the axisymmetric instabilities [94] and crystallization [60] and has even been used to extract extensional viscosity of polymeric fluids at very high strain rates.

For highly strain-hardening fluids, Yu et al. [95] demonstrated that the diameter of the jet decreased with a power-law exponent of -1/2, rather than -1/4 or -1, as discussed earlier for Newtonian fluids. This -1/2 power-law scaling for jet thinning in viscoelastic fluids has been explained in

terms of a balance between electromechanical stresses acting on the surface of the jet and the viscoelastic stress associated with extensional strain hardening of the fluid. Additionally, theoretical studies of viscoelastic fluids predict a change in the shape of the jet due to non-Newtonian fluid behavior. Both Yu et al. [95] and Han et al. [96] have demonstrated that substantial elastic stresses can be accumulated in the fluid as a result of the high-strain rate in the transition from the meniscus into the jetting region. This elastic stress stabilizes the jet against external perturbations. Further downstream the rate of stretching slows down, and the longitudinal stresses relax through viscoelastic processes. The relaxation of stresses following an extensional deformation, such as those encountered in electrospinning, has been studied in isolation for viscoelastic fluids [97]. Interestingly, Yu et al. [95] also observed that, elastic behavior notwithstanding, the straight jet transitions into the whipping region when the jet diameter becomes of the order of 10 mm.

1.5.2 THE WHIPPING JET (JET INSTABILITY)

While it is in principle possible to draw out the fibers of small diameter by electrospinning in the cone-jet mode alone, the jet does not typically solidify enough en route to the collector and succumbs to the effect of force imbalances that lead to one or more types of instability. These instabilities distort the jet as they grow. A family of these instabilities exists, and can be analyzed in the context of various symmetries (axisymmetric or nonaxisymmetric) of the growing perturbation to the jet.

Some of the lower modes of this instability observed in electrospinning have been discussed in a separate review [81]. The "whipping instability" occurs when the jet becomes convectively unstable and its centerline bends. In this region, small perturbations grow exponentially, and the jet is stretched out laterally. Shin et al. [62] and Fridrikh et al. [63] have demonstrated how the whipping instability can be largely responsible for the formation of solid fiber in electrospinning. This is significant, since as recently as the late 1990s the bifurcation of the jet into two more or less equal parts (also called "splitting" or "splaying") were thought to be the mechanism through which the diameter of the jet is reduced, leading to the fine fibers formed in electrospinning. In contrast to "splitting" or "splaying," the appearances of secondary, smaller jets from the primary jet have been observed more frequently and in situ [64, 98]. These secondary jets occur when the conditions on the surface of the jet are such that perturbations in the local field, for example, due to the onset of the slight bending of the jet, is enough to overcome the surface tension forces and invoke a local jetting phenomenon.

The conditions necessary for the transition of the straight jet to the whipping jet has been discussed in the works of Ganan-Calvo [99], Yarin et al. [64], Reneker et al. [66] and Hohman et al. [60].

During this whipping instability, the surface charge repulsion, surface tension, and inertia were considered to have more influence on the jet path than Maxwell's stress, which arises due to the electric field and finite conductivity of the fluid. Using the equations reported by Hohman et al. [60, 61] and Fridrikh et al. [63] obtained an equation for the lateral growth of the jet excursions arising from the whipping instability far from the onset and deep into the nonlinear regime. These developments have been summarized in the review article of Rutledge and Fridrikh.

The whipping instability is postulated to impose the stretch necessary to draw out the jet into fine fibers. As discussed previously, the stretch imposed can make an elastic response in the fluid, especially if the fluid is polymeric in nature. An empirical rheological model was used to explore the consequences of nonlinear behavior of the fluid on the growth of the amplitude of the whipping instability in numerical calculations [63, 79]. There it was observed that the elasticity of the fluid significantly reduces the amplitude of oscillation of the whipping jet. The elastic response also stabilizes the jet against the effect of surface tension. In the absence of any elasticity, the jet eventually breaks up and forms an aerosol. However, the presence of a polymer in the fluid can stop this breakup if:

$$\tau / \left(\frac{\rho h^3}{\gamma}\right)^{1/2} \ge 1 \tag{4}$$

Where τ is the relaxation time of the polymer, ρ is the density of the fluid, h is a characteristic radius, and γ is the surface tension of the fluid.

