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An Elementary Introduction to Electrospinning

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Abstract: *This review is an elementary introduction to the concepts of electrospinning and new developments. Particular attention is paid throughout the paper to giving an intuitive grasp for the basic mechanism of electrospinning, especially the mechanisms of the vibration-electrospinning, the megnetio-electrospinning, and bubble-electrospinning. Finally nanomechanics and E-infinity theory in high energy physics are considered to be the most potential candidates for theoretical analysis of electrospinning.*

Keywords: *electrospinning, nanofiber, nano-effect.*

1. WHAT IS NANOTECHNOLOGY?

The important of nanotechnology was recognized in the US as an emerging technology. A National Nanotechnology Initiative (*NNI, http://www.nano.gov*) has been launched in the US with an investment of over $1 billion in nanotechnology research over the past few years. Nanotechnology has been caught much attention recently, and it can be applied to all aspects of science, engineering and life as well. But what is nanotechnology?

There are many definitions of nanotechnology, hereby we adopt El-Naschie's definition [1].

The naive and direct answer to the frequently posed question what exactly is Nanotechnology is to say that it is a technology concerning processes which are relevant to physics, chemistry and biology taking place at a length scale of one divided by 100 million of a meter[1].

$$1\text{nanometer} = 10^{-9}\text{ meter}$$

Etymology

Greek nanos or nannos means "little old man" or "dwarf", from nannas, meaning uncle. A metric prefix meaning one billionth of a unit or 10^{-9}. A single human hair is around 80,000 nanometres in.

An obvious phenomenon is the remarkably large surface-to-volume ratio of nanomaterials. Consider a fiber with radius of 1 mm and length of 10mm, its surface is

$$S = 2\pi rL = 2\pi \times 10^{-3} \times 10^{-2} = 2\pi \times 10^{-5} m^2$$

Now we divide the fiber into nanofibers with radius of 10nm. The number of the nanofibers can be calculated as

$$n = r^2 / r_0^2 = 10^{-6} / 10^{-16} = 10^{10}$$

So the total surface of the nanofibers is

$$S_0 = 2\pi n r_0 L = 2\pi \times 10^{10} \times 10^{-8} \times 10^{-2} = 2\pi m^2$$

The volume keeps unchanged, while the surface increases remarkably:

$$S_0 / S = 10^5$$

Maybe a little bit more enlightening although equally naive is to say, according to El Naschie[1], that nanotechnology is the art of producing little devices , machines and systems that have novel properties, such as extremely small electronic devices and circuits built from individual atoms and molecules, DNA computer, MEMS motor, nanosensor, nanowires, nano-satellite missions, and others, somewhat at the atomic, molecular, or macromolecular scales. Atoms are roughly Angstroms in size (a hydrogen atom is about 1 Å in diameter, a carbon atom is about 2 Å in diameter , and the diameter of oxygen atom is ca. 1.75 Å). One Angstrom (Å) is one ten-billionth of a meter or one-tenth of a nanometer.

1nm = 10 Å

In molecular scale or Angstrom scale, quantum-like phenomena occur. In a scientific sense, El Naschie[1] defined nanotechnology as a technology applied in the grey area between classical mechanics and quantum mechanics. Classical mechanics is the mechanics governing the motion of all the objects we can see with our naked eye. This is a mechanics which obeys deterministic laws (Newton Laws) and which we can control to a very far extent. By contrast, quantum mechanics which is the mechanics controlling the motion of things like the electron, the proton, the neutron and the like is completely probabilistic. We know nothing about the motion of the electron except that there is a probability that the electron may be here or there. Even crazier than this, if we know the exact location of an electron, it is impossible to know its speed, and if we know the exact speed of the electron it is impossible to know its exact location. Such a relationship is called the Heisenberg uncertainty principle.

Nanotechnology links to both deterministic classic mechanics and chaotic quantum mechanics[1]. There should a law controlling the change from a classical object like a stone to a quantum object like an electron. Somewhere between these two scales these changes happen, but this does not happen suddenly. There is a grey area between these two scales which is neither classical nor quantum[1].

To model quantum processes, we can use the deterministic chaotic geometry, which is used in E-infinite theory [2, 3, 4]. Consider an extremely simple quadratic equation in iterated form [5].

