FUNDAMENTAL IDEAS FOR THE NANOFIBRE THEORY

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Abstract.

In the paper some fundamental ideas are proposed for a nanofiber theory. The conditions for the preparation of tle polymer bulk of the nanofibre precursors is formulated. The elemental theory goes out from the homogenous electric field acting on the sphere droplets which are changed in succesive steps to elipsoids by increasing the main axis ratios to a straight line which proceeds, as in reality, to the nanofiber.

The results show, that the main contribution to the sphere drawing is dependent on the acting of electric field. The drawing effect of the sphere is also dependent on the material characteristics such as the polarisability, surface tension and dynamic viskosity .

1.Introduction

Contemporary technology is oriented to the so called nanotechnology, which means the technology is based on an atomic and molecular scale. In the nanotechnology it is interested as early as the chemistry before long time. The concept of nanotechnology appeared in physics work in the year 1959 by R.P.Feynman (NCF 1965 [1]). Since that time it has been used and applied quite generally in condensed state physics and chemistry [2], [3], [4] and other sciences for the production of the electronic components. The most intensive interest is being oriented to the point (1D) and area (2D) solid state electronics and technology. The nanophysics is also being applied to the construction of very high strength material components. Since 1917, when the principles were formulated in the first patent in 1934 [1] and to their current state [2], nanofibers are prepared and produced aminy others using electrospinning technology .

2. Some fundamental properties of nanofibers

The basic property of nanofibers is the geometrical one, its radius (diameter). Nanofibers are defined as fibers with a diameter ranging below a micrometer, mostly going from 400nm – 800nm, which is also the interval of wave lengths of the visible spectrum. The limiting radius of nanofibers is the radius of their polymer molecules. Nanofibers belong to the nanoaggregates t.i., the aggregates, at least one of which has the dimension of the diameter of the order ~nanometers. The smallest nanofibers are the polymer molecules with the approximately ~ 0,15 nm , what the structure elements of nonofibers are. Thus the smallest

limit diameter of used nanofibers can be estimated to the value ~ 10nm. These 10nm fibers can contain approximately 4 400; 30nm - 40 000; 50nm - 111 000; 100nm - 444 000; 500 nm -11 million and 800nm - 28 million macromolecular fibers. The densities of nanofibers are being done from 70 to 90 percent of the crystalline structure, the diffusion coeffients are 100 to 1000 times greater then crystalline one, as well as what the specific thermal capacity does. A very important property of a nanofiber is also its surface. With 5nm nonofibers the surface is 50 percent; at 10nm it is only 33 percent of the fiber bulk.
Other important mechanical properties of nanofibers are their flexibility and stiffness. The fiber´s flexibility Φ is defined through the relation

$$\Phi = 1/MR = 64/\pi E d^4 = 4\pi/ES^2 = 4\pi\rho^2/ET^2, \quad S=\pi d^2/4 \qquad (1)$$

In (1) as the M torque, the product of tle acting force F with the arm R making a fiber curvature with the radius R, d as the fiber diameter and E its Young´s modulus. According the formula (1) the nanofiber´s flexibility is very high and can achieve for the carbon HM fibers of the diameters 10nm and 100nm the following very high values of Φ: $\Phi_{10} = 6.79.10^{21}$ ($Pa^{-1}.m^{-3}$) and $\Phi_{100}=6.9.10^{17}$ ($Pa^{-1}.\ m^{-3}$).
The basic properties listed imply the following secondary ones: dopeability, dyeability, surface adsorbility, absorbility, catalibility and others. All are very important for the nanotechnology of the atomic doping for the electronic nanofiber constituents such as for example diods, transistors, lasers, CCD elements [3], [4] , [5]. These electronic element were discovered in 20th century and are the subject of the Nobel prizes [6]. Further inteligent textiles and new textile electronic elements can be prepared from nanofibers. Therefore, high production of nanofibers with a high quality needs to be produced also taking in electronic elements. For these purposes theoretical knowledge of the nanofiber technology has to be proposed. In this contribution an elemental outline of simple nanofiber theory is suggested.