1.6 ELECTROSPINNING DRAWBACKS

Electrospinning has attracted much attention both to academic research and industry application because electrospinning (1) can fabricate continuous fibers with diameters down to a few nanometers, (2) is applicable to a wide range of materials such as synthetic and natural polymers, metals as well as ceramics and composite systems, (3) can prepare nanofibers with low cost and high yielding [47].

Despite the simplicity of the electrospinning technology, industrial applications of it are still relatively rare, mainly due to the notable problems of very low fiber production rate and difficulties in controlling the process [50, 67]. The usual feed-rate for electrospinning is about 1.5 mL/hr. Given a solution concentration of 0.2 g/mL, the mass of nanofiber collected from a single needle after an hour is only 0.3 g. In order for electrospinning to be commercially viable, it is necessary to increase the production rate of the nanofibers. To do so, multiple-spinning setup is necessary to increase the yield while at the same time maintaining the uniformity of the nanofiber mesh [48].

Optimization of the alignment and morphology of the fibers, which is produced by fitting the composition of the solution and the configuration of the electrospinning apparatus such as voltage, flow rate, etc., can be useful to improve the efficiency of this method [85]. Mathematical and theoretical modeling and simulating procedure will assist to offer an in-depth insight into the physical understanding of complex phenomena during electrospinningand might be very useful to manage contributing factors toward increasing production rate [75, 86].

Presently, nanofibers have attracted the attention of researchers due to their remarkable micro and nano structural characteristics, high surface area, small pore size, and the possibility of their producing three dimensional structure that enable the development of advanced materials with sophisticated applications [73].

Controlling the property, geometry, and mass production of the nanofibers, is essential to comprehend quantitatively how the electrospinning process transforms the fluid solution through a millimeter diameter capillary tube into solid fibers which are four to five orders smaller in diameter [74]. As mentioned above, the electrospinning gives us the impression of being a very simple and easily controlled technique for the production of nanofibers. But, actually the process is very intricate. Thus, electrospinning is usually described as the interaction of several physical instability processes. The bending and stretching of the jet are mainly caused by the rapidly whipping which is an essential element of the process induced by these instabilities. Until now, little is known about the detailed mechanisms of the instabilities and the splaying process of the primary jet into multiple filaments. It is thought to be responsible that the electrostatic forces overcome surface tensions of the droplet during undergoing the electrostatic field and the deposition of jets formed nanofibers [47].

Though electrospinning has been become an indispensable technique for generating functional nanostructures, many technical issues still need to be resolved. For example, it is not easy to prepare nanofibers with a same scale in diameters by electrospinning; it is still necessary to investigate systematically the correlation between the secondary structure of nanofiber and the processing parameters; the mechanical properties, photoelectric properties and other property of single fiber should be systematically studied and optimized; the production of nanofiber is still in laboratory level, and it is extremely important to make efforts for scaled-up commercialization; nanofiber from electrospinning has a the low production rate and low mechanical strength which hindered it's commercialization; in addition, another more important issue should be resolved is how to treat the solvents volatilized in the process.

Until now, lots of efforts are putted on the improvement of electrospinning installation, such as the shape of collectors, modified spinnerets and so on. The application of multi-jets electrospinning provides a possibility to produce nanofibers in industrial scale. The development of equipments, which can collect the poisonous solvents and the application of melt electrospinning, which would largely reduce the environment problem, create a possibility of the industrialization of electrospinning. The application of water as the solvent for electrospinning provides another approach to reduce environmental pollution, which is the main fact hindered the commercialization of electrospinning. In summary, electrospinning is an attractive and promising approach for the preparation of functional nanofibers due to its wide applicability to materials, low cost and high production rate [47].

1.7 MODELLING OF THE ELECTROSPINNING PROCESS

The electrospinning process is a fluid dynamics related problem. Controlling the property, geometry, and mass production of the nanofibers, is essential to comprehend quantitatively how the electrospinning process transforms the fluid solution through a millimeter diameter capillary tube into solid fibers which are four to five orders smaller in diameter [74]. Although information on the effect of various processing parameters and constituent material properties can be obtained experimentally, theoretical models offer in-depth scientific understanding which can be useful to clarify the affecting factors that cannot be exactly measured experimentally. Results from modeling also explained how processing parameters and fluid behavior lead to the nanofiber of appropriate properties. The term "properties" refers to basic properties (such as, fiber diameter, surface roughness, fiber connectivity, etc.), physical properties (such as, stiffness, toughness, thermal conductivity, electrical resistivity, thermal expansion coefficient, density, etc.) and specialized properties (such as, biocompatibility, degradation curve, etc. for biomedical applications) [48, 73].

