Review

Mathematical models for continuous electrospun nanofibers and electrospun nanoporous microspheres

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Abstract: A brief review of mathematical models of electrospinning is given. The nano-effect and electrospinning dilation are presented to explain how to prepare extremely high strength continuous nanofibers and nanoporous microspheres, respectively. According to the established models, vibration-electrospinning is introduced to improve electrospinability, Siro-electrospinning is suggested to mimic the spinning procedure of a spider and magneto-electrospinning is used to control the instability arising in the electrospinning process. A new theory linked to both classical mechanics and quantum mechanics should be developed to explain certain special phenomena in electrospinning. E-infinity theory is considered to be a potential theory to deal with quantum-like properties and nano-effect on the nanoscale. The emphasis of this brief review is upon the authors' recent work, and the references are not exhaustive.

Keywords: electrospinning; nanofiber; nanoporous microspheres; nano-effect; dragline silk; magneto-electrospinning; vibration-electrospinning; Sirofil; Siro-electrospinning; E-infinity theory

INTRODUCTION

Nanofibers and nanoporous microspheres have remarkably large surface-to-volume ratio, and the nano-effect has been demonstrated for unusual strength, high surface energy, surface reactivity and high thermal and electric conductivity.[1–3] These characteristics improve performance for many applications. Electrospinning[4–13] is a process which produces polymer nanofibers and nanoporous microspheres.[1–3] Electrospinning has the unique ability to produce nanofibers and nanoporous microspheres of different materials in various fibrous assemblies. The relatively high production rate and simplicity of the setup make electrospinning highly attractive to both academia and industry. A variety of nanofibers and nanoporous microspheres can be made for applications in air filtration, water filtration, agricultural nanotechnology, energy storage, healthcare, biotechnology, environmental engineering, defense and security and invisibility devices (e.g. stealth plane). The procedure involves applying a very high voltage to a capillary and pumping a polymer solution through it. Nanofibers of the polymer are collected as a nonwoven fabric on a grounded plate below the capillary.

In this paper we give a brief review of mathematical models for electrospinning and their applications. The work is mainly based on the three invited lectures given at the 4th World Congress of Nonlinear Analysts (2004), the 3rd MIT Conference on Computational Fluid and Solid Mechanics (2005) and the 1st International Conference on Science and Technology for Sustainable Development of the Greater Mekong Sub-region (2006).

ONE-DIMENSIONAL STEADY MODEL

One can write the one-dimensional steady model for an electrospinning jet as follows:[14–17]

$$\pi r^2 u\rho = Q \tag{1}$$

$$2\pi r\sigma u + \pi r^2 kE = I \tag{2}$$

$$u\frac{\partial u}{\partial z} = -\frac{1}{\rho}\frac{\partial p}{\partial z} + \frac{2\sigma E}{\rho r} + \frac{\partial \tau}{\partial z} \tag{3}$$

where Q is the mass flow rate, u the velocity, ρ the density, E the applied voltage, I the current, p the internal pressure of the fluid, τ the viscous force, σ the surface density of the charge and r the radius of the jet at axial coordinate z.

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SPIVAK–DZENIS MODEL

Spivak and co-workers established a model of a steady-state jet in the electrospinning process:[18,19]

Equation of mass balance gives
$$\nabla \cdot \boldsymbol{u} = 0 \tag{4}$$

Linear momentum balance is
$$\rho(\boldsymbol{u} \cdot \nabla)\boldsymbol{u} = \nabla T^{\mathrm{m}} + \nabla T^{\mathrm{e}} \tag{5}$$

Electric charge balance reads
$$\nabla \cdot \boldsymbol{J} = 0 \tag{6}$$

The right-hand side of Eqn (5) is the sum of viscous and electric forces.

WAN–GUO–PAN MODEL

The Wan–Guo–Pan model[20] considers the couple effects of heat, electricity and hydrodynamics. A complete set of balance laws governing the general thermoelectrohydrodynamics flows was derived by and Ko and Dulikravich[21] and Chen.[22] It consists of modified Maxwell's equations governing the electrical field in a moving fluid, the modified Navier–Stokes equations governing heat and fluid flow under the influence of electric field and constitutive equations describing behavior of the fluid. The governing equations are[20]

$$\frac{\partial q_{\mathrm{e}}}{\partial t} + \nabla \cdot \boldsymbol{J} = 0 \tag{7}$$

$$\rho \frac{\mathrm{D}\boldsymbol{u}}{\mathrm{D}t} = \nabla \cdot \boldsymbol{t} + \rho \boldsymbol{f} + q_{\mathrm{e}}\boldsymbol{E} + (\nabla \boldsymbol{E}) \cdot \boldsymbol{P} \tag{8}$$

$$\rho c_{\mathrm{p}} \frac{\mathrm{D}T}{\mathrm{D}t} = Q_{\mathrm{h}} + \nabla \cdot \boldsymbol{q} + \boldsymbol{J} \cdot \boldsymbol{E} + \boldsymbol{E}\frac{\mathrm{D}\boldsymbol{P}}{\mathrm{D}t} \tag{9}$$

The current is composed of three parts: (1) the Ohmic bulk conduction current, $\mathcal{J}_{\mathrm{c}} = \pi r^2 kE$; (2) the surface convection current, $\mathcal{J}_{\mathrm{s}} = 2\pi r\sigma u$; and (3) the current caused by temperature gradient, $\mathcal{J}_{\mathrm{T}} = \pi r^2 \sigma_{\mathrm{T}} \partial T/\partial z$.