$$x_{i+1} = \lambda x_i (1 - x_i)$$

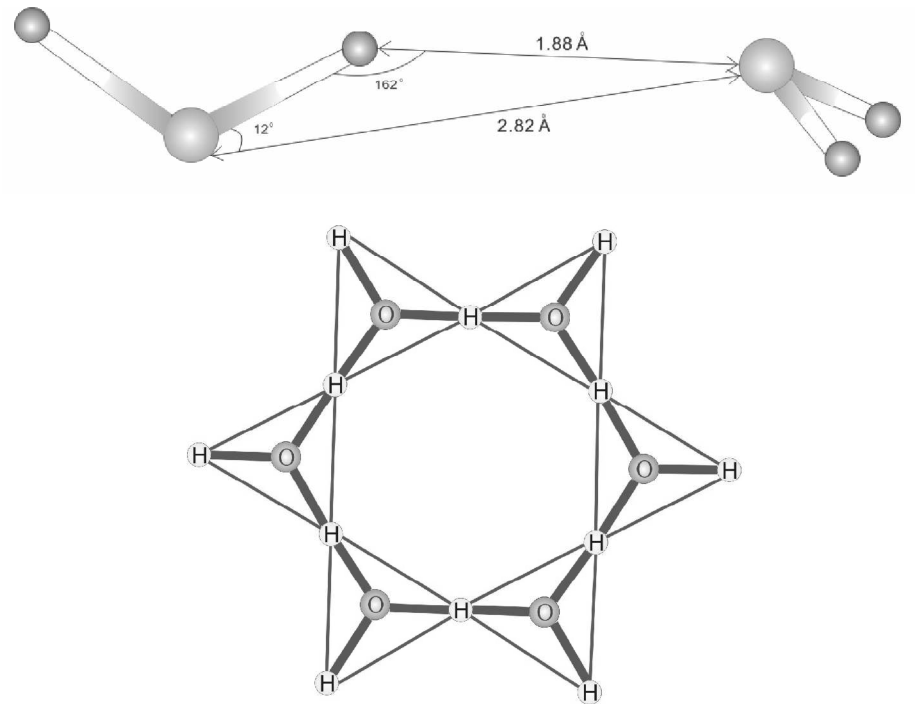


Figure 1: Aqua Technology in Angstrom-scale, shaping the World atom by atom

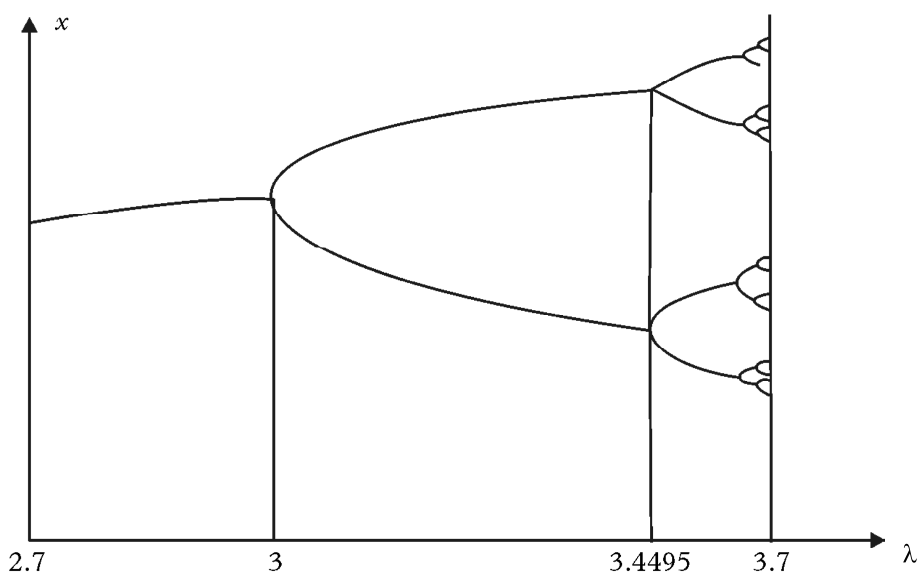


Figure 2: From Deterministic Path to Chaotic Path

where • is a parameter. The incredible complexity displayed by the bifurcation diagram of this equation as • varies was one of the most amazing discoveries in this field (see Fig. 2).

The main application of E-infinity theory shows miraculous scientific exactness, especially in determining theoretically coupling constants and the mass spectrum of the standard model of elementary particles. The absolute zero temperature, for example, can be derived using E-infinity as [1-5]

$$T_0 = (4)\ (10)\ (1/\phi)^4 - 1K$$

or the mass of an expectation proton is[1-5]

$$m_p = (20)\ (1/\phi)^8 \ \text{Mev.}$$

where $\phi = (\sqrt{5} - 1)/2$ is the golden mean.

In nano-scale, some new properties occur, and in many instances the origins of the new properties are, at present, not fully understood. Scale is of utter importance in physics as well as nanotechnology. Different scales lead to different laws (or theories) and thus results in different dimensions as illustrated in the following formula.

Dimensions = $3 + 1 + \phi^3 = 4.236...$

Newton: three dimensional absolute space.

Einstein : four dimensional continuous space-time.

El-Naschie: infinite dimensional discontinuous space-time.

E-infinity theory can give an excellent explanation of the hierarchy of motion in electrospinning process[6] as illustrated in Fig. 3.

In view of El-Naschie's E-infinite theory, systems in nano-scale may possess entirely new physical and chemical characteristics that result in properties that are neither well described by those of a single molecule of the substance, nor by those of the bulk material. Similar phenomenon is observed in quantum scale, in such a scale Einstein's spacetime resembles a stormy ocean and his original Riemannian smooth manifold is only an approximation [7]. This is the very reason for Einstein's failure to unify gravity with electromagnetism.

Consider a dragline silk with diameter of 3×10^{-6} meter, which is made of many nano-fibers with diameter of about 20nm[8]. We can estimate the number of nano-fibers in the assembly, which reads

$$n = \left(\frac{3 \times 10^{-6}}{20 \times 10^{-9}}\right)^2 \approx 2 \times 10^4$$

That means there are tens of thousands of nanofibers in the assembly !

