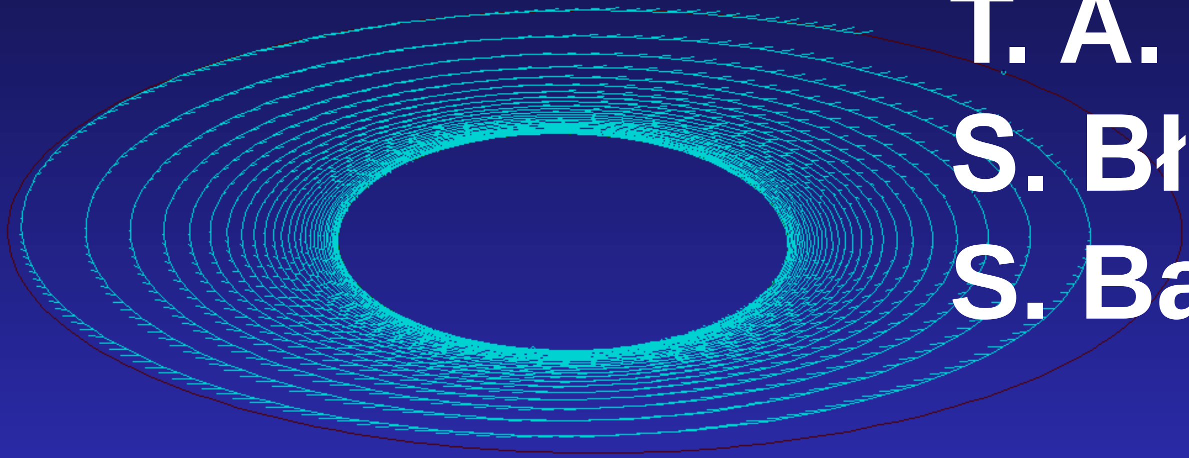
Department of Mechanics and Physics of Fluids



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Experiments and Modelling of Electrospinning Process

NANOFIBRES

Nanofibres background

1. Nanofibres properties

   - Increase of the surface to volume ratio -> solar and light sails and mirrors in space
   - Reduction of characteristic dimension -> nano-biotechnology, tissue engineering, chemical catalysts, electronic devices
   - Bio-active fibres: catalysis of tissue cells growth
   - Mechanical properties improvement -> new materials and composite materials by alignment in arrays and ropes

2. Nanofibres production:

   - Air-blast atomisation
   - Pulling from melts
   - Electrospinning of polymer solutions