3. Some theoretical suppositions

The proposed elemental theory of nanofibers is based on the following supposition:
1. The original material is polymeric with the long molecules.
2. The polymer used can be offered as dielectric (isolator), or conductive one.
3. The polymeric material occurs in a fluid state (solution or melt)
4. The polymeric material has to be prepared in a prespinning state (molecule orientation)
5. Drawing nanofiber is carried out through a homogenous or nonhomogenous electrostatic field.
6. The nanofibers can be produced from fluid droplets , from a jet creating the thin flow of polymer fluid, from the fluid with ferromagnetic or ferroelectric nanoparticles placed in magnetic and/or magnetic and/or electric fields (liquids with magnetic and electret particles).
7. The basic shape for the nanofiber theory the sphere is assumpted.
8. Besides the electric drawing force, the resistive forces through the surface tension γ and the inner friction presented with dynamic viscosity η are take effekt.
When either five or all of the eight are fulfilled, the liquid (fluid) is called nanofiber precursor.

4. Simplified nanofiber theory

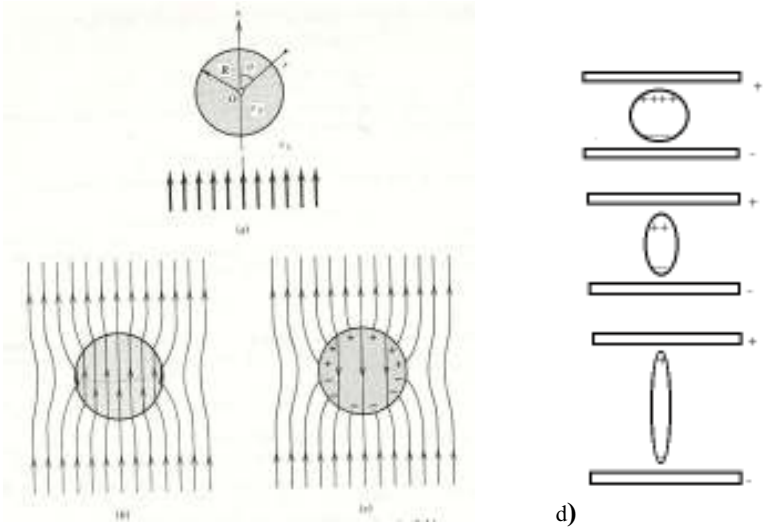


Fig.1 a) Material droplet in the homogenous electric field $\mathbf{E}_0$. Initial state, b) course of vector $\mathbf{D} = \varepsilon \mathbf{E}$, c) course of the intensity vector **E,** d) the change of the sphere to the epipsoids with increasing intensity **E**.

The polymer in a solution and/or in a melt as a droplet is inserted in an even (homogenous) electrical field and, the situation as drawn in Fig.1 is created.
The dielectric and/or conductive liquid sphere placed in homogenous electric field is deformed to an ellipsoid (Fig.1) and in the final step to a straight line. The original intensity vector $\mathbf{E}_0 = E_0\mathbf{z}$ is being oriented in the *z* axis direction with the unit vector **z**. The permitivity, and the field intensity outside the sphere is designated ε_1, $\mathbf{E}_1$ and inside ε_2, $\mathbf{E}_2$. In the initial field of action, the sphere material polarization is described through the polarisation vector $\mathbf{P} = \sigma \mathbf{z}$ **,** where σ is the area charge density . The electrical field action can be expanded to two components parallel and perpendicular ones. The parallel component induces the sphere´s drawing and perpendicular the droplet stressing. The parallel force draws sphere and perpendicular stretches it and so nanofiber is created. The perpendicular force creates so called Taylor cones appeared as the first nanofiber stage (see for example [2]). Now the force balance will be made. Three forces on the droplet are acting as follows:
1. The surface tension force F_S , 2. electric field force F_E and 3. The inner friction force F_i . Then the total force acting on the droplet is $F = F_S+F_E+F_i$. Using Newton´s inner friction law , obtains: $F_i = - 2\pi\eta rL\, dv/dx \rightarrow -2\pi\eta rL\, \Delta v/\Delta x = -2\pi\eta rL\, \Delta v/2r = -\pi\eta L\Delta v$. The quantity η is the dynamic viscosity and Δv is the flow velocity change, L is the material length. For the zero approximation and simplification of solution the inner friction force F_i is ignored in the further development of the theory ($\Delta v \rightarrow 0$).
Because $F_S = 2\pi R\gamma$ and $F_E = \sigma S E = PSE = \alpha S E^2 = 4\pi\alpha R^2 E^2$ for the total force F are relations obtained, where α is the polarisability, P the polarisation of the precursor fiber material and for the total force the following relation holds

$$F = 4\pi\alpha R^2 E^2 - 2\pi R\gamma - 2\pi\eta rL = 2\pi R(2\alpha R E^2 - \gamma - 2\pi\eta rL/R). \quad (2)$$