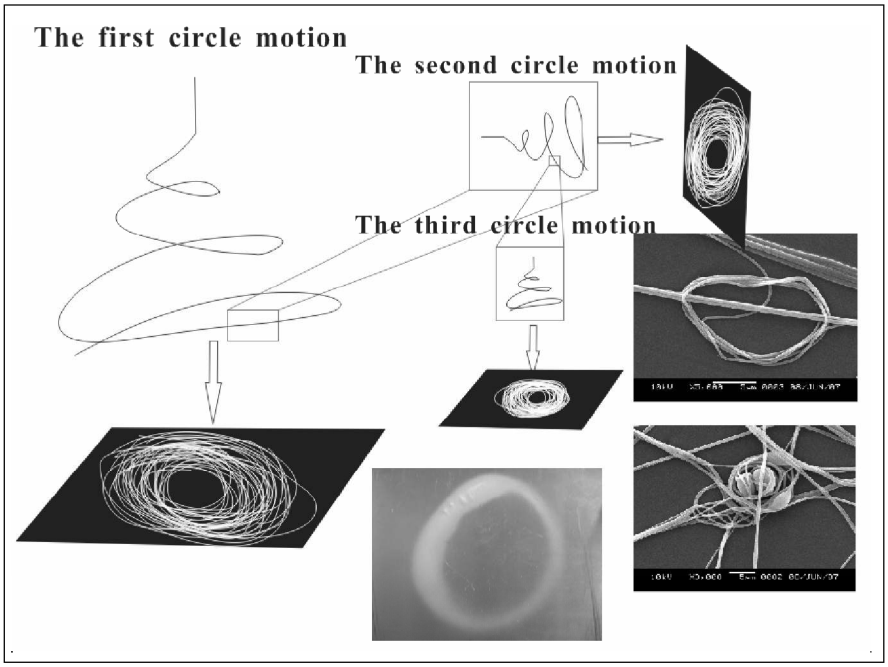


Figure 3: Hierarchy of Motion in Electrospinning Process

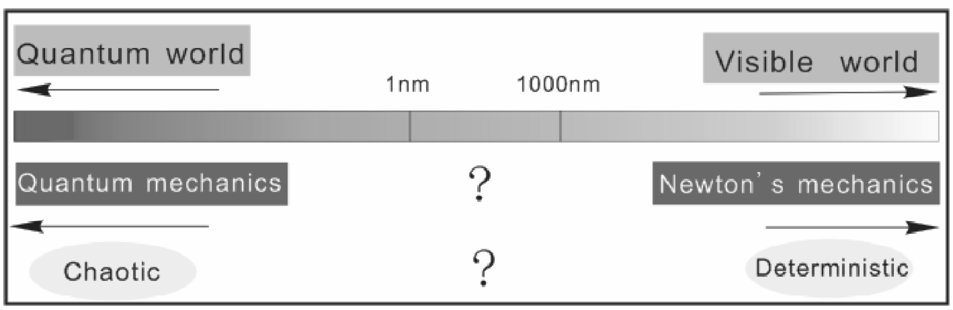


Figure 4: Nanomechanics, is it Chaotic or Deterministic?

Similar to the Hall-Petch relationship[9], the nanofiber strength depends upon fiber diameter in nano-scale (from few nanometers to tens of nanometers)[9]:

$$\tau = \tau_0 + \frac{k_\tau}{d^{1/2}}$$

where k_τ is the fitting parameters (material constants), τ_0 is the strength of the bulk material respectively, d is the fiber diameter.

Comparing the strength of a single fiber with diameter of 3×10^{-6} meter, τ_{SF}, with that of a dragline assembly consisting of 2×10^4 nanofibers with diameter of 20×10^{-9} meter, τ_{DA}, we estimate[8]

$$\frac{\tau_{DA} - \tau_0}{\tau_{SF} - \tau_0} = 2.4\times10^6$$

Extraordinarily high strength of a dragline assembly is predicted compared with a single fiber with same section area and same material.

The finding shows it is a challenge to developing technologies capable of preparing for nanofibers within 50 nm.

2. WHAT IS ELECTROSPINNING?

There are various approaches to producing nanofibers, for example, the drawing technology for producing micro/nanofibers using a micropipette with a diameter of a few micrometers; template synthesis of carbon nanotubes, nanofiber arrays and electronically conductive polymer nanostructures; thermally induced phase separation method for producing nano-porous nanofibers.

Electrospinning is the cheapest, the most straightforward way to produce nanomaterial. The electrospun nanofibers are of indispensable importance for the scientific and economical revival of developing countries.

Structured polymer fibers with diameters in the range from several micrometers down to tens of nanometers are of considerable interest for various kinds of applications. It is now possible to produce a low cost, high-value, high-strength fiber from a biodegradable and renewable waste product for easing the environmental concerns. For instance, pore structured electrospun nanofibrous membrane as wound dressing can exudates fluid from the wound so as to prevent either building up under the covering, or wound desiccation. The electrospun nanofibrous membrane shows controlled liquid evaporation, excellent oxygen permeability, and promoted fluid drainage capacity, meanwhile still can inhibit exogenous microorganism invasion because its ultra-fine pores. Other examples include thin fibers for filtration application, bone tissue engineering, drug delivery, catalyst supports, fiber mats serving as reinforcing component in composite systems, fiber templates for the preparation of functional nanotubes.

In 1934, a process was patented by Formhals entitled as "Process and apparatus for preparing artificial threads" [10], wherein an experimental setup (see Fig. 5) was outlined for the production of polymer filaments using electrostatic force. When used to spin fibers this way, the process is termed as electrospinning.

Electrospinning is a novel process for producing superfine fibers by forcing a viscous polymer/composite/sol-gel solution or melt through a spinnerette with an electric field to a droplet of the solution (most often at a metallic needle tip), see Fig.6. The electric field draws this droplet into a structure called a Taylor cone. If the viscosity and surface tension of the solution are appropriately tuned, varicose breakup is avoided (if there is varicose breakup electrospray occurs) and a stable jet is formed.

Electrospinning traces its roots to electrostatic spraying, and now electrospinning represent attractive approaches for polymer biomaterials processing with the opportunity for control over morphology, porosity, and compositions using simple equipment. Because