Classical liquid jet

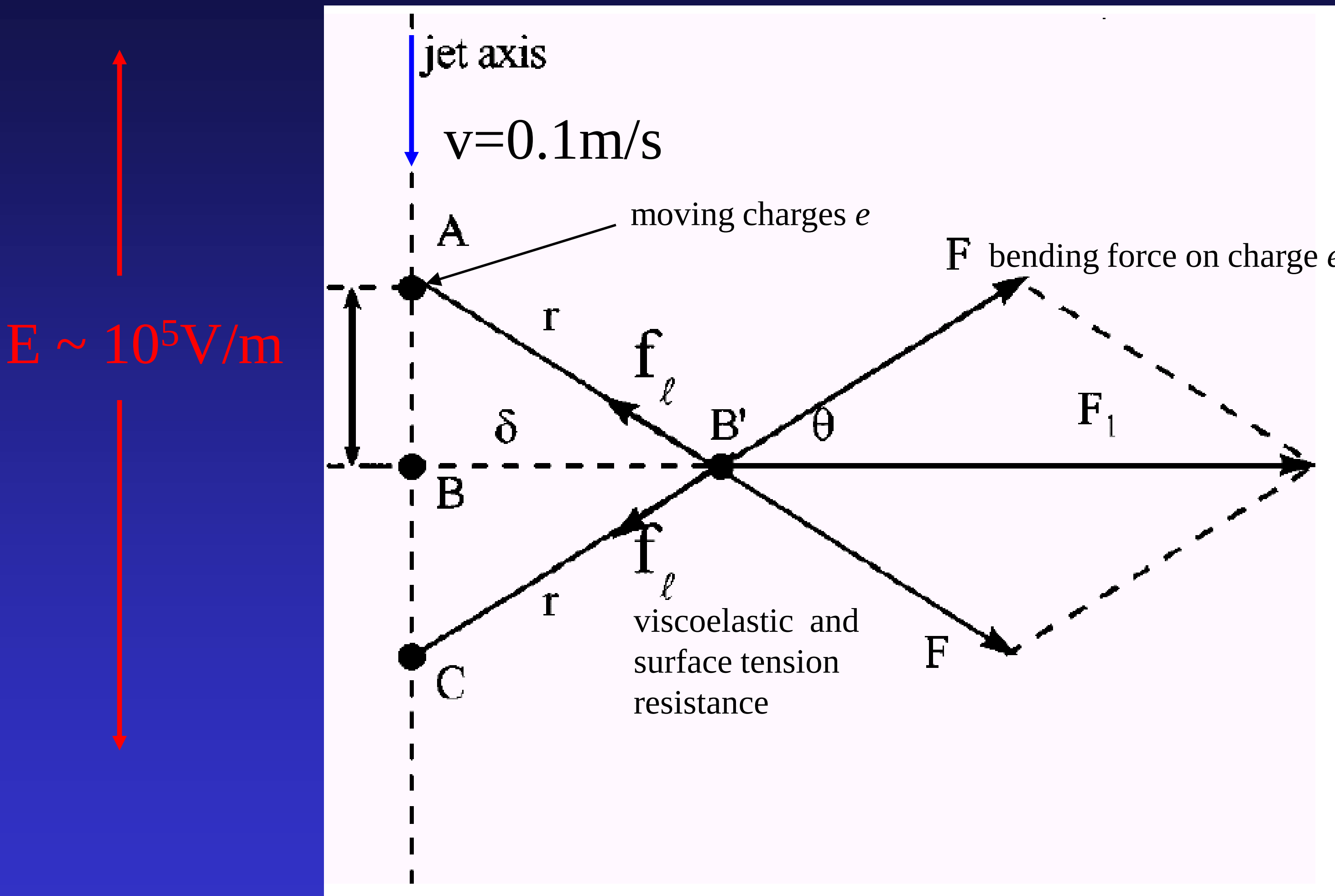
Orifice – 0.1mm

Primary jet diameter ~ 0.2mm

Micro-jet diameter ~ 0.005mm

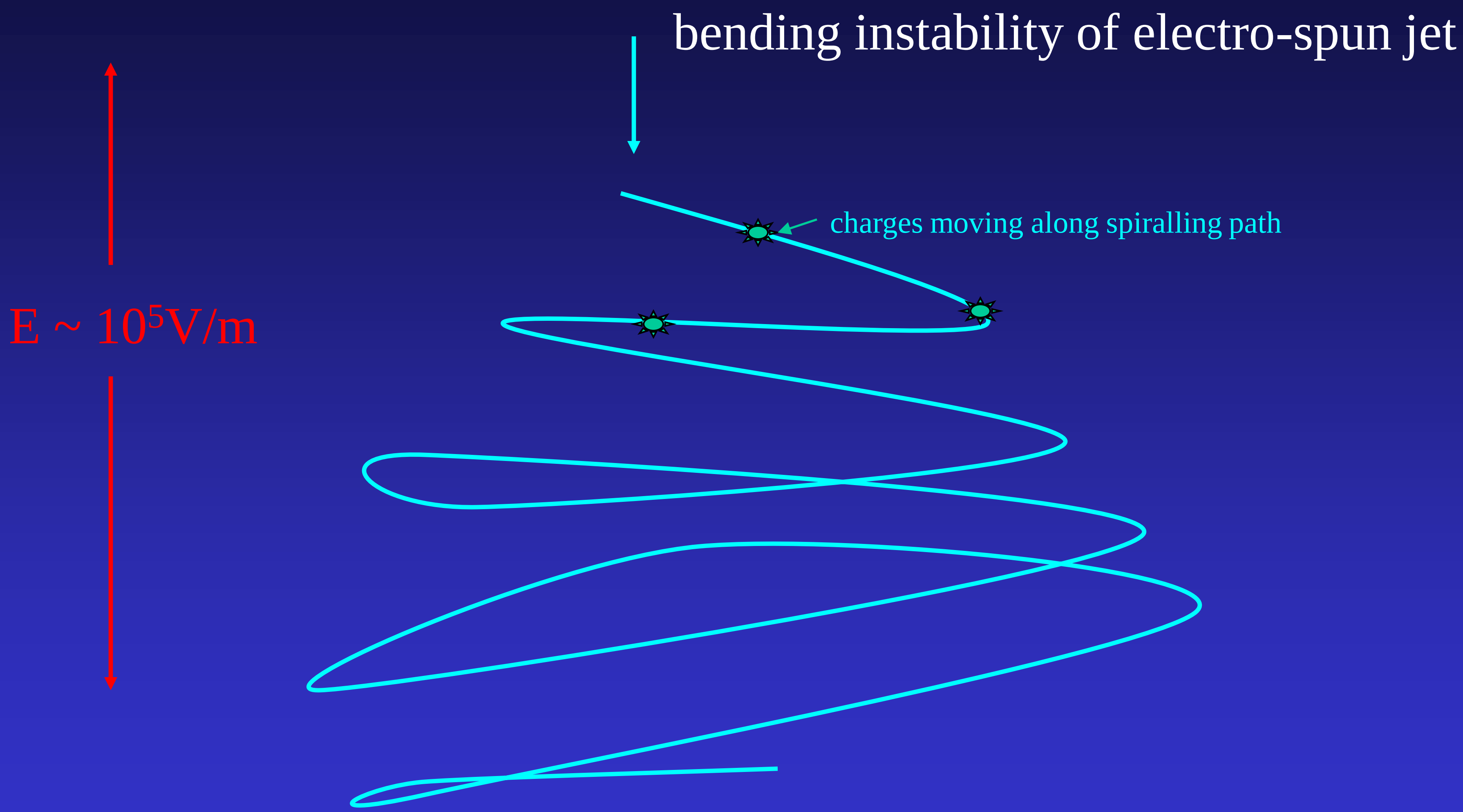
- Gravitational, mechanical or electrostatic pulling limited to l/d ~ 1000 by capillary instability
- To reach nano-range:
  jet thinning $\sim 10^{-3}$
  draw ratio $\sim 10^{6}$!