This force is responsible for the stretching of the nanofibers. The total sphere´s extension ΔL can be estimated using Hook´s law in the form $F/S = E_Y \Delta L/2R$, and the maximal value ΔL_{max} is possible to calculate using the relation

$$\Delta L_{max}=4(2\alpha RE^2-\gamma-2\pi\eta rL/R)/E_Y. \quad (3)$$

E_Y is the Young´s modulus of the fluid material.
The quantities γ and η with the increasing temperature approximate to zero and can be ignored. Then the equations (2) and (3) are reduced to

$$F = 4\pi\alpha R^2 E^2 \quad \text{and} \quad \Delta L_{max}=8\alpha RE^2 \quad (4)$$

and F is dependent only on the electric intensity´s square and electrical polarisability α.
In an ideal case the sphere of the radius R is totally transformed to the nanofiber length L, which is determined through the relation

$$L = (2/3) R^3/ r \quad (5)$$

R is sphere´s radius and r the fiber radius. For the droplet 10^{-3}m the maximal nanofiber length ~ 0,6m can be produced.
In (2) the resistive inner friction force
$F_i = -S \eta\Delta v/\Delta x = -2\pi rL\Delta v/2r= -\pi\eta L\Delta v \rightarrow 0$ pro $\Delta v \rightarrow 0$ and can also be ignored in the zero approximation .
From formula (2) it can also be deduced that the nanofiber elongation is dependent on material characteristics as the polarisability α, surface tension γ, dynamic viscosity η and fluid Young´s modulus E_Y are. That means for the easy nanofiber production the polymer with high polarizibility, low surface tension γ , dynamic viscosity η and high Young´s modulus are requested.
This elemental theory is only theory of zero order approximation for the quasistatic estimation. In new possibilities for the preparation of nanofibers and their theories will be proposed also using a nonhomogeneous electric field and magnetic and/or electric fields acting on the ferromagnetic and ferroelectric nanoparticles.
The nanofiber theory can also be developed using computer modeling [7].

5. Possibilities of application

Nanofiber applications are very broad. At this time most applications are in the web fabrics and medical and technical application, such as for example filtration. Future are the development of single nanofibers and their application to woven, knitting together with other periodic fabrics to optoelectronics and to intelligent textile production. This will also lead to nanotextile technology.
There are also proposals to create nanofibers directly on models of bodies and directly create whole clothing.
Very attractive in the future will also be the technical nanotextile applications and some carbon nanofibers and fullerene nanotubes with great strength which can be used to the construction of cosmic cables for their applications to cosmic lift. In future prepared nanowovens can be used for their nanoelectronic properties to electronic devices.

6. Continuation

6.1 Introduction

The new technology of nanofiber preparation is proposed and increased. But the theoretical works are at time only initiated. For the polymer nanofiber drawing it is necessary to act on the fluid polymer with the external forces to accelerate the drawing process. This can be done using the gravitational force and better the force electrostatic the praxis is showing.
In the paper [8] the formula for the acting force F for the fiber formation during the electrospinning process was derived. The acting of external electrostatic force completed also with the gravitational force causing also the nanofiber formation. The formulas the equations of motion of the nanofibers was derived implies as it was in [9] shown. The first equation of motion are derived for the nanofibers of the radius r_N and for the electrospinning is as follows

$$F = 4\pi\alpha\, r_N^2\, E^2 = m\, d^2\mathbf{r}/dt^2 = 4\pi\alpha\, r_N^2\, E^2$$