The disadvantage of this model is that no thermal effect is considered in Eqn (8), which can be modified as

$$\rho \frac{\mathrm{D}\boldsymbol{u}}{\mathrm{D}t} = \nabla \cdot \boldsymbol{t} + \rho \boldsymbol{f} + q_{\mathrm{e}}\boldsymbol{E} + (\nabla \boldsymbol{E}) \cdot \boldsymbol{P} + \zeta \nabla T \tag{10}$$

ALLOMETRIC MODEL

We know from Ohm's law that current flows down a voltage gradient in proportion to the resistance in the circuit. Current is therefore expressed as

$$I = \frac{E}{R} = gE \tag{11}$$

where I is the current, E is the voltage, R is the resistance and g is the conductance. The resistance, R, in Eqn (11) is expressed in the form

$$R = \frac{kL}{A} \tag{12}$$

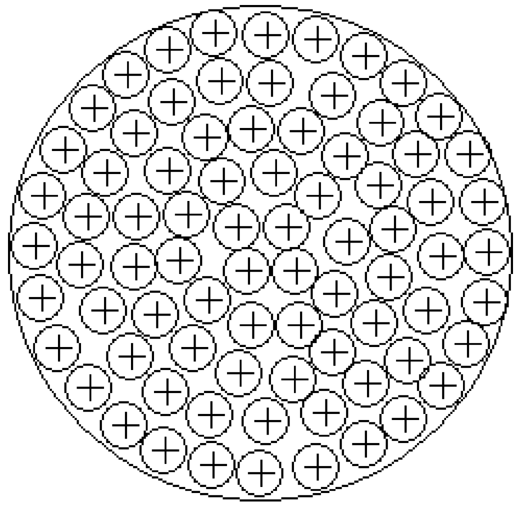

Figure 1. Conductance of an ideal electronically charged jet: $g_{\mathrm{c}} \sim r^2$, where r is the radius of the conductor.

where A is the area of the conductor, L its length and k a resistance parameter.

Actually Eqn (11) is valid only for metal conductors where there are plenty of electrons in the conductor. However, in an electrospinning jet, the current is not caused by electrons, so Eqn (11) should be modified in order to accurately describe the polymer conduction. An allometric scaling law between the conductance and the radius of the jet has been proposed[23] in the form

$$g \sim r^{\alpha} \tag{13}$$

where α is a scaling exponent. The above modification is also valid for nerve fibers.[24]

When $\alpha = 2$, one has the case of a metal-like conductor, so for the Ohmic bulk conduction current (Fig. 1), we have $I_{\mathrm{c}} = \pi r^2 kE$, where k is the dimensionless conductivity of the fluid.

When $\alpha = 1$, no free ions or electrons exist in the bulk, and the current is caused by surface charge distributed along the surface which is in motion (Fig. 2). So for the surface convection current, we have $I_{\mathrm{s}} = 2\pi r\sigma u$. The conduction of an actual electronically charged jet lies between Ohmic bulk conduction and surface convection (Fig. 3), so the value of α lies between 1 and 2.

We can also assume that the scaling relationship between the conductance and polymer concentration has the form (see the experimental data in Kim *et al.*[25])

$$g \sim c^{\beta} \tag{14}$$

where c is the polymer concentration and β is a scaling exponent. So the conductance for an electrospinning jet can be expressed as

$$g = \lambda c^{\beta} r^{\alpha} \tag{15}$$

where λ is a constant.

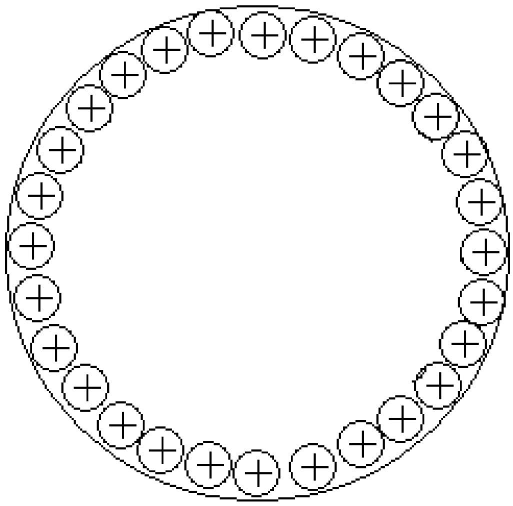

Figure 2. Conductance of an ideal surface: $g_s \sim r$.