Electro-spinning



Moving charges (ions) interacting with electrostatic field amplify bending instability, surface tension and viscoelasticity counteract these forces

Electro-spinning



Bending instability enormously increases path of the jet, allowing to solve problem: how to decrease jet diameter 1000 times or more without increasing distance to tenths of kilometres

Electro-spinning

Simple model for elongating viscoelastic thread

$$\frac{d\sigma}{dt} = G\frac{d\ell}{\ell dt} - \frac{G}{\mu}\sigma$$

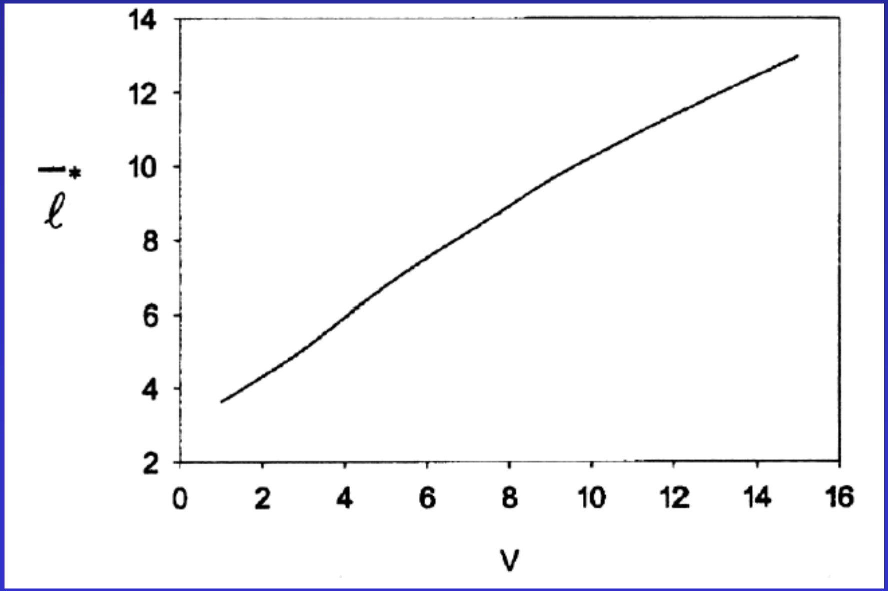
Stress balance: *μ - viscosity, G – elastic modulus stress, σ stress tensor, dl/dt – thread elongation*

$$m\frac{dv}{dt} = -\frac{e^2}{\ell^2} - \frac{eV_0}{h} + \pi a^2\sigma,$$

Momentum balance: *V_o – voltage, e – charge, a – thread radius, h- distance pipette-collector*