$$nm_{mu}\, d^2\mathbf{r}/dt^2 = 4\pi\alpha'\, r_N\, E^2 \qquad (2)$$

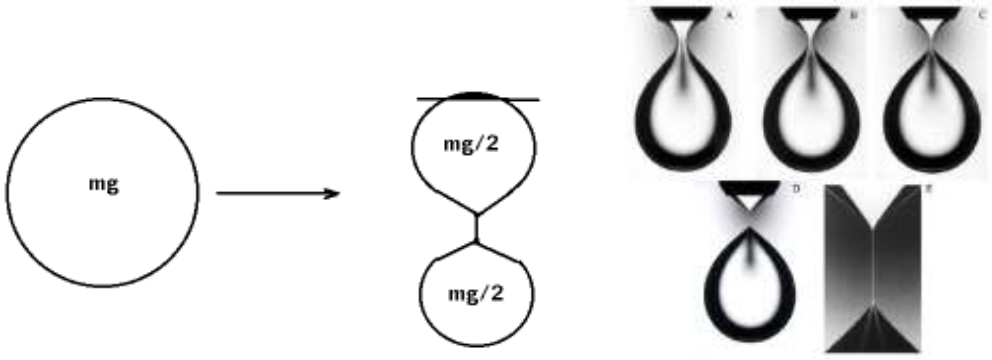
where α means the polymer polarisability, m_{mu} mer unit mass of one polymer molecule, n is positive integer number of mer units which is depending on time, α' is mer unit polarisability, E is the intensity of applied electric field intensity. This quantity changes in some problems also with time. This equation of motion is simplified so, that influence of surface tension is after the Öetves equation is neglected [12], [13]and the same is made with the viscosity after the Boltzman relation [7]. The equation (2) can be viewed as the zero approximation of the problem. From it is seen, that the operation of the electrostatic field is very high.
The simplest possibility of nanofiber preparation technology is free fall of the polymer droplet. The acting drawing force is in this case the gravitational one. The experimental conditions for this case are shown on the fig.2a,b. Now it is also being derived the equation of nanofiber motion after work of gravitational force on nanofiber drawing. For the elementary derivation of equation of motion it is supposed the division of polymer spherical drop forming in the capillary nose on two equally droplets, as it is shown on the fig.2a, b. For the gravitational spinning force F_G the equation of motion of a half
of droplet is as follows

$$F_G = mg/2 \quad \text{and} \quad (m/2)d^2\mathbf{r}/dt^2 = m\mathbf{g}/2 \qquad (3)$$

This is an equation of the uniformly accelerated motion, where m is polymer mass of droplet and **g** gravitational acceleration. The solution for trajectory **r**(t) and fiber velocity **v**(t) are the relations of elementary uniformly accelerated motion

$$\mathbf{r}(t) = (\mathbf{g}/2)t^2 \quad \text{and} \quad \mathbf{v}(t) = \mathbf{g}t \qquad (4)$$

During one second in ideal condition in vacuum the nanofiber can be drawn to 5m with the velicity 10m/s.



a) b)

Fig.2 The spinning of nanofibers with gravitational field a) drop division, b) gravitational spinning

In this case the air resistance, streaming, and elastic coherent forces was neglected and therefore in real case the velocity and also the nonofiber formation will be considerably slower. In the gravitational drawing force field the trajectory of fiber is a straigth line. Otherwise it is in the in the preparation of polymer nanofibers through the electrostatic spinning. At the electrostatic spinning the fiber trajectories are complicated as conical spiral shown on fig.2.

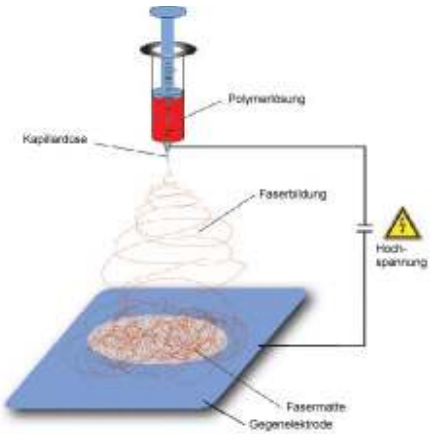


Fig.3 One exemple of the path of fiber during electrospinning process in real case.

6.2. Solution of equation of motion of nanofiber element

For the solution of the equation (2) for the special polymer nanofibers their material quantity n, m_{mu} , α' a r_N have to be known. The quantity α and α' are achieved from the following relation

$$\alpha = (3/4\pi)\,(M/\rho)(\varepsilon_r - 1)/(\varepsilon_r + 2)\,,\ \alpha = P/E\ ,\ \alpha' = \alpha\, V_{mu}\,,\ [3] \qquad (5)$$

$$\alpha = 3\varepsilon_0\,(\varepsilon_r - 1)/(\varepsilon_r + \varepsilon_r)/N_0\,, \qquad (6)$$

where N_0 is the number of dipolmoments n_d in volume unit , V_{mu} is the volume of mer unit, α' is the polarisability of mer unit, ε_r relative permitivity, M molar mass of mer unit , ρ is the density, P polarization and E intensity of electrostatic field.