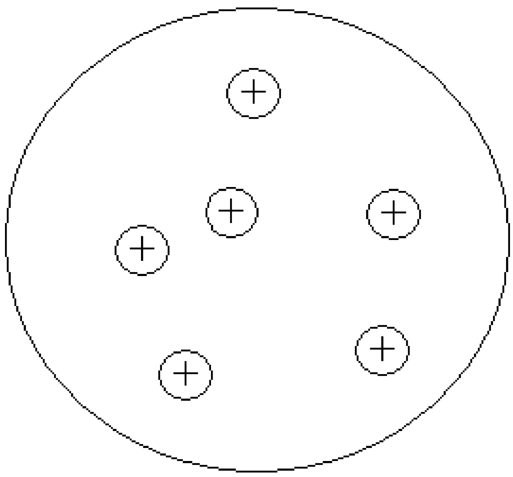

Figure 3. Conductance of an actual electronically charged jet.

The current balance in the jet can be expressed as follows:

$$2\pi r\sigma u + \lambda c^{\beta} r^{\alpha} E = I \tag{16}$$

This equation first appeared in the literature giving implications for the polymer concentration and nonmetal conductive effect on the electrospinning process.

We also establish a mathematical model for AC electrospinning.[26] Based on the established models, numerical analysis[27] and analytical analysis[28–34] can be easily carried out. By approximate one-dimensional models, we establish the relationships among voltage, current, solution flow rate and diameter of the electrospun fibers.[28–34] Instability arising in electrospinning is theoretically studied,[31] and in order to control the instability in electrospinning, magneto-electrospinning is suggested.[35]

ELECTROSPINABILITY AND VIBRATION-ELECTROSPINNING

This section is concerned with showing the possibility of producing ultrafine fibers from solutions with high viscosity or even in the gel state, which is difficult to be spun by traditional electrospinning, by vibration-electrospinning.[36–39] Electrospinning is a simple but powerful method for making very thin polymer fibers, but not every polymer can be prepared for electrospinning. Generally speaking solutions of polymers with too low or too high a molecule weight (dilute unentangled or concentrated entangled solutions) cannot be electrospun into continuous fibers.[39]

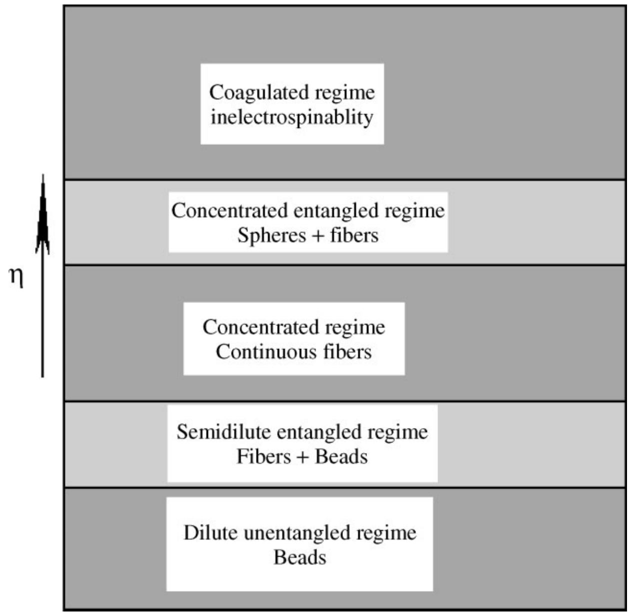

Figure 4. Electrospinability of different concentrations.

Chain entanglements are one of many parameters that can significantly influence fiber formation during polymer electrospinning.[40] At polymer concentrations higher than the critical concentration, above which polymer entanglement can occur, it was found polymer fibers could be electrospun, provided the spin-dope solution was sufficiently viscous.[39] Electrospinability mainly depends upon the solution viscosity, as illustrated in Fig. 4.

McKee *et al*. expanded the range of this technique by making fibers from small molecules, namely phospholipids.[40] McKee *et al*. showed that at concentrations above the onset of entanglements of the wormlike micelles, electrospun fibers were fabricated with diameters of the order of 1–5 μm.[40]

Our analysis[36] shows that viscosity affects markedly the diameter of electrospun fibers, and it was shown that the fiber diameter depends allometrically on solution viscosity in the form

$$d \propto \eta^{\alpha} \tag{17}$$

where d is the diameter of the electrospun fiber, η the viscosityand α the scaling exponent. The exponent value might differ between different polymers. For acrylic solution, Baumgarten[41] found that the scaling exponent is about 1/2.

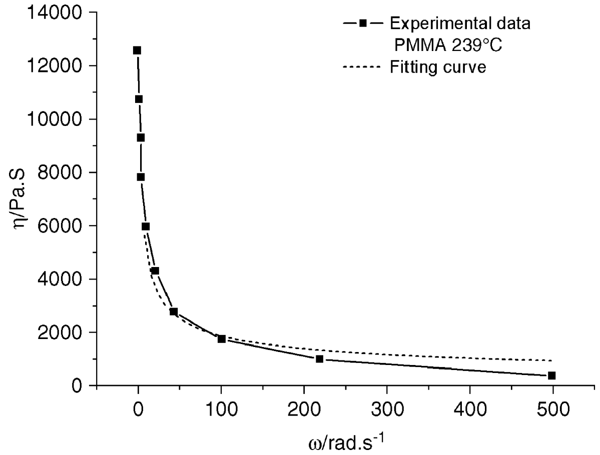

Figure 5. Solution viscosity (η) of poly(methyl methacrylate) (PMMA) *versus* the vibration frequency (ω).