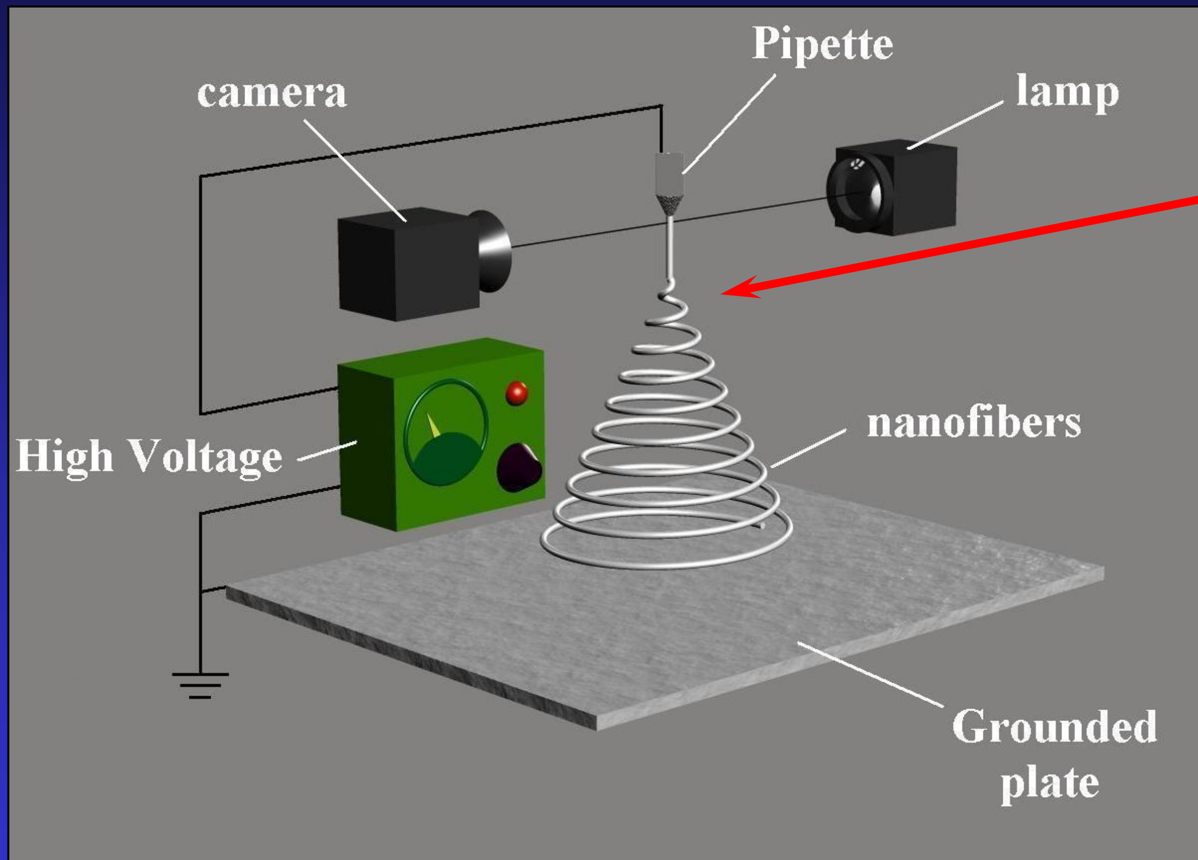
$$\frac{d\ell}{dt} = -v.$$

Kinematic condition for thread velocity v



Non-dimensional length of the thread as a function of electrostatic potential

Nanofibres – basic setup



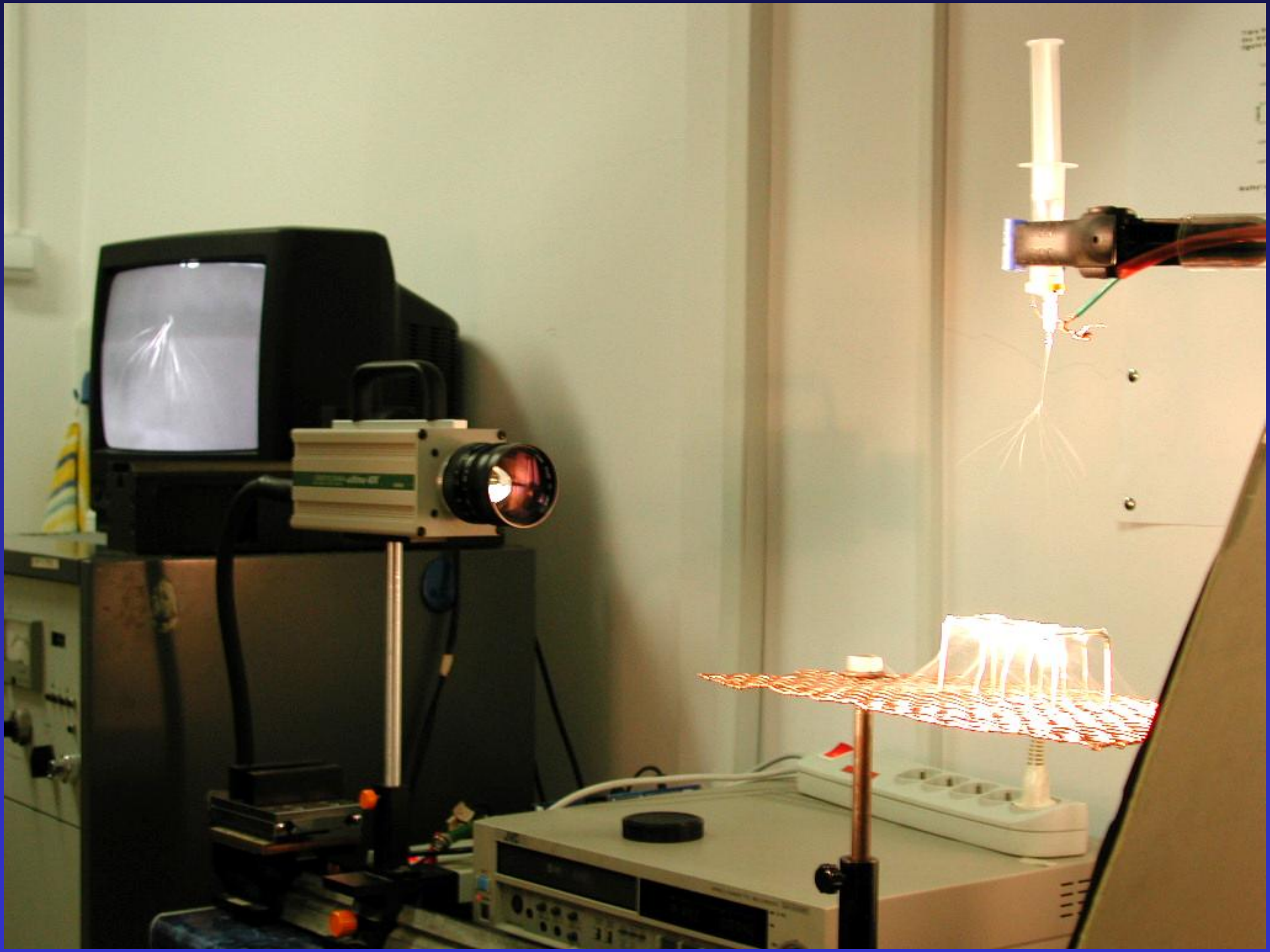
liquid jet

~ 10^5 Volt/m

Nanofibres – howto?