Evaluation of the quantity n , m_{mu} , α' a r_N and other quantity for some important polymers
The quantity n is positive number achieving the values step by step 1,2,3, … . Quantity m_{mu} is mass of mer unit and for it holds $m_{mu} = \rho V_{mu}$, ρ is polymer density, V_{mu} the volume of mer unit $\alpha' = \alpha V_{mu}$, r_N is the radius of nanofiber (see fig.4). To calculate the volumen of mer unit V_{mu} It is necessary to go out from the polymer structure formula, which for the calculated

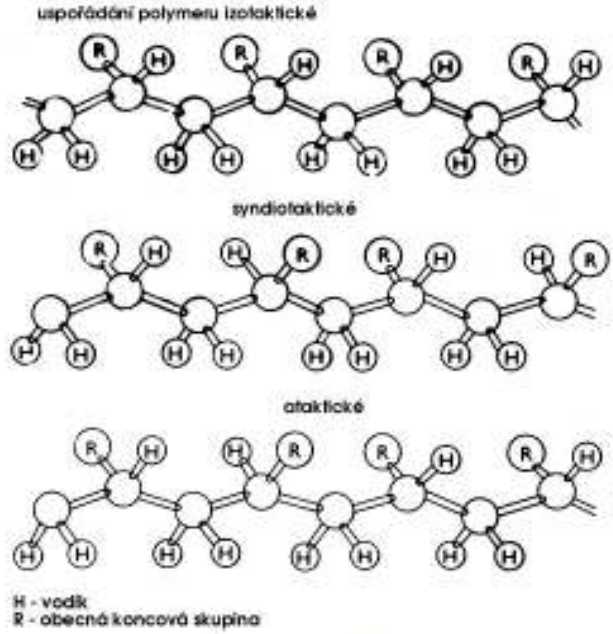


Fig.4 General formulae of linear polymer. R denotes different groups. For PE ,H, for PP CH_3 and so on.

polymer polyethylene, polypropylene and polyvinylalcohol is as follows in fig.3. From the fig.3 it is possible to estimate already V_{mu} . The calculation is supported on the cylindrical model on fig.4. This smooth model can produce the higher velocity then the corresponding real mer unit.

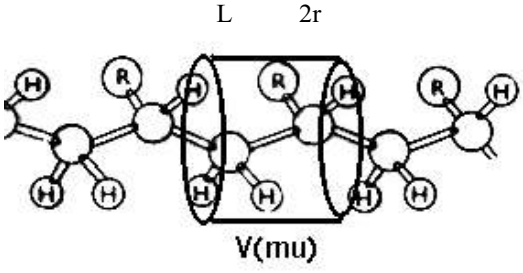


Fig.5 To the definition of $V(mu) = V_{mn}$, L length and r_{mu} of the cylinder approximated mer unit

Using the model on fig.5, it is possible to calculate V_{mu} and other quantity for polyethelene, polypropylene, for polyvinylalcohol and polyamid 4.6.

Polyethylene (PE)
The cardinal data for volume of mer unit r_{mu} and L was calculated from the data deduced from [10], tom 2, chap.18, tab.18.3 is L=0,31nm, r_{mu} = 0,11nm and from the tab.18.4 L=0,5nm, r_{mu} = 0,25nm. From these values the V_{mu} is calculated and has the value V_{mu} = 0,118nm^3 and the corresponding $m_{mu} = 0{,}0118.\rho = 0{,}90.0{,}118.10^{-20}$kg = $1{,}062.10^{-21}$kg.
The necessary molecule polarisability of polyethylene α_{PE} is calculated using the formulas (9.22), (9.23) from [3] (tom 1, chap.9.p.280) of the form

$\alpha_{PE} = 3\varepsilon_0 (\varepsilon_r - 1)/(\varepsilon_r + \varepsilon_r)/N_0$, N_0 is the number of dipolmoments n_d in volume unit (7)

where $\varepsilon_0 = 8{,}85.10^{-12}$F/m , $\varepsilon_{rPE} = 2{,}30$ and $N_0 = n_{dmu}/ V_{mu} = 4/0{,}118\text{nm}^3 = 3{,}39.10^{26}$
After substitution all values in (3) it results $\alpha_{PE} = 8{,}0.10^{-39}$F.m^2.

Polypropylen (PP)
Using the data from [10], tom 2, chap.18, tab.18.3 corresponding quantity for the solution of equation of motion can be calculated and the results for the volume V_{PP}, mass m_{PP} and radius r_{PP} of the polypropylene mer unit are as follows
$V_{PP} = 0{,}093.10^{-27}$m^3 , $m_{PP} = 0{,}087.10^{-27}$kg, $r_{PP} = 0{,}046.10^{-9}$m and $\alpha'_{PP} = \alpha_{PP} V_{PP.}$ For the calculation of α , the equations (5), (6) are being used.