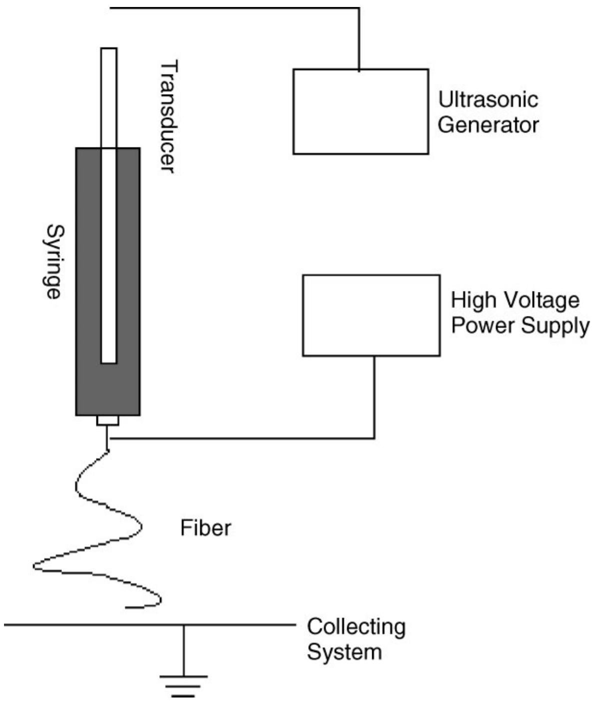

Figure 6. Schematic of vibration technology in polymer electrospinning. (This apparatus is patented: Wan YQ, Zhang J, He JH and Yu J, Chinese Patent 200420020596.3. To use this principle to prepare electrospun fibers, a transfer agreement must be made).

The viscosity of the polymer solution can be dramatically reduced by vibration technology[42,43] (Fig. 5), leading to finer nanofibers. One can also prepare nanofibers via vibration-electrospinning from solutions with high viscosity, where the traditional electrospinning becomes invalid.[37–39] The experimental setup for vibration-electrospinning is illustrated in Fig. 6.

ELECTROSPINNING DILATION AND ELECTROSPUN NANOPOROUS MICROSPHERES

During the electrospinning process, the charged jet is accelerated by a constant external electric field, and the spinning velocity probably reached maximum and perhaps exceeds the velocity of sound in air in a very short time before the spinning becomes unstable. According to the conservation of mass equation

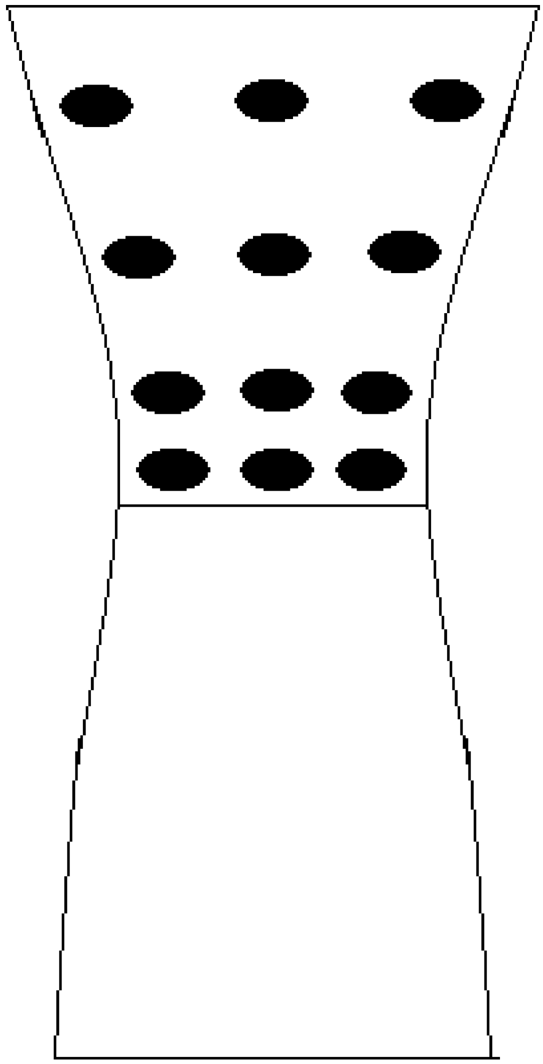

Figure 7. Macromolecular chains are compacted during electrospinning.

$$\pi r^2 \rho u = Q \tag{18}$$

where r is the radius of the jet, u the velocity, Q the flow rate and ρ the density, the radius of the jet decreases with the increase of the velocity of the incompressible jet. When the velocity reaches its maximum, the radius of the jet is minimized, and macromolecules of the polymers are compacted together tighter and tighter, as illustrated in Fig. 7. There must exist a critical minimal radius r_{cr} for all electrospin jets, $r \le r_{cr}$ for continuous ultrafine fibers, and the critical maximal velocity is $u_{cr} = Q/\pi\rho r_{cr}^2$. However, the velocity can exceed this critical value u_{cr} if a higher voltage is applied.