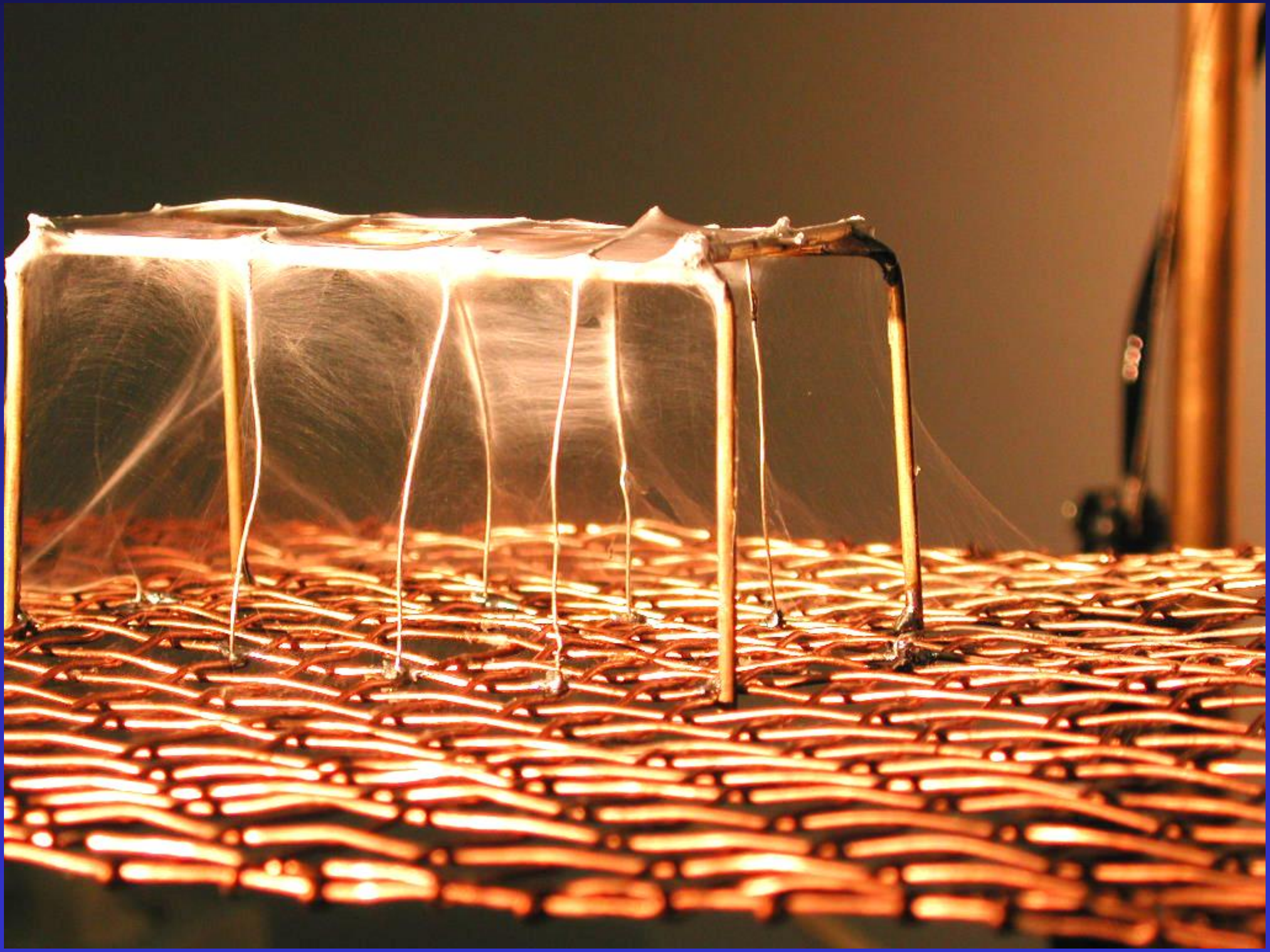
1. Viscoelastic fluid:
   - Dilute solution (4 – 6)% of polyethylene oxide (molar weight $4 \cdot 10^5$ g/mol), in 40% ethanol –water solvent
2. Electrostatic field
   - high voltage power supply (5-30kV)
   - plastic syringe
   - metal grid to collect fibres
3. Visualization
   - high speed camera (4000 – 40000 fps)
   - high resolution „PIV” camera (1280x1024pixels)
   - CW Argon laser, double pulse Nd:Yag laser, projection lens