For example, the developed models can be used for the analysis of mechanisms of jet deposition and alignment on various collecting devices in arbitrary electric fields [100].

The various method formulated by researchers are prompted by several applications of nanofibers. It would be sufficient to briefly describe some of these methods to observed similarities and disadvantages of these approaches. An abbreviated literature review of these models will be discussed in the following sections.

1.7.1 ASSUMPTIONS

Just as in any other process modeling, a set of assumptions are required for the following reasons:

- a) to furnish industry-based applications whereby speed of calculation, but not accuracy, is critical;
- b) to simplify and therefore, enabling checkpoints to be made before more detailed models can proceed; and

c) for enabling the formulations to be practically traceable.

The first assumption to be considered as far as electrospinning is concerned is conceptualizing the jet itself. Even though the most appropriate view of a jet flow is that of a liquid continuum, the use of nodes connected in series by certain elements that constitute rheological properties has proven successful [64, 66]. The second assumption is the fluid constitutive properties. In the discrete node model [66], the nodes are connected in series by a Maxwell unit, that is, a spring and dashpot in series, for quantifying the viscoelastic properties.

In analyzing viscoelastic models, we apply two types of elements: the dashpot element, which describes the force as being in proportion to the velocity (recall friction), and the spring element, which describes the force as being in proportion to elongation. One can then develop viscoelastic models using combinations of these elements. Among all possible visco-elastic models, the Maxwell model was selected by [66] due to its suitability for liquid jet as well as its simplicity. Other models are either unsuitable for liquid jet or too detailed.

In the continuum models a power law can be used for describing the liquid behavior under shear flow for describing the jet flow [101]. At this juncture, we note that the power law is characterized from a shear flow, while the jet flow in electrospinning undergoes elongational flow. This assumption will be discussed in detail in following sections.

The other assumption that should be applied in electrospinning modeling is about the coordinate system. The method for coordinate system selection in electrospinning process is similar to other process modeling, the system that best bring out the results by (i) allowing the computation to be performed in the most convenient manner and, more importantly, (ii) enabling the computation results to be accurate. In view of the linear jet portion during the initial first stage of the jet, the spherical coordinate system is eliminated. Assuming the second stage of the jet to be perfectly spiraling, due to bending of the jet, the cylindrical coordinate system would be ideal. However, experimental results have shown that the bending instability portion of the jet is not perfectly expanding spiral. Hence the Cartesian coordinate system, which is the most common of all coordinate system, is adopted. Depending on the processing parameters (such as applied voltage, volume flow rate, etc.) and the fluid properties (such as surface tension, viscosity, etc.) as many as 10 modes of electrohydrodynamically driven liquid jet have been identified [102]. The scope of jet modes is highly abbreviated in this chapter because most electrospinning processes that lead to nanofibers consist of only two modes, the straight jet portion and the spiraling (or whipping) jet portion. Insofar as electrospinning process modeling is involved, the following classification indicates the considered modes or portion of the electrospinning jet.

- 1. Modeling the criteria for jet initiation from the droplet [64, 103];
- 2. Modeling the straight jet portion [104, 105] Spivak et al. [101, 106];
- 3. Modeling the entire jet [60, 61, 66, 107].

A schematic of the jet flow variety, which occurs in electrospinning process presented in Fig. 1.2.



FIGURE 1.2 Geometry of the jet flow.

1.7.2 CONSERVATION RELATIONS

Balance of the producing accumulation is, particularly, a basic source of quantitative models of phenomena or processes. Differential balance equations are formulated for momentum, mass and energy through the contribution of local rates of transport expressed by the principle of Newton's, Fick's and Fourier laws. For a description of more complex systems like electrospinning that involved strong turbulence of the fluid flow, characterization of the product property is necessary and various balances are required [108].

The basic principle used in modeling of chemical engineering process is a concept of balance of momentum, mass and energy, which can be expressed in a general form as:

$$A = I + G - O - C \tag{5}$$

where, A is the accumulation built up within the system; I is the input entering through the system surface; G is the generation produced in system volume; O is the output leaving through system boundary; and C is the consumption used in system volume.