In the case when the radius of the jet reaches the value of the critical value, $r = r_{cr}$, and the jet speed exceeds its critical value, $u > u_{cr}$, in order to keep the conservation of mass equation, the jet

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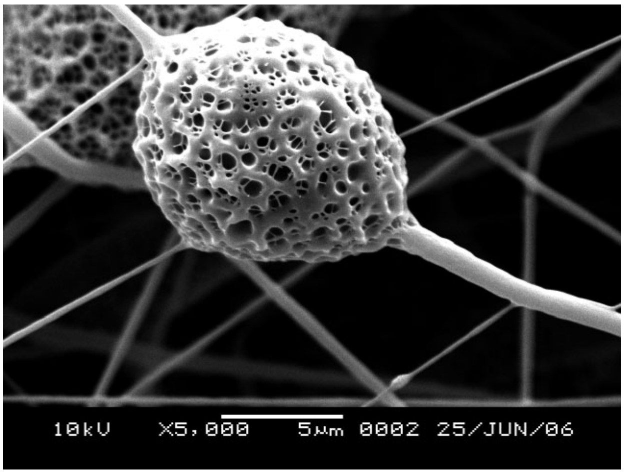

Figure 8. Electrospinning dilation phenomenon of PBS electrospun fibers.[2]

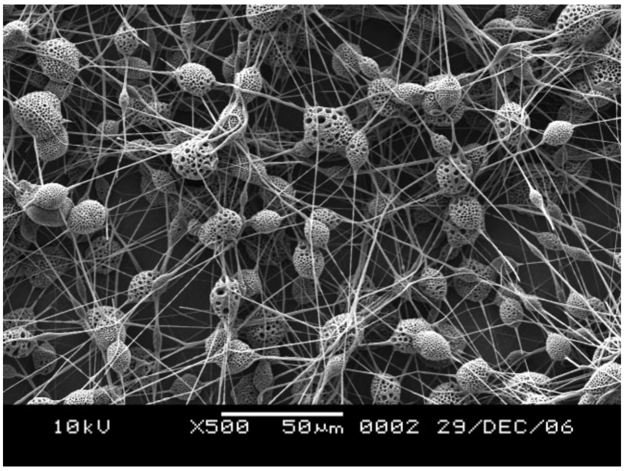

Figure 9. Electrospun nanoporous microspheres, where a kind of traditional Chinese drug called *Yunnan Baiyo* was used as an additive.[3]

dilates by decreasing its density, leading to porosity of electrospun fibers[1–3] (Figs 8 and 9); we call this phenomenon electrospinning dilation. Nanoporous microspheres are especially useful for invisibility devices (e.g. stealth planes)[1–3] and drug delivery.[44]

NANO-EFFECT IN ELECTROSPINNING

Electrospun nanofiber technology bridges the gap between deterministic laws (Newtonian mechanics) and probabilistic laws (quantum mechanics).[45,46] Our research reveals that fascinating phenomena arise when the diameter of the electrospun nanofibers is less than 100 nm.[1] In our previous experiments, we found an uncertainty phenomenon: at almost the same conditions, we could not obtain exactly the same nanofibers, beads or microspheres (see Figs 2(a) and (b) in reference 3), similar to Heisenberg's uncertainty principle in quantum mechanics.

The nano-effect has been demonstrated for unusual strength, high surface energy, surface reactivity and high thermal and electric conductivity. Similar to the

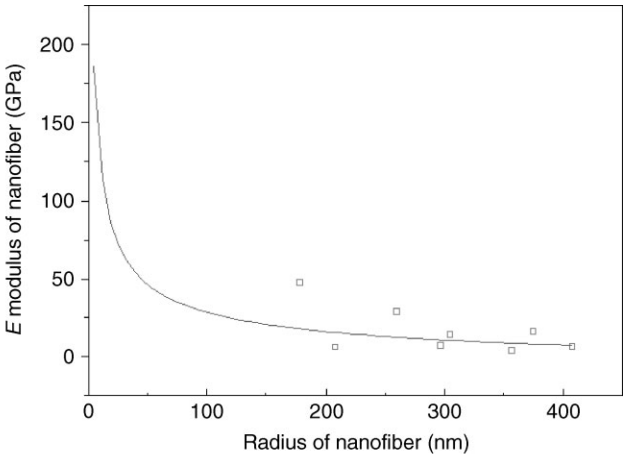

Figure 10. *E* modulus of nanofibers. (Redrawn according to the experimental data of Gu *et al*.[47] The squares are the experimental data).