Nanofibres – basic setup



Nanofibres collection

Nanofibres collection

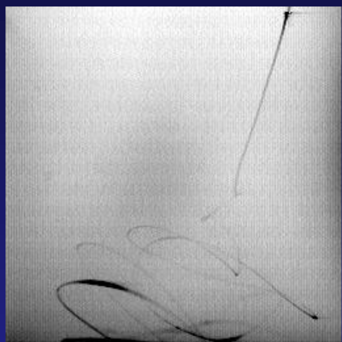


Electrospinning observed at 30fps

5 cm

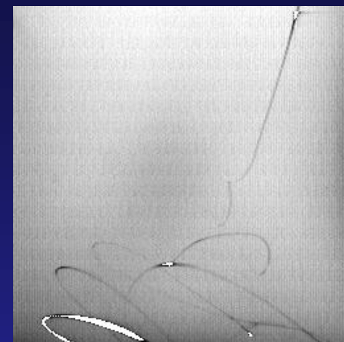
Average velocity of the fibres: 2 m/s

Electrospinning observed at 4500fps



0.0 ms

8.9 ms

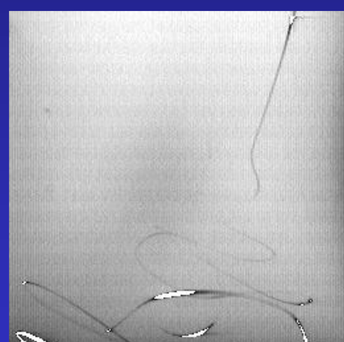


17.8 ms

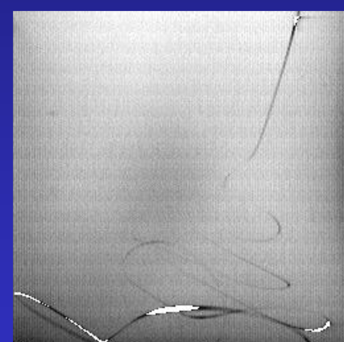
26.7 ms

35.6 ms

44.4 ms



53.3 ms



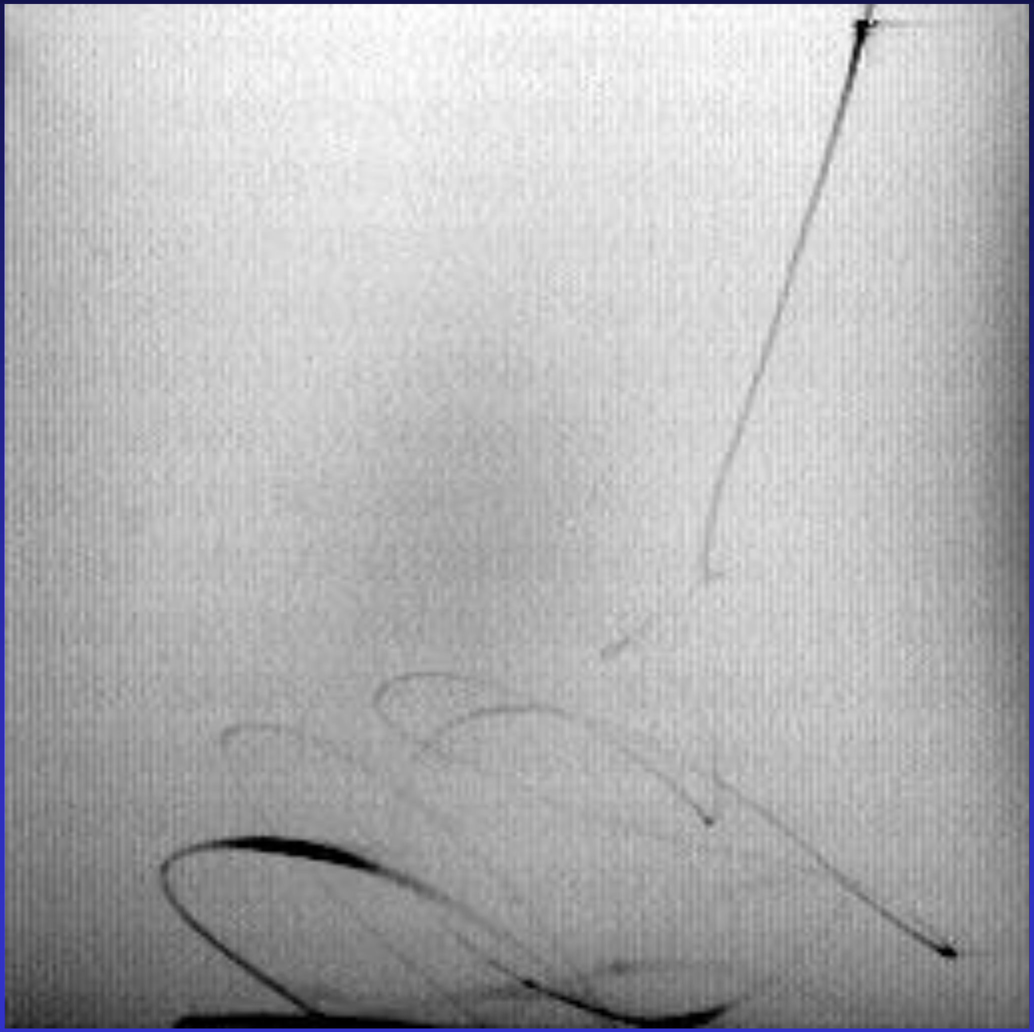
62.2 ms

71.1 ms

80.0 ms

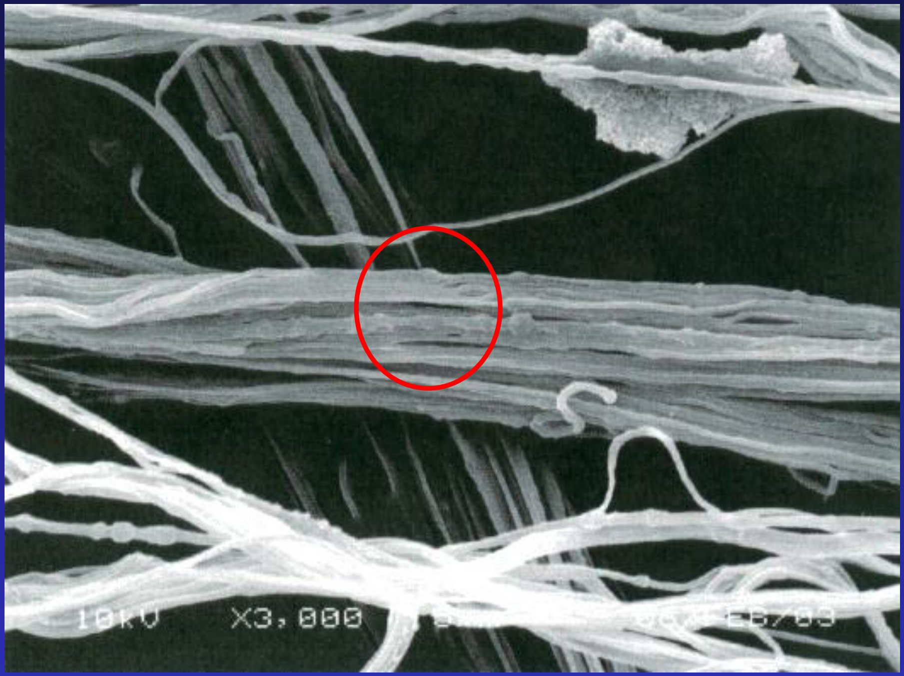
Electrospinning observed at 4500fps

5 cm



Average velocity of the fibre: 2 m/s

Electron microscopy

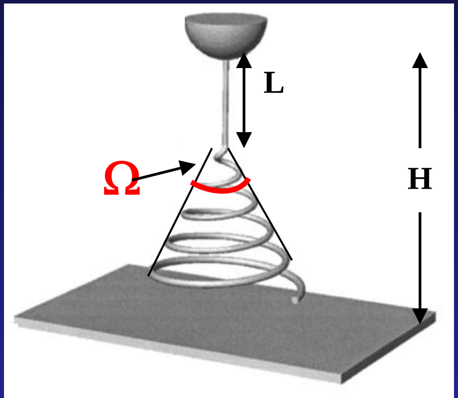


PEO nanofibres

Parametric study

Model validation varying following parameters:

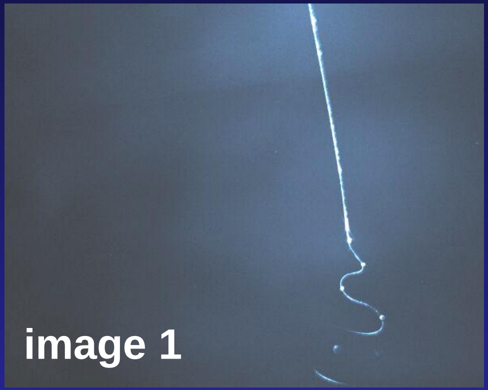
- L – length of the rectilinear part
- Ω – angle of the envelope cone (image analysis)
- U – velocity of the fibre by PIV method
- a – fibre diameter (image analysis)
- structure of collected woven (failure modes)
- elongation strength of single fibre measured by air jet

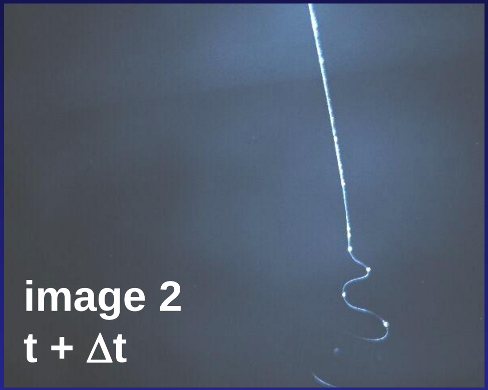


Effect of

- Electrostatic potential *V*
- Distance pipette-collector *H*
- Solution concentration *c*
- Distance from the pipette *x*

Parametric study



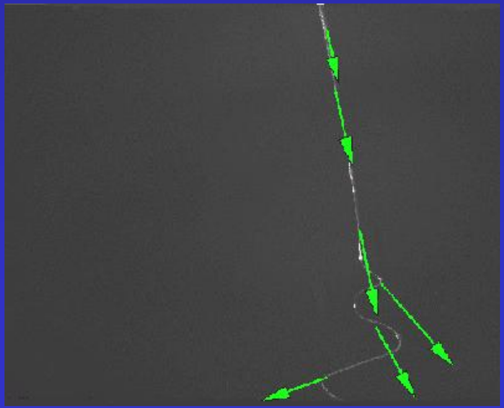


PIV

cross – correlation

Δt = 500 μs

- concentration of PEO: 3%
- Voltage: 8 kV
- H = 215 mm
- polymer solution with the addition of fluorescent particles (0.3μm polymer microspheres)
- light source: Nd:Yag laser