The form of expression depends on the level of the process phenomenon description [108–109]

According to the electrospinnig models, the jet dynamics are governed by a set of three equations representing mass, energy and momentum conservation for the electrically charge jet [110].

In electrospinning modeling for simplification of describing the process, researchers consider an element of the jet and the jet variation versus time is neglected.

1.7.2.1 MASS CONSERVATION

The concept of mass conservation is widely used in many fields such as chemistry, mechanics, and fluid dynamics. Historically, mass conservation was discovered in chemical reactions by Antoine Lavoisier in the late eighteenth century, and was of decisive importance in the progress from alchemy to the modern natural science of chemistry. The concept of matter conservation is useful and sufficiently accurate for most chemical calculations, even in modern practice [111].

The equations for the jet follow from Newton's Law and the conservation laws obey, namely, conservation of mass and conservation of charge [60].

According to the conservation of mass equation,

$$\pi R^2 \upsilon = Q \tag{6}$$

$$\frac{\partial}{\partial t} \left(\pi R^2 \right) + \frac{\partial}{\partial z} \left(\pi R^2 \upsilon \right) = 0 \tag{7}$$

For incompressible jets, by increasing the velocity the radius of the jet decreases. At the maximum level of the velocity, the radius of the jet reduces. The macromolecules of the polymers are compacted together closer while the jet becomes thinner as it shown in Fig. 1.3. When the radius of the jet reaches the minimum value and its speed becomes maximum to keep the conservation of mass equation, the jet dilates by decreasing its density, which called electrospinning dilation [112–113].



FIGURE 1.3 Macromolecular chains are compacted during the electrospinning.

1.7.2.2 ELECTRIC CHARGE CONSERVATION

An electric current is a flow of electric charge. Electric charge flows when there is voltage present across a conductor. In physics, charge conservation is the principle that electric charge can neither be created nor destroyed. The net quantity of electric charge, the amount of positive charge minus the amount of negative charge in the universe, is always conserved. The first written statement of the principle was by American scientist and statesman Benjamin Franklin in 1747 [114]. Charge conservation is a physical law, which states that the change in the amount of electric charge in any volume of space is exactly equal to the amount of charge in a region and the flow of charge into and out of that region [115].

During the electrospinning process, the electrostatic repulsion between excess charges in the solution stretches the jet. This stretching also decreases the jet diameter that this leads to the law of charge conservation as the second governing equation [116].

In electrospinning process, the electric current, which induced by electric field, is included into two parts, conduction and convection.

The conventional symbol for current is *I*:

$$I = I_{conduction} + I_{convection} \tag{8}$$

Electrical conduction is the movement of electrically charged particles through a transmission medium. The movement can form an electric current in response to an electric field. The underlying mechanism for this movement depends on the material.

$$I_{conduction} = J_{cond} \times S = KE \times \pi R^2$$
(9)

$$J = \frac{I}{A(s)} \tag{10}$$

$$I = J \times S \tag{11}$$

Convection current is the flow of current with the absence of an electric field.

$$I_{convection} = J_{conv} \times S = 2\pi R(L) \times \sigma v \tag{12}$$

$$J_{conv} = \sigma v \tag{13}$$

So, the total current can be calculated as:

$$\pi R^2 K E + 2\pi R v \sigma = I \tag{14}$$

$$\frac{\partial}{\partial t}(2\pi R\sigma) + \frac{\partial}{\partial z}\left(\pi R^2 K E + 2\pi R \nu \sigma\right) = 0$$
(15)

1.7.2.3 MOMENTUM BALANCE

In classical mechanics, linear momentum or translational momentum is the product of the mass and velocity of an object. Like velocity, linear momentum is a vector quantity, possessing a direction as well as a magnitude:

$$P = m\upsilon \tag{16}$$

Linear momentum is also a conserved quantity, meaning that if a closed system (one that does not exchange any matter with the outside and is not acted on by outside forces) is not affected by external forces, its total linear momentum cannot change. In classical mechanics, conservation of linear momentum is implied by Newton's laws of motion; but it also holds in special relativity (with a modified formula) and, with appropriate definitions, a (generalized) linear momentum conservation law holds in electro-dynamics, quantum mechanics, quantum field theory, and general relativity [114]. For example, according to the third law, the forces between two particles are equal and opposite. If the particles are numbered 1 and 2, the second law states:

$$F_1 = \frac{dP_1}{dt} \tag{17}$$

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$$F_2 = \frac{dP_2}{dt} \tag{18}$$