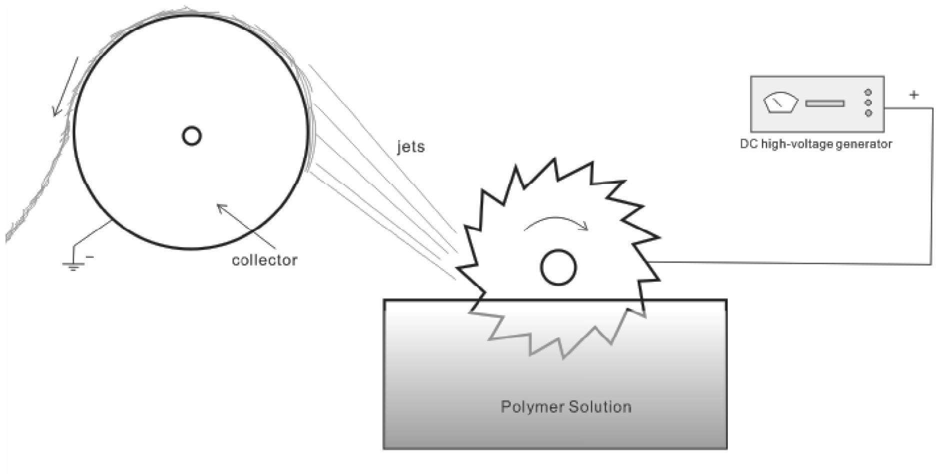


Figure 5: Formhals's Electrospinning Set-up

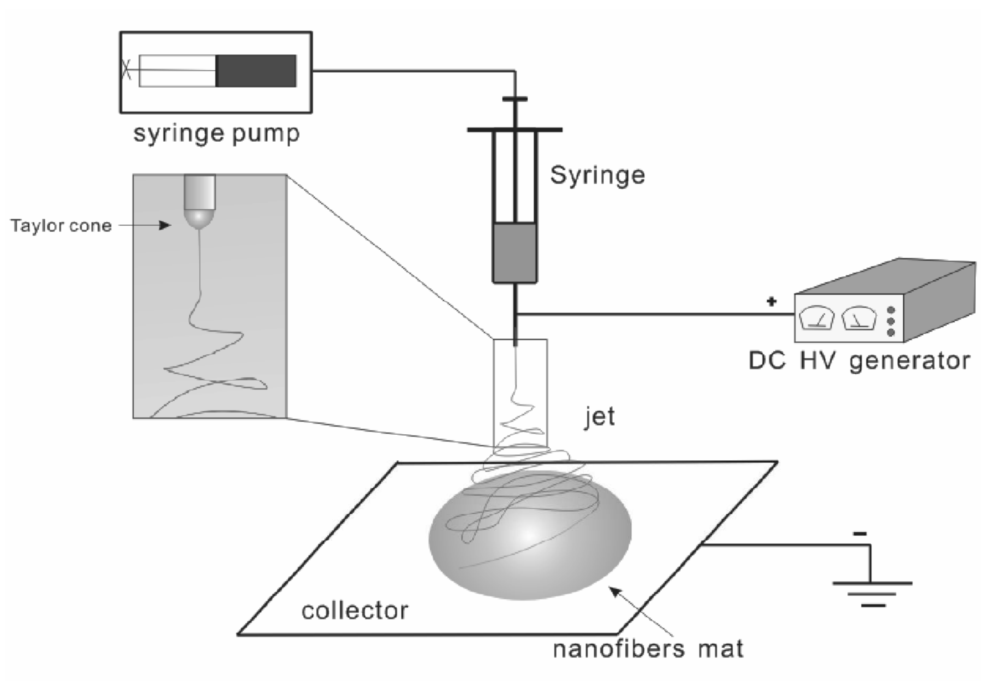


Figure 6: The Most Frequently used Electrospinning Set-up

Taylor cone [11]

A Taylor cone is caused by equilibrium between the electronic force of charged surface and the surface tension. A higher applied voltage leads to an elongated cone, when it exceeds its threshold voltage, a jet is emanated.

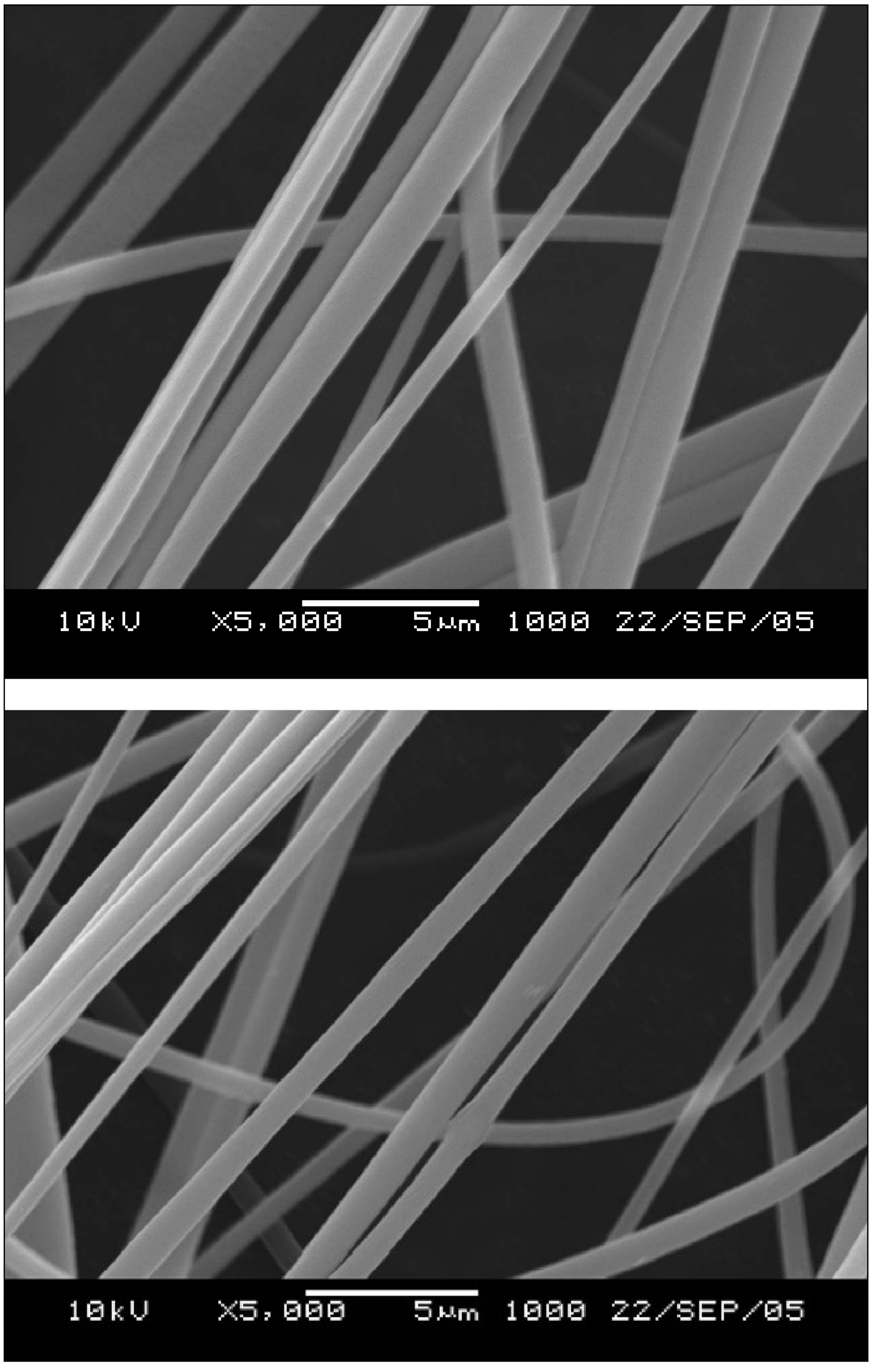


Figure 7: SEM Photograph of Electrospun Fibers

electrospinning is one of the few techniques to prepare long fibers of nano- to micrometer diameter, great progress has been made in recent years.