Hall–Petch relationship, the nanofiber strength and surface energy depend upon fiber diameter at the nanoscale (from a few to tens of nanometers):[1]

$$\tau = \tau_0 + \frac{k_\tau}{d^\alpha} \tag{19}$$

$$E = E_0 + \frac{k_E}{d^\beta} \tag{20}$$

where k_τ and k_E are the fitting parameters (material constants), τ_0 and E_0 are the strength and surface energy of the bulk material respectively, d is the fiber diameter ($0 < d < 100$ nm) and $\alpha > 0$ and $\beta > 0$ are scaling exponents.

Gu *et al*. measured the Young's modulus of a single electrospun polyacrylonitrile (PAN) fiber using an atomic force microscopy (AFM) cantilever.[47] We re-analyzed the data revealing the nano-effect happening near 150 nm (Fig. 10).

SPIDER-SPUN FIBER AND SIRO-ELECTROSPINNING

Recently spider silk has attracted much attention due to its unmatched mechanical character and potential applications in various fields.[48–55] Actually dragline silk is made of many nanofibers with diameters of about 20 nm (Fig. 11); thus it can make full use of nano-effects.

Spiders have evolved far superior methods for processing polymers into materials. These methods allow nearly optimal utilization of the quantum-like properties or nano-effect of the polymer chains. Imagine a silk-like material with the diameter of a pencil so strong it could stop a Boeing 747 in flight; the stress and strain of dragline treads can reach up to 1500 MPa and 500% respectively. However, electrospun nonwoven silk fibers have markedly lower stress and strain.[56–59] Generally electrospun nanofibers are large enough (a few hundred to thousands of nanometers) to show no nano-effect.

Spider spinning is controlled by changing pH (from 6.9 to 4.8) and viscosity (from a high value to a low one). It is a challenge to develop technologies capable of preparing nanofibers less than 100 nm.

To mimic spider spinning, a primary mathematical model for spider dragline has been published,[60,61] and Siro-electrospinning (Fig. 12) has been suggested,[1] since Sirospun or Sirofil spinning is very similar to spider spinning. Two-strand spun yarns[62,63] are now widely used in the worsted industry. The strands are textured to improve the bulk of the resultant yarns, which have been demonstrated to possess more desirable properties.

E-INFINITY THEORY: A CHALLENGE FOR NANOSCALE TECHNOLOGY AND SCIENCE

At the nanoscale, the nano-effect arises similar to that in the quantum world. For example, unusual current conduction properties arise when the size of wires are reduced below a certain critical thickness (nanoscale); smaller wires may conduct more current. This nano-effect is very similar to Arnold diffusion, where the higher the dimensionality the stronger is the Arnold diffusion.[64]

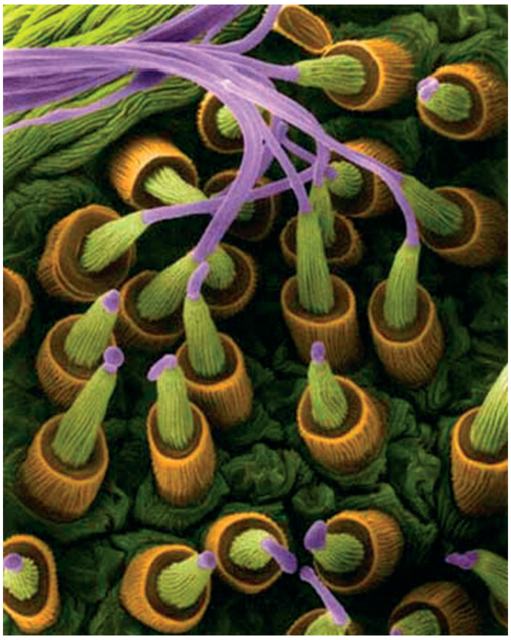

Figure 11. Spider spinning. The diameter of a single nanofiber is about 20 nm, and many nanofibers are combined together to form the visible spider silk. (Image © Dennis Kunkel Microscopy, Inc).

We should develop a new theory linked to both classical mechanics and quantum mechanics. The new theory might be El Naschie's E-infinite theory.[45]

In view of El Naschie's E-infinite theory,[64–72] systems at the nanoscale 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.[1] At the nanoscale, quantum-like phenomena occur. Nanotechnology is, according to El Naschie's definition,[44] a technology applied in the gray area between classical mechanics and quantum mechanics. Classical mechanics is the mechanics governing the motion of all the objects we can see with the naked eye. This is a mechanics which obeys deterministic laws (Newton's laws) and which we can control to a very large 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.

Nanotechnology links both deterministic classic mechanics and chaotic quantum mechanics.[1] There should be 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 gray area between these two scales which is neither classical nor quantum. And E-infinity theory is a strong candidate theory to deal with this gray area.