Therefore:

$$\frac{dP_1}{dt} = -\frac{dP_2}{dt} \tag{19}$$

$$\frac{d}{dt}(P_1 + P_2) = 0 (20)$$

If the velocities of the particles are v_{11} and v_{12} before the interaction, and afterwards they are v_{21} and v_{22} , then,

$$m_1 \upsilon_{11} + m_2 \upsilon_{12} = m_1 \upsilon_{21} + m_2 \upsilon_{22} \tag{21}$$

This law holds no matter how complicated the force is between the particles. Similarly, if there are several particles, the momentum exchanged between each pair of particles adds up to zero, so the total change in momentum is zero. This conservation law applies to all interactions, including collisions and separations caused by explosive forces. It can also be generalized to situations where Newton's laws do not hold, for example in the theory of relativity and in electrodynamics [104, 117]. The momentum equation for the fluid can be derived as follow:

$$\rho(\frac{d\upsilon}{dt} + \upsilon\frac{d\upsilon}{dz}) = \rho g + \frac{d}{dz} \left[\tau_{zz} - \tau_{rr}\right] + \frac{\gamma}{R^2} \cdot \frac{dr}{dz} + \frac{\sigma}{\varepsilon_0} \frac{d\sigma}{dz} + (\varepsilon - \varepsilon_0)(E\frac{dE}{dz}) + \frac{2\sigma E}{r}$$
(22)

But commonly the momentum equation for electrospinning modeling is formulated by considering the forces on a short segment of the jet [104, 117].

$$\frac{d}{dz}(\pi R^2 \rho \upsilon^2) = \pi R^2 \rho g + \frac{d}{dz} \Big[\pi R^2 (-\rho + \tau_{zz}) \Big] + \frac{\gamma}{R} \cdot 2\pi R R' + 2\pi R (t_t^e - t_n^e R')$$
(23)



FIGURE 1.4 Momentum balance on a short section of the jet.

As it is shown in the Fig. 1.4. the element's angels could be defined as α and β . According to the mathematical relationships, it is obvious that:

$$\alpha + \beta = \frac{\pi}{2} \tag{24}$$

$$\sin\alpha = \tan\alpha$$

$$\cos\alpha = 1$$
(25)

Due to the Fig. 1.4, relationships between these electrical forces are as below:

$$t_n^e \sin \alpha \cong t_n^e \tan \alpha \cong -t_n^e \tan \beta \cong -\frac{dR}{dz} t_n^e = -R' t_n^e$$
(26)

$$t_t^e \cos \alpha \cong t_t^e \tag{27}$$

So the effect of the electric forces in the momentum balance equation can be presented as:

$$2\pi RL(t_t^e - R't_n^e)dz \tag{28}$$

(Notation: In the main momentum equation, final formula is obtained by dividing into dz.)

Generally, the normal electric force is defined as:

$$t_n^e \cong \frac{1}{2}\overline{\epsilon}E_n^2 = \frac{1}{2}\overline{\epsilon}(\frac{\sigma}{\overline{\epsilon}})^2 = \frac{\sigma^2}{2\overline{\epsilon}}$$
(29)

A little amount of electric forces is perished in the vicinity of the air.

$$E_n = \frac{\sigma}{\overline{\epsilon}} \tag{30}$$

The electric force can be presented by:

$$F = \frac{\Delta We}{\Delta I} = \frac{1}{2} (\varepsilon - \overline{\varepsilon}) E^2 \times \Delta S$$
(31)

The force per surface unit is:

$$\frac{F}{\Delta S} = \frac{1}{2} (\varepsilon - \overline{\varepsilon}) E^2$$
(32)

Generally, the electric potential energy is obtained by:

$$Ue = -We = -\int F.ds \tag{33}$$

$$\Delta We = \frac{1}{2} (\varepsilon - \overline{\varepsilon}) E^2 \times \Delta V = \frac{1}{2} (\varepsilon - \overline{\varepsilon}) E^2 \times \Delta S.\Delta I$$
(34)

So, finally it could be resulted:

$$t_n^e = \frac{\sigma^2}{2\overline{\varepsilon}} - \frac{1}{2} (\varepsilon - \overline{\varepsilon}) E^2$$
(35)

$$t_t^e = \sigma E \tag{36}$$

1.7.2.4 COULOMB'S LAW

Coulomb's law is a mathematical description of the electric force between charged objects, which is formulated by the 18th-century French physicist Charles-Augustin de Coulomb. It is analogous to Isaac Newton's law of gravity. Both gravitational and electric forces decrease with the square of the distance between the objects, and both forces act along a line between them [118]. In Coulomb's law, the magnitude and sign of the electric force are determined by the electric charge, more than the mass of an object. Thus, a charge, which is a basic property matter, determines how electromagnetism affects the motion of charged targets [114].