We define nanofiber in this book as a slender, elongated threadlike object or structure in nano-scale, from several hundreds nanometer to several thousands nanometer.

Nanofiber is an emerging, interdisciplinary area of research with important commercial applications, and will, most assuredly, be a dominant technology in new-world economies.

Materials in nanofiber form have exceptionally high level of specific surface area which enables high proportion of atoms on fiber surface, this will result in quantum efficiency, nanoscale effect of unusually high surface energy, surface reactivity, high thermal and electric conductivity, and high strength….

Electrospun fibers can be used to make nonwoven fabrics, reinforced fibers, support for enzymes, drug delivery systems, fuel cells, conducting polymers and composites, photonics, sensorics, medicine, pharmacy, wound dressing, filtration, tissue engineering, catalyst supports, fiber mats serving as reinforcing component in composite systems, fiber templates for the preparation of functional nanotubes, just say few.

3. WHAT AFFECTS ELECTROSPINNING?

We have difficulty in preciously controlling over diameter, morphology, and porosity of the electrospun fibers, we should develop a new theory linked to classical mechanics and quantum mechanics. As a first step to the new theory, we should define dimensions needed for theoretical analysis in a suitable scale, it is certainly different from our three dimensional space or 4 dimensions of spacetime, and thus El-Naschie's E-infinite theory[1] is needed.

Notice that Einstein's special relativity forbids discontinuous space, leading to the failure of unification of gravity with electromagnetism. El Naschie set up to solve the contradiction and the result was his famous E-infinity theory[1]. According to El Naschie, space and time are discontinuous. The main conceptual idea of E-infinity theory is in fact a sweeping generalization of what Einstein did in his general theory of relativity, namely introducing a new geometry for space–time which differs considerably from the space–time of our sensual experience. As El Naschie points out that on extremely small scales, at very high observational resolution equivalent to a very high energy, space–time resembles a stormy ocean[1].

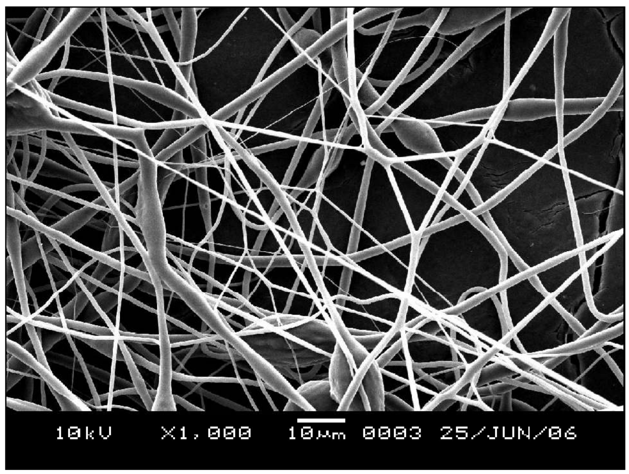
We like to stress that E-infinity theory is stressing the fact that everything we see or measure in nature is resolution dependent. Hereby we show continuum water on angstrom-scale becomes discontinuous.

One Angstrom (Å) is one ten-billionth of a meter or one-tenth of a nanometer [nm] nanometer. Atoms are roughly Angstroms in size (a hydrogen atom is about 1 Å in diameter, a carbon atom is about 2 Å in diameter , and the diameter of oxygen atom is ca. 1.75 Å). At such a resolution, the world of water must look like Universe which is full of empty.

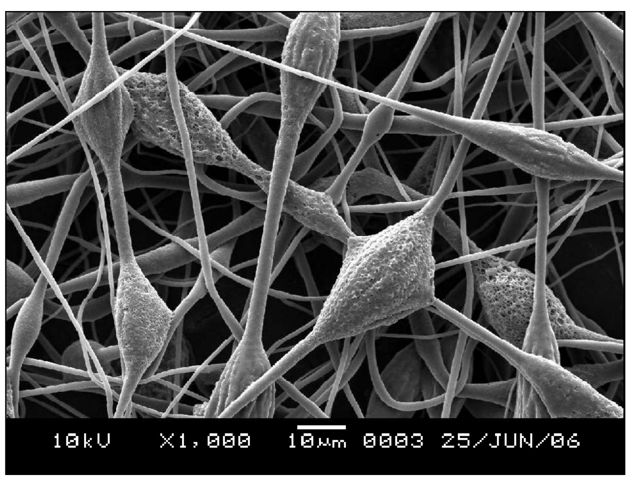
In macro-scale, pure water is definitely continuous with 3 dimensions of space, but on Angstrom-scale, the fractal dimension reads.

$$D = \frac{\ln 7.359}{\ln 2.82} = 1.92$$

That means the pure water is full of empty in the three dimensional space. In nano-scale, quantum-like phenomenon can be observed. In our previous experiment, we found uncertainty phenomenon: at almost the same conditions, we could not obtain exactly same nanofibers, beads, or micro-spheres, see Fig.8(a) and (b), similar to Heisenberg's uncertainty principle in quantum mechanics[12].



(a) Beads are Formed.



(b) Enlarged Beads with Surface Porosity are Formed.

Figure 8: Different Morphology SEM Photographs of PBS Electrospun Fibers at the Same Conditions. The Concentration and Voltage are 12wt% and 10kV. The Diameter of the Inner Needle Orifice is 0.5mm.

Of course deterministic characteristic also exists in nano-scale. The following parameters affect the electrospinning process:

Molecular weight, viscosity, conductivity, surface tension, applied electric potential, flow rate, solvent, concentration, distance between the capillary and collection screen. A complete mathematical analysis is available on the forthcoming chapters.

4. VIBRATION-ELECTROSPINNING [13,14]

Vibration technology [13, 14] has been introduced into polymer processing for many years. Initially, it was only applied in researches for polymer melt viscosity measurement. Subsequently, the principle of melt vibration was introduced into practical applications including injection molding, extrusion and compression molding/thermoforming for reduction of viscosity to lowering processing temperature and pressure to the elimination of melt defects and weld lines, and enhancement of mechanical properties by modification of the amorphous and semicrystalline texture and orientational state.