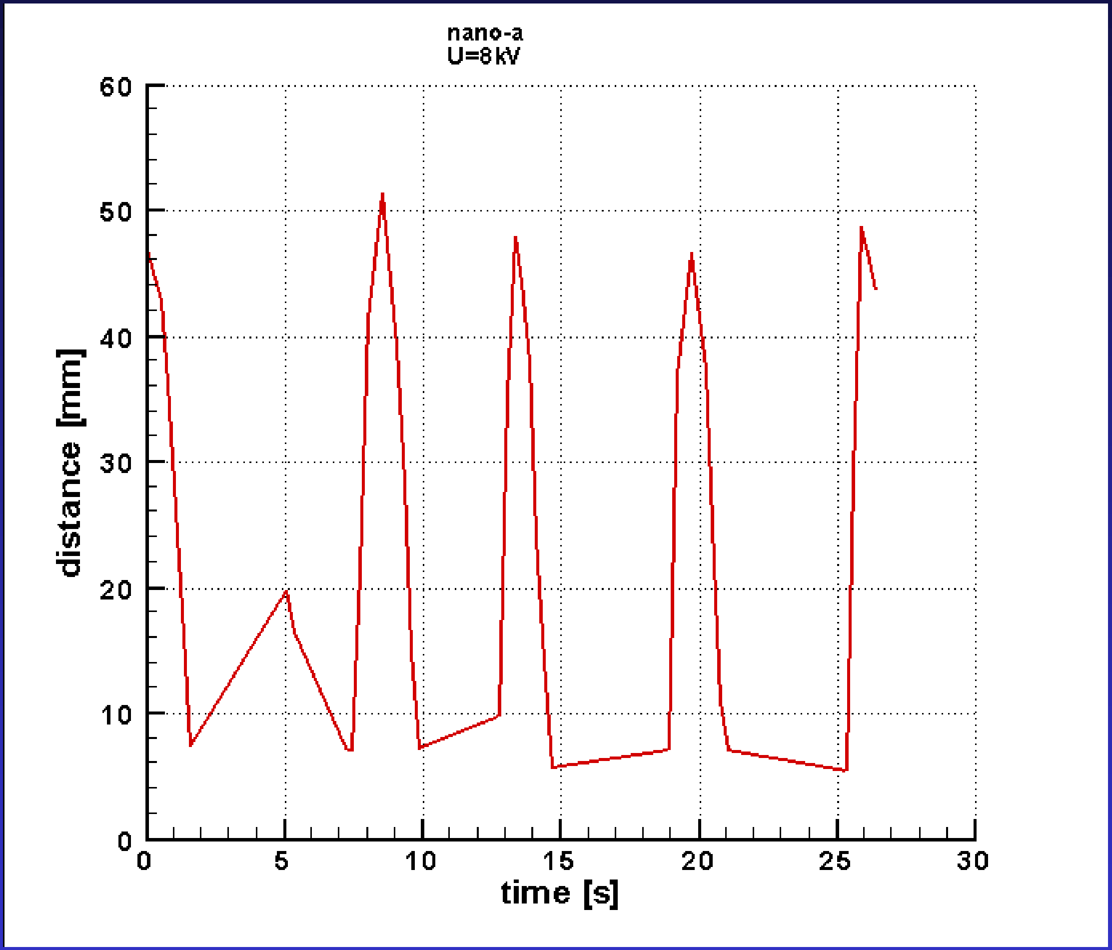


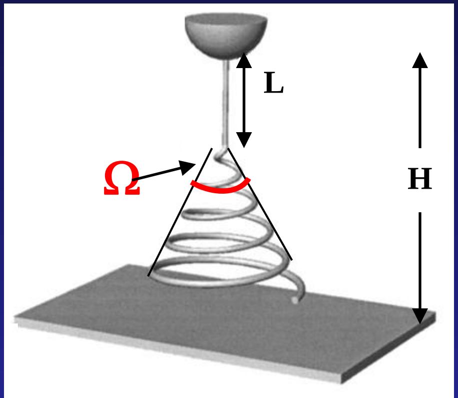
Average velocity of the fibres: 2 m/s

Tested polymers

Test	Polymer	Solvent	Concen tration	Voltage [kV]	Electrospinning
I	**PEO** poly(ethylene oxide)	40% water 60% ethanol mixture	3 – 4 %	3 – 12	good and stable process for voltage up to 10kV
II	**DBC** dibutyrylo chitin	ethanol	9 %	6 – 16	fairly good
III	**TAC** cellulose triacetate	methylo chloride	20 %	3 – 30	polymer too viscous
			7 %	10 – 30	difficult
IV	**PAN** polyacrylonitrile	dimethyl-formamide (DMF)	15 %	5 – 25	very good
V	**Glycerol**	water	88 %	20 – 30	difficult, lack of solidification cause that the liquid jet is separated into small droplets (electrospray)

Parametric study