Electrospinning provides a simple approach to fabricating nanofibers and assemblies with controllable hierarchical structures. Figure 13 illustrates a schematic representing a section of a nanofiber where the large circle and medium-sized circles refer to aggregated macromolecules and the small circles on the fiber surface represent atoms. This will result in quantum-like properties of unusually high surface

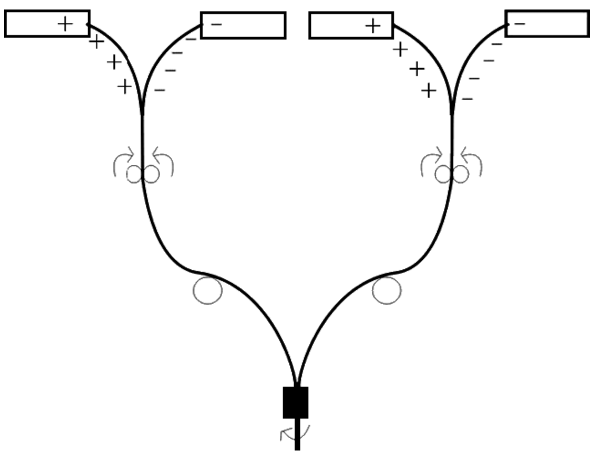

Figure 12. Siro-electrospinning.

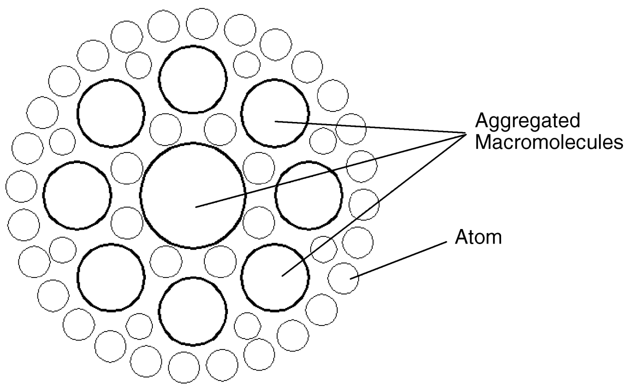

Figure 13. Section of nanofiber, with aggregated macromolecules in the center and a high proportion of atoms on the fiber surface, as 'artificial atoms' which behave with quantum-like properties.

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energy, surface reactivity and high thermal and electric conductivity.

E-infinite theory is a powerful tool in dealing with hierarchical structures. For a heuristic tutorial guide to E-infinity theory, readers are referred elsewhere.[64–67]

CONCLUSIONS

A real mathematical model, or, more accurately, a real physical model, might initiate a revolution in understanding of dynamic and quantum-like phenomena in the electrospinning process. A new theory is much needed which bridges the gap between Newton's world and the quantum world.