Ibar[15] observed the effect of low-frequency vibration during processing for PMMA (Fig. 9). The result showed that increasing frequency makes the solution viscosity decreased. The lower the frequency was the bigger the viscosity differences were among variety temperatures. In the regime of low frequency, the solution viscosity decreased quickly, in the regime of frequency from 100-500rad/s, the increase of frequency did not work obviously. However, frequencies higher than 200rad/s would decrease viscosity gradient caused by temperature. Ibar explained the effect of vibration frequency and amplitude on melt viscosity in terms of shear-thinning criteria.

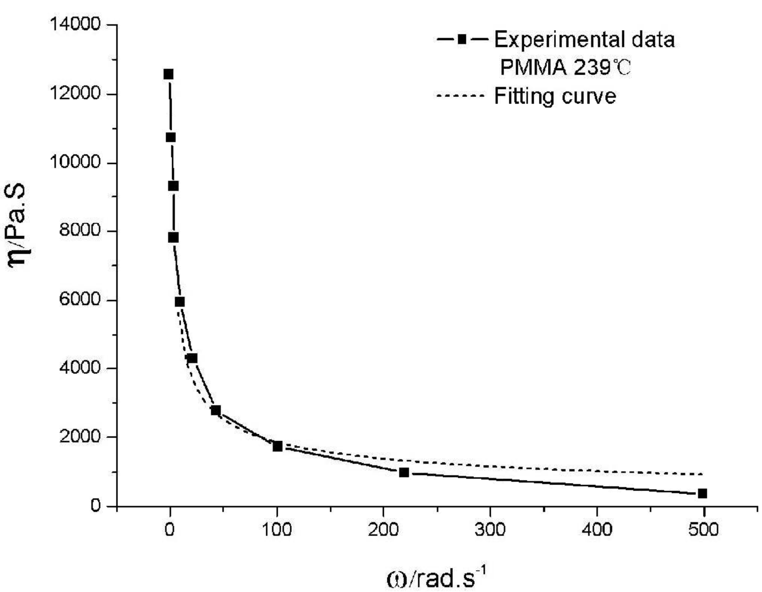


Figure 9: Solution Viscosity (η) of PMMA vs. the Vibration Frequency (ω) [15]

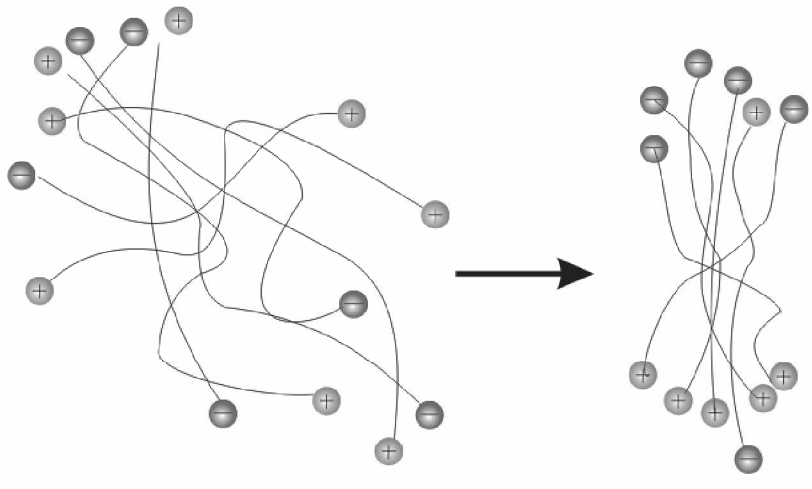


Figure 10: Electronic Field acts on Entangled Macromolecule

(a) without an electric field; (b) with an electric field plus vibrating force which leads to high molecular orientation due to electronic force, and a result high mechanical properties are estimated.

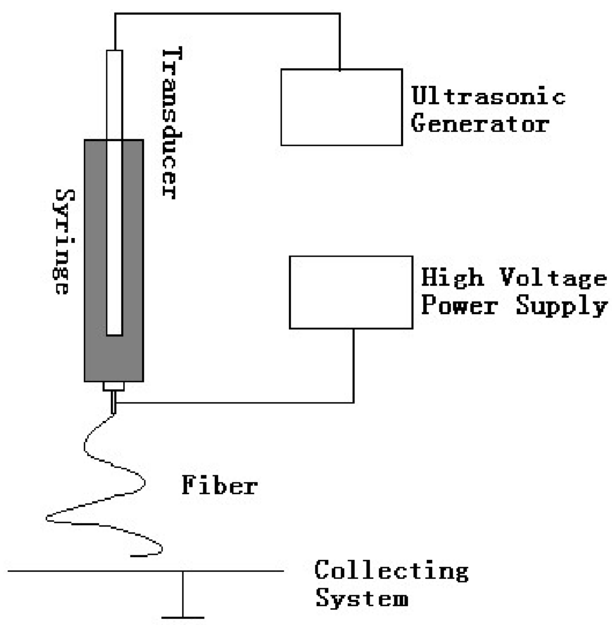


Figure 11: Schematic of Vibration Technology in Polymer Electrospinning (this Apparatus was Patented: Wan, Y.Q., Zhang, J., He, J.H., Yu, J.Y. , CHN Patent 200420020596.3, to use this Principle to Prepare Electrospun Fibers, Transfer Agreement must be Made).

When a vibrating force is applied to a concentrated and entangled polymer solution or melt, the weak van der Waals force connecting with macromolecules becomes weaker, and entanglement is relaxed, so that viscous force between the macromolecules decreases dramatically, resulting in the reduction of viscosity.

According to the experimental observation, we have the following allometric scaling.

$$\eta \propto \omega^{-\beta}$$

where β is a scaling exponent that varies with the polymer's characteristics. For PMMA solution at 239°C Ibar's experiment [15] showed $\eta \propto \omega^{-2/5}$. Our experiment revealed $\eta \propto \omega^{-7/10}$ for PAN/DMF solution.

When an additional vibrating force is applied to conducting polymer solutions or melts, dramatic reduction in viscosity occurs.

The voltage is applied to polarize dielectrics, where the charges are not completely free to move, but the positive and negative charges that compose the body may be displaced in relation to one another when a vibrating force is applied, see Fig. 4. 2.

Due to its lower viscosity, we need a relative lower voltage to eject jet from the spinnerette.