6.3 Solution of equation of motion for nanofiber electrospinning

Knowing the numerical value of all quantities appearing in the equation of motion (2) and after substitution them to this equation the following equation of motion of mer unit is resulting in

$nm_{mu}\, d^2\mathbf{r}/dt^2 = 4\pi\alpha'\, r_N{}^2\, E^2$, $d^2\mathbf{r}/dt^2 = a = 4\pi\alpha'\, r_N{}^2\, E^2/\, nm_{mu}$ (4)

with the solution

$\mathbf{r} = (4\pi\alpha'\, r_N{}^2\, E^2/2nm_{mu})\, t^2\, \mathbf{n}_0$, $\mathbf{v} = (4\pi\alpha'\, r_N{}^2\, E^2/\, nm_{mu})\, t\, \mathbf{v}_0$ (5)

Because the acceleration a is for the n=const constant, the motion of nanofiber is rectilinear and uniformly accelerated with the acceleration $a = 4\pi\alpha\, r_N{}^2 E^2/\, nm_{mu}$, which for the polyethylene and for the intensity of homogenous electrostatic field E = 300kV/m is
$a_{PE} = 4\pi\, \alpha_{PE}\, r_{NPE}{}^2 E^2/\, nm_{muPE} = 4\pi.\, 8{,}0.10^{-39}\text{F.m}^2\, .(0{,}11\text{nm})^2.(3{,}0.10^5\ \text{V/m})^2\, /1.\ 1{,}062.10^{-21}$kg
$= 2{,}1.10^5$m/s^2 and for the length of trajectory L and the velocity v it is obtaining the values
$L = 1{,}05.10^5\ t^2$ (m/s^2) , $v = 2{,}1.10.^5\ t$ (m/s). The values are calculated for the drawing of virtual monomolecular nanofiber from the spherical clue to the linear macromolecule. The molecular mass is increasing with time t , that is meaning the quantity n in (4) is increasing as much as 10^4times
The further L and v lowering is caused through the fact, that the nanofibers have the diameter from 10nm to 100nm what represents further L and v decreasing until 10^3 times and thus the calculated values of L and v is approximating to the real ones. The further slackening of L and v is possible to the fact, that it is been worked with ideal smooth macromolecules which have negligible inner friction in comparison with real molecule (see fig.4,5) a the same id done with the cohesive elastic force in nanofiber and with inner friction force quantified through the dynamical viscosity. For the polypropylene, polyamid 6.4 and polyvinylalcohol

It is obtaining the similar results, because all their numerical values are similar as the tab.1 is showing

Tab.1 Values of polymer quantities for the calculation done PE,PP,PVA a PAD 6.4 ([15])

Material,density		volume of mer unit	radius of macromolecule	length of mer unit
PE	$0{,}9.10^3$ (kg/m^3),	$2{,}1.10^{-29}$ (m^3)	$2{,}18.10^{-10}$ (m)	$1{,}4\ .10^{-10}$ (m)
PP	$0{,}91.10^3$	$9{,}3.10^{-29}$	$4{,}6.10^{-10}$	$1{,}4\ .10^{-10}$
PVA	$1{,}28.10^3$	$1{,}4.10^{-29}$	$2{,}46.10^{-10}$	$1{,}4\ .10^{-10}$
PAD 6.4	$1{,}14.10^3$	$1{,}68.10^{-27}$	$4{,}6.10^{-10}$	$16{,}8.10^{-10}$

6.4 Precursor formation

The rersults of solution of nanofiber motion equation are being implied under the supposition, that the macromolecules are reposing free in the polymer. In reality there are operating intermolecular forces creating inner friction and so brake the drawing process. For the enhancing the nonofiber production it is necessary to order the polymer macromolecules in parallel state so called precursor formation for the increase of nanofiber production.

6.5 Result discussion, conclusion

In the contribution the equation of motion of nanofiber drawing process has been solved after the simplified supposition. Nonofiber drawing in gravirational field gives the exact solution in agreement with experimental results. The nanofiber trajectories are straith lines. But the velocity and length production are too high. The explanation for this discrepancy is offering.
The trajectory of nanofibers cannot be explained with the acting of the homogenous electrostatic field. For explaining of spiral conical trajectories on fig.2 the nonhomogenous electrostatic field for the equation of motion has to be applied. This will be done in part 3.

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