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REFERENCES

1 Ramakrishna S, Fujihara K, Teo WE, Yong T, Ma ZW and Ramaseshan R, *Mater Today* **9**:40 (2006).
2 Burger C, Hsiao BS and Chu B, *Annu Rev Mater Res* **36**:333 (2006).
3 Teo WE and Ramakrishna S, *Nanotechnology* **17**:R89 (2006).
4 Reneker DH and Chun I, *Nanotechnology* **7**:216 (1996).
5 Doshi J and Reneker DH, *J Electrostat* **35**:151 (1995).
6 Reneker DH, Yarin AL, Fong H and Koombhongse S, *J Appl Phys* **87**:4531 (2000).
7 Fong H, Chun I and Reneker DH, *Polymer* **40**:4585 (1999).
8 Deitzel JM, Kleinmeyer J, Harris D and Tan NCB, *Polymer* **42**:261 (2001).
9 Sutasinpromprae J, Jitjaicham S, Nithitanakul M, Meechaisue C and Supaphol P, *Polym Int* **55**:825 (2006).
10 Allcock HR, Steely LB and Singh A, *Polym Int* **55**:621 (2006).
11 He JH, Liu Y, Xu L and Yu JY, *Chaos Solitons Fract* **32**:1096 (2007).
12 Xu L, He JH and Liu Y, *Int J Nonlinear Sci* **8**:199 (2007).
13 He JH, Wan YQ and Xu L, *Chaos Solitons Fract* **33**:26 (2007).
14 Hohman MM, Shin M, Rutledge G and Brenner MP, *Phys Fluids* **13**:2201 (2001).
15 Hohman MM, Shin M, Rutledge G and Brenner MP, *Phys Fluids* **13**:2221 (2001).
16 Ganan-Calvo AM, *Phys Rev Lett* **79**:217 (1997).
17 Ganan-Calvo AM, *J Fluid Mech* **335**:165 (1997).
18 Spivak AF and Dzenis YA, *Appl Phys Lett* **73**:3067 (1998).
19 Spivak AF, Dzenis YA and Reneker DH, *Mech Res Commun* **27**:37 (2000).
20 Wan YQ, Guo Q and Pan N, *Int J Nonlinear Sci* **5**:5 (2004).
21 Ko JH and Dulikravich GS, *Int J Nonlinear Sci* **1**:247 (2000).
22 Chen ZH, *Int J Nonlinear Sci* **5**:17 (2004).
23 He JH, *Polymer* **45**:9067 (2004).
24 He JH, *Neurosci Lett* **373**:48 (2005).
25 Kim CK, Kim HY, Lee KH, Kim KW and Lee BM, *Proceedings of the Textile Institute 83rd World Conference* (83rd TIWC), Shanghai, China, 23–27 May, pp. 995.
26 He JH, Wu Y and Pan N, *Int J Nonlinear Sci* **6**:243 (2005).
27 Zeng YC, Wu Y, Pei ZG and Yu CW, *Int J Nonlinear Sci* **7**:385 (2006).
28 He JH and Wan YQ, *Polymer* **45**:6731 (2004).
29 He JH, Wu Y and Zuo WW, *Polymer* **46**:12637 (2005).
30 Wan YQ, He JH and Yu JY, *Iran Polym J* **15**:265 (2006).
31 He JH, Wan YQ and Yu JY, *Int J Nonlinear Sci* **5**:243 (2004).
32 He JH, Wan YQ and Yu JY, *Polymer* **46**:2799 (2005).
33 Qin XH, Wan YQ, He JH, Zhang J, Yu JY and Wang SY, *Polymer* **45**:6409 (2004).
34 Liu Y, He JH, Xu L and Yu JY, *Int J Electrospun Nanofibers Appl* **1**:7 (2007).
35 Wu Y, Yu JY, He JH and Wan YQ, *Chaos Solitons Fract* **32**:5 (2007).
36 He JH, Wan YQ and Yu JY, *Int J Nonlinear Sci* **5**:253 (2004).
37 Wan YQ, He JH, Wu Y and Yu HY, *Mater Lett* **60**:3296 (2006).
38 Wan YQ, He JH, Yu JY and Wu Y, *J Appl Polym Sci* **103**(6):3840 (2007).
39 Wan YQ, He JH, Xu L and Yu JY, *Int J Electrospun Nanofibers Appl*, **1**:17 (2007).
40 McKee MG, Layman JM, Cashion MP and Long TE, *Science* **311**:353 (2006).
41 Baumgarten PK, *J Colloid Interf Sci* **36**:71 (1971).
42 Zhang J, *Int J Nonlinear Sci* **5**:37 (2004).
43 Zhang J and Qu JP, *Int J Nonlinear Sci* **5**:97 (2004).
44 Wu Y, He JH, Xu L and Yu JY, *Int J Electrospun Nanofibers Appl*, **1**:1 (2007).
45 El Naschie MS, *Chaos Solitons Fract* **30**:769 (2006).
46 Alani DI and Mougharbel ZA, *Chaos Solitons Fract* **30**:51 (2006).
47 Gu SY, Wu QL, Ren J and Vancso GJ, *Macromol Rapid Commun* **26**:716 (2005).
48 Vollrath F and Knight DP, *Nature* **410**:541 (2001).
49 Bell FI, Mcewen IJ and Viney C, *Nature* **416**:37 (2002).
50 Jin HJ and Kaplan DL, *Nature* **424**:1057 (2003).
51 Lazaris A, Arcidiacono S, Huang Y, Zhou JF, Duguay F and Chretien N, *Science* **295**:472 (2002).
52 Service RF, *Science* **295**:419 (2002).
53 Gatesy J, Hayashi C, Motriuk D, Woods J and Lewis R, *Science* **291**:2603 (2001).
54 Xu M and Lewis RV, *Proc Natl Acad Sci* **87**:7120 (1990).
55 Gosline JM, Denny MW and DeMont ME, *Nature* **309**:551 (1984).
56 Ohgo K, Zhao C, Kobayashi M and Asakura T, *Polymer* **44**:841 (2003).
57 Sukigara S, Gandhi M, Ayutsede J, Micklus M and Ko F, *Polymer* **44**:5721 (2003).
58 Min BM, Lee G, Kim SH, Nam YS, Lee TS and Park WH, *Biomaterials* **25**:1289 (2004).
59 Foelix RF, *Biology of Spiders*, 2nd edn. Oxford University Press, New York (1996).
60 He JH and Xie KL, *Fact Univ Ser: Mech Autom Control Robotics* **5**:53 (2006).
61 He JH, in *16th European Conference of Fracture*, ed. by Katica SH. University of Nis, Serbia, pp. 39 (2006).
62 He JH, Yu YP, Yu JY, Li WR, Wang SY and Pan N, *Text Res J* **75**:181 (2005).
63 He JH, Yu YP, Pan N, Cai XC, Yu JY and Wang SY, *Mech Res Commun* **32**:197 (2005).
64 El Naschie MS, *Chaos Solitons Fract* **30**:579 (2006).
65 El Naschie MS, *Chaos Solitons Fract* **30**:622 (2006).
66 El Naschie MS, *Chaos Solitons Fract* **30**:636 (2006).
67 El Naschie MS, *Chaos Solitons Fract* **30**:656 (2006).
68 El Naschie MS, *Int J Nonlinear Sci* **7**:119 (2006).
69 El Naschie MS, *Int J Nonlinear Sci* **7**:101 (2006).
70 El Naschie MS, *Int J Nonlinear Sci* **6**:335 (2005).
71 El Naschie MS, *Int. J. Nonlinear Sci.*, **8**:11 (2007).
72 El Naschie MS, *Int. J. Nonlinear Sci.*, **8**:5 (2007).