From relations(4.1) and (4.2), we have the following power law [13]:

$$d \propto \omega^{-\delta},$$

where δ is the scaling exponent that varies among different polymers.

The main advantages of the vibration-electrospinning are: (1) dramatic reduction of viscosity, so that the jet length can be controlled by frequency; (2) finer fibers can be produced than those obtained by traditional electrospinning apparatus under the same conditions, or the patented apparatus can even spin such fibers that traditional apparatus can not be spun, or can spin fibers with same diameter by much lower voltage; (3) the patented electrospinning process, as that in polymer extrusion, can enhance mechanical properties of electrospun fibers by modification of the amorphous and semicrystalline texture and orientational state.

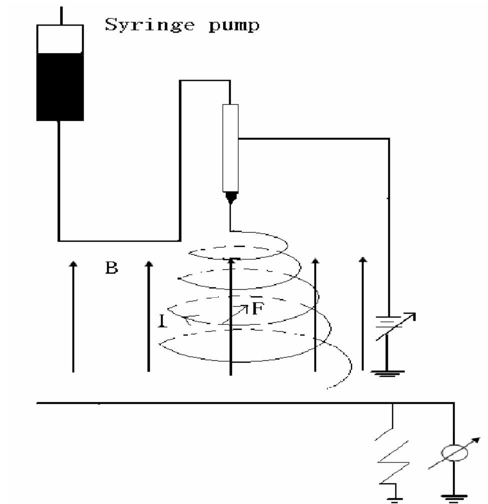
6. MEGNETIO-ELECTROSPINNING [16]

If we apply a magnetic field in the electrospinning process, as illustrated in Fig.12, an Ampere force is generated due to the current in the polymer jet:

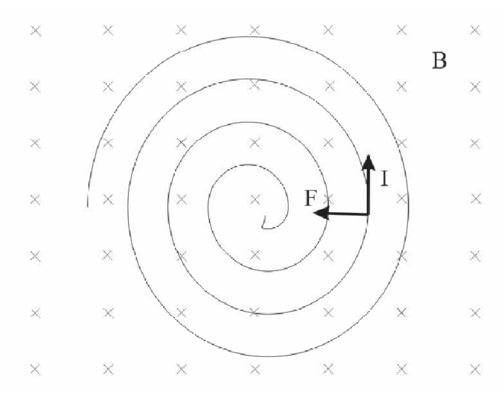
$$\vec{F} = L\vec{I} \times \vec{B}$$

where I is current, floating inside the conductor, B is the value of magnetic field induction, and L is the conductor length.

The resultant force of electric force and the viscous force of the jet flow enlarges the whipping circle. If we apply a magnetic field in the electrospinning, the problem can be completely overcome. The current in the jet, under the magnetic field, produces a



(a) Application of a Magnetic Field to the Electrospinning



(b) Ampere Force in the Electronic Jet Induced by the Magnetic Field

(c) The Whipping Circle is Shrunken using a Magnetic Field.

Figure 12: Effect of Magnetic Field on Electrospinning.

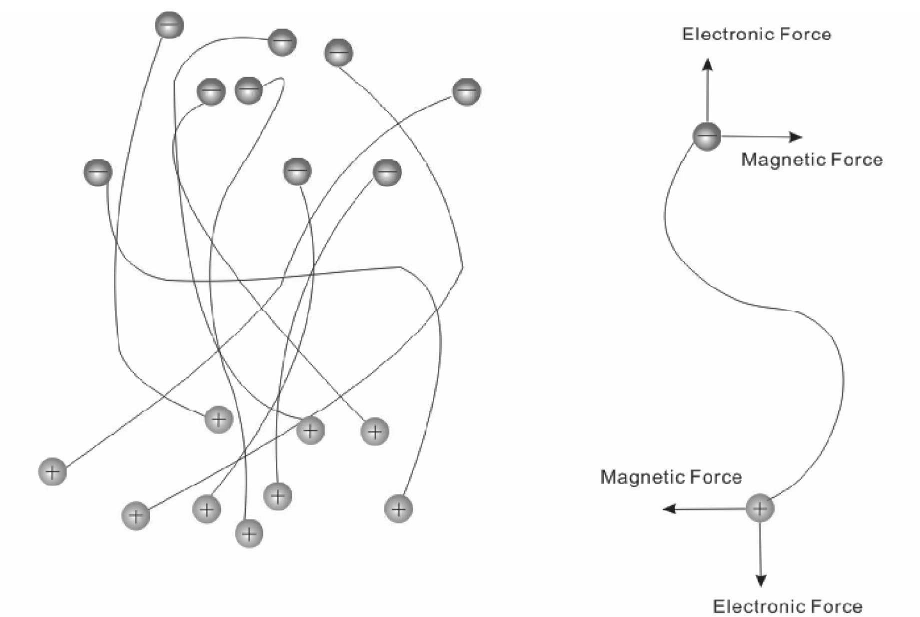


Figure 13: Macromolecules under the Coupled Forces of Electronic Force and Magnetic Force.

centripetal force, i.e., the direction of the Ampere force is always towards the initial equilibrium point (see Fig. 13), leading to the shrinking of the radius of whipping circle.

The magnetic force is perpendicular to the velocity, so it contributes no work for the moving jet, and the shrunken circle means less energy waste in the instability process, the saved energy is used to increase the kinetic energy of the moving jet. According to Eq. (2.1) $r^2 \sim 1/u$, the radius becomes much smaller than that without magnetic field.

The produced magnetic force can ameliorate inner structure of macromolecules, resulting in remarkable amelioration of nanofiber's strength.

7. BUBBLE-ELECTROSPINNING [17, 18]

Hinted by the mechanism of the spider-spinning, we design a new approach to overcoming the bottleneck in present electrospinning technology, that is to minimize the surface tension of the electrospun solutions mimicking the spider-spinning. Our system[17,18] consists of a vertical solution reservoir with a gas tube feeding from the bottom, in which a metal electrode fixed along the centerline of the tube, and a grounded collector over the reservoir, see Fig.14. It has been found that many small bubbles with different sizes were produced on the solution surface.