Coulomb force is thought to be the main cause for the instability of the jet in the electrospinning process [119]. This statement is based on the Earnshaw's theorem, named after Samuel Earnshaw [120], which claims that "A charged body placed in an electric field of force cannot rest in stable equilibrium under the influence of the electric forces alone." This theorem can be notably adapted to the electrospinning process [119]. The instability of charged jet influences on jet deposition and as a consequence on nanofiber formation. Therefore, some researchers applied developed models to the analysis of mechanisms of jet deposition and alignment on various collecting devices in arbitrary electric fields [66].

The equation for the potential along the centerline of the jet can be derived from Coulomb's law. Polarized charge density is obtained:

$$\rho_{p'} = -\vec{\nabla}.\vec{P}' \tag{37}$$

Where P' is polarization:

$$\vec{P}' = (\varepsilon - \overline{\varepsilon})\vec{E} \tag{38}$$

By substituting P' in Eq. (38):

$$\rho_{P'} = -(\overline{\varepsilon} - \varepsilon) \frac{dE}{dz'} \tag{39}$$

Beneficial charge per surface unit can be calculated as below:

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$$\rho_{P'} = \frac{Q_b}{\pi R^2} \tag{40}$$

$$Q_b = \rho_b . \pi R^2 = -(\overline{\varepsilon} - \varepsilon) \pi R^2 \frac{dE}{dz'}$$
(41)

$$Q_b = -(\overline{\varepsilon} - \varepsilon)\pi \frac{d(ER^2)}{dz'}$$
(42)

$$\rho_{sb} = Q_b.dz' = -(\overline{\varepsilon} - \varepsilon)\pi \frac{d}{dz'}(ER^2)dz'$$
(43)

The main equation of Coulomb's law:

$$F = \frac{1}{4\pi\varepsilon_0} \frac{qq_0}{r^2} \tag{44}$$

The electric field is:

$$E = \frac{1}{4\pi\varepsilon_0} \frac{q}{r^2} \tag{45}$$

The electric potential can be measured:

$$\Delta V = -\int E.dL \tag{46}$$

$$V = \frac{1}{4\pi\varepsilon_0} \frac{Q_b}{r} \tag{47}$$

According to the beneficial charge equation, the electric potential could be rewritten as:

$$\Delta V = Q(z) - Q_{\infty}(z) = \frac{1}{4\pi\overline{\varepsilon}} \int \frac{(q - Q_b)}{r} dz'$$
(48)

$$Q(z) = Q_{\infty}(z) + \frac{1}{4\pi\overline{\varepsilon}} \int \frac{q}{r} dz' - \frac{1}{4\pi\overline{\varepsilon}} \int \frac{Q_b}{r} dz'$$
(49)

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$$Q_b = -(\overline{\varepsilon} - \varepsilon)\pi \frac{d(ER^2)}{dz'}$$
(50)

The surface charge density's equation is:

$$q = \sigma.2\pi RL \tag{51}$$

$$r^2 = R^2 + (z - z')^2 \tag{52}$$

$$r = \sqrt{R^2 + (z - z')^2}$$
(53)

The final equation, which obtained by substituting the mentioned equations is:

$$Q(z) = Q_{\infty}(z) + \frac{1}{4\pi\overline{\varepsilon}} \int \frac{\sigma . 2\pi R}{\sqrt{(z-z')^2 + R^2}} dz' - \frac{1}{4\pi\overline{\varepsilon}} \int \frac{(\overline{\varepsilon} - \varepsilon)\pi}{\sqrt{(z-z')^2 + R^2}} \frac{d(ER^2)}{dz'}$$
(54)

It is assumed that β is defined:

$$\beta = \frac{\varepsilon}{\overline{\varepsilon}} - 1 = -\frac{(\overline{\varepsilon} - \varepsilon)}{\overline{\varepsilon}}$$
(55)

So, the potential equation becomes:

$$Q(z) = Q_{\infty}(z) + \frac{1}{2\overline{\varepsilon}} \int \frac{\sigma R}{\sqrt{(z-z')^2 + R^2}} dz' - \frac{\beta}{4} \int \frac{1}{\sqrt{(z-z')^2 + R^2}} \frac{d(ER^2)}{dz'}$$
(56)

The asymptotic approximation of χ is used to evaluate the integrals mentioned above:

$$\chi = \left(-z + \xi + \sqrt{z^2 - 2z\xi + \xi^2 + R^2}\right)$$
(57)

where c is "aspect ratio" of the jet (L = length, R0 = Initial radius). This leads to the final relation to the axial electric field:

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$$E(z) = E_{\infty}(z) - \ln \chi \left(\frac{1}{\overline{\varepsilon}} \frac{d(\sigma R)}{dz} - \frac{\beta}{2} \frac{d^2 (ER^2)}{dz^2} \right)$$
(58)

1.7.2.5 FORCES CONSERVATION

There exists a force, as a result of charge build-up, acting upon the droplet coming out of the syringe needle pointing toward the collecting plate, which can be either grounded or oppositely charged. Furthermore, similar charges within the droplet promote jet initiation due to their repulsive forces. Nevertheless, surface tension and other hydrostatic forces inhibit the jet initiation because the total energy of a droplet is lower than that of a thin jet of equal volume upon consideration of surface energy. When the forces that aid jet initiation (such as electric field and Coulombic) overcome the opposing forces (such as surface tension and gravitational), the droplet accelerates toward the collecting plate. This forms a jet of very small diameter. Other than initiating jet flow, the electric field and Coulombic forces tend to stretch the jet, thereby contributing towards the thinning effect of the resulting nanofibers.

In the flow path modeling, we recall the Newton's Second Law of motion,

$$m\frac{d^2P}{dt^2} = \sum f \tag{59}$$

where, *m* (equivalent mass) and the various forces are summed as,

$$\sum f = f_{C} + f_{E} + f_{V} + f_{S} + f_{A} + f_{G} + \dots$$
(60)

where, subscripts *C*, *E*, *V*, *S*, *A* and *G* correspond to the Coulombic, electric field, viscoelastic, surface tension, air drag and gravitational forces respectively. A description of each of these forces based on the literature [66] is summarized in Table 1.1. Here, V_0 = applied voltage; *h* = distance from pendent drop to ground collector; σ_v = viscoelastic stress; and v = kinematic viscosity.

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Forces	Equations
Coulombic	$f_C = \frac{q^2}{l^2}$
Electric field	$f_E = -\frac{qV_0}{h}$
Viscoelastic	$f_V = \frac{d\sigma_V}{dt} = \frac{G}{I}\frac{dI}{dt} - \frac{G}{\eta}\sigma_V$
Surface tension	$f_{S} = \frac{\alpha \pi R^{2} k}{\sqrt{x_{i}^{2} + y_{i}^{2}}} \left[i \left x \right Sin(x) + i \left y \right Sin(y) \right]$
Air drag	$f_A = 0.65\pi R \rho_{air} v^2 \left(\frac{2\nu R}{\nu_{air}}\right)^{-0.81}$
Gravitational	$f_G = \rho g \pi R^2$

TABLE 1.1 Description of itemized forces or terms related to them.

1.7.3 CONSTITUTIVE EQUATIONS

In modern condensed matter physics, the constitutive equation plays a major role. In physics and engineering, a constitutive equation or relation is a relation between two physical quantities that is specific to a material or substance, and approximates the response of that material to external stimulus, usually as applied fields or forces [121]. There are a sort of mechanical equation of state, and describe how the material is constituted mechanically. With these constitutive relations, the vital role of the material is reasserted [122]. There are two groups of constitutive equations: Linear and nonlinear constitutive equations [123]. These equations are combined with other governing physical laws to solve problems; for example in fluid mechanics the flow of a fluid in a pipe, in solid state physics the response of a crystal to an electric field, or in structural analysis, the connection between applied stresses or forces to strains or deformations [121].