The mechanism of the new electrospinning process is deceptively simple: in the absence of an electric field, the aerated solution forms various bubbles on the surface. When an electric field is present, it induces charges into the bubble surface, these quickly relax to the bubble surface. The coupling of surface charge and the external electric field creates a tangential stress, resulting in the deformation of the small bubble into a protuberance-induced upward-directed reentrant jet. Once the electric field exceeds the critical value needed to overcome the surface tension, a fluid jet ejects from the apex of the conical bubble. The threshold voltage needed to overcome the surface tension depends upon the size of the bubble and inlet air pressure. The most fascinating character of the surface tension of a bubble is independent of the properties of the electrospun solutions, such as viscosity. This new technology is of critical importance for the new generation of electrospinning, especially for the specialists in design, manufacturing and using nanofibers.

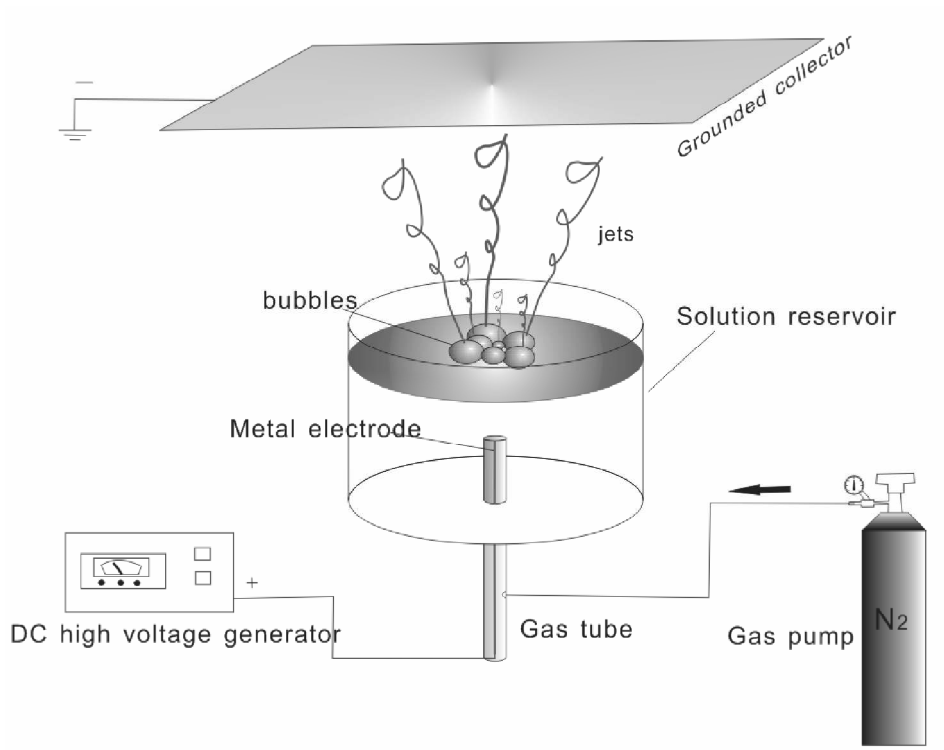


Figure 14: The Experimental Setup of the Aerated Solution Electrospinning. This Principle to Prepare for Nano Products was Patented (CHN Patent No. 200710036447.4). To use this Principle to Prepare for Nano-porous Products, Transfer Agreement Must be Made).

8. APPLICATIONS

An important characteristic of electrospinning is the ability to make fibers with diameters in the range of manometers to a few microns. Consequently these fibers have a large surface area per unit mass so that nanowoven fabrics of these nanofibers collected on a screen can be used for example, for filtration of submicron particles in separation industries and biomedical applications, wound dressing,, tissue engineering scaffolds, artificial blood vessels, photonics, sensorics, pharmacy, drug delivery, catalyst supports, fiber mats serving as reinforcing component in composite systems, fiber templates for the preparation of functional nanotubes, and others. The use of electrospun fibers at invisibility device (e.g. stealth plane) and at critical places in advanced composites to improve crack resistance is also promising.

9. GLOBAL INTEREST IN THE FIELD OF ELECTROSPINNING

According to data basis of Web of Science on July 15, 2006, publications on electrospinning is rocketing.

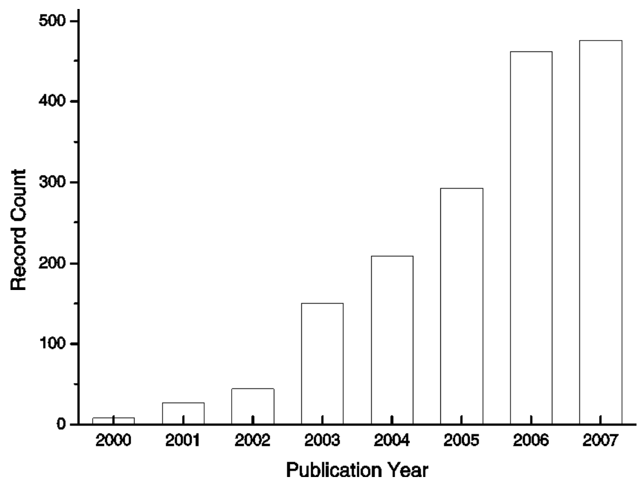


Figure 15: Increase of Publication in Electrospinning.

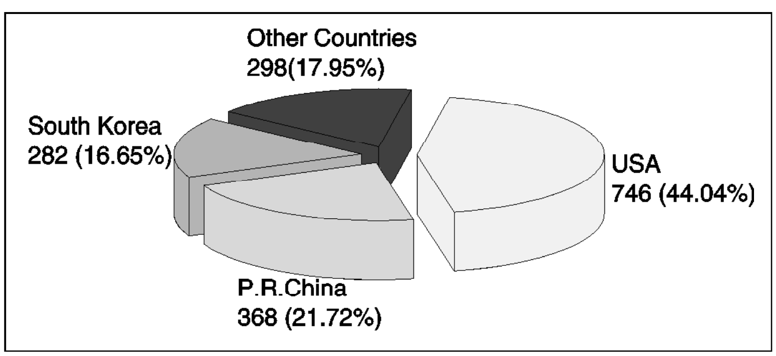


Figure 16: Global Interest in Electrospinning.

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