The first constitutive equation (constitutive law) was developed by Robert Hooke and is known as Hooke's law. It deals with the case of linear elastic materials. Following this discovery, this type of equation, often called a "stress-strain relation" in this example, but also called a "constitutive assumption" or an "equation of state" was commonly used [124]. Walter Noll advanced the use of constitutive equations, clarifying their classification and the role of invariance requirements, constraints, and definitions of terms like "material," "isotropic," "aeolotropic," etc. The class of "constitutive relations" of the form stress rate = f (velocity gradient, stress, density) was the subject of Walter Noll's dissertation in 1954 under Clifford Truesdell [121]. There are several kinds of constitutive equations, which are applied commonly in electrospinning. Some of these applicable equations are discussed as following:

1.7.3.1 OSTWALD–DE WAELE POWER LAW

Rheological behavior of many polymer fluids can be described by power law constitutive equations [123]. The equations that describe the dynamics in electrospinning constitute, at a minimum, those describing the conservation of mass, momentum and charge, and the electric field equation. Additionally, a constitutive equation for the fluid behavior is also required [76]. A Power-law fluid, or the Ostwald–de Waele relationship, is a type of generalized Newtonian fluid for which the shear stress, τ , is given by:

$$\tau = \kappa' \left(\frac{\partial \upsilon}{\partial y}\right)^m \tag{61}$$

which $\partial v/\partial y$ is the shear rate or the velocity gradient perpendicular to the plane of shear. The power law is only a good description of fluid behavior across the range of shear rates to which the coefficients are fitted. There are a number of other models that better describe the entire flow behavior of shear-dependent fluids, but they do so at the expense of simplicity, so

the power law is still used to describe fluid behavior, permit mathematical predictions, and correlate experimental data [117, 125].

Nonlinear rheological constitutive equations applicable for polymer fluids (Ostwald–de Waele power law) were applied to the electrospinning process by Spivak and Dzenis [77, 101, 126].

$$\hat{\tau}^{c} = \mu \left[tr(\dot{\hat{\gamma}}^{2}) \right]^{(m-1)/2} \dot{\hat{\gamma}}$$
(62)

$$\mu = \kappa \left(\frac{\partial \upsilon}{\partial y}\right)^{m-1} \tag{63}$$

Viscous Newtonian fluids are described by a special case of equation above with the flow index m = 1. Pseudoplastic (shear thinning) fluids are described by flow indices $0 \le m \le 1$. Dilatant (shear thickening) fluids are described by the flow indices m > 1 [101].

1.7.3.2 GIESEKUS EQUATION

In 1966, Giesekus established the concept of anisotropic forces and motions into polymer kinetic theory. With particular choices for the tensors describing the anisotropy, one can obtained Giesekus constitutive equation from elastic dumbbell kinetic theory [127, 128]. The Giesekus equation is known to predict, both qualitatively and quantitavely, material functions for steady and nonsteady shear and elongational flows. However, the equation sustains two drawbacks: it predicts that the viscosity is inversely proportional to the shear rate in the limit of infinite shear rate and it is unable to predict any decrease in the elongational viscosity with increasing elongation rates in uniaxial elongational flow. The first one is not serious because of the retardation time, which is included in the constitutive equation but the second one is more critical because the elongational viscosity of some polymers decreases with increasing of elongation rate [129, 130].

In the main Giesekus equation, the tensor of excess stresses depending on the motion of polymer units relative to their surroundings was connected to a sequence of tensors characterizing the configurational state of the different kinds of network structures present in the concentrated solution or melt. The respective set of constitutive equations indicates [131, 132]:

$$S_k + \eta \frac{\partial C_k}{\partial t} = 0 \tag{64}$$

The Eq. (65) indicates the upper convected time derivative (Oldroyd derivative):

$$\frac{\partial C_k}{\partial t} = \frac{DC_k}{Dt} - \left[C_k \nabla \upsilon + (\nabla \upsilon)^T C_k \right]$$
(65)

(Note: The upper convective derivative is the rate of change of any tensor property of a small parcel of fluid that is written in the coordinate system rotating and stretching with the fluid.)

 C_{ν} also can be measured as follows:

$$C_k = 1 + 2E_k \tag{66}$$

According to the concept of "recoverable strain" S_{μ} may be understood as a function of E_k and vice versa. If linear relations corresponding to Hooke's law are adopted.

$$S_k = 2\mu_k E_k \tag{67}$$

So,

$$S_k = \mu_k (C_k - 1) \tag{68}$$

The Eq. (55) becomes:

$$S_k + \lambda_k \frac{\partial S_k}{\partial t} = 2\eta D \tag{69}$$

$$\lambda_k = \frac{\eta}{\mu_k} \tag{70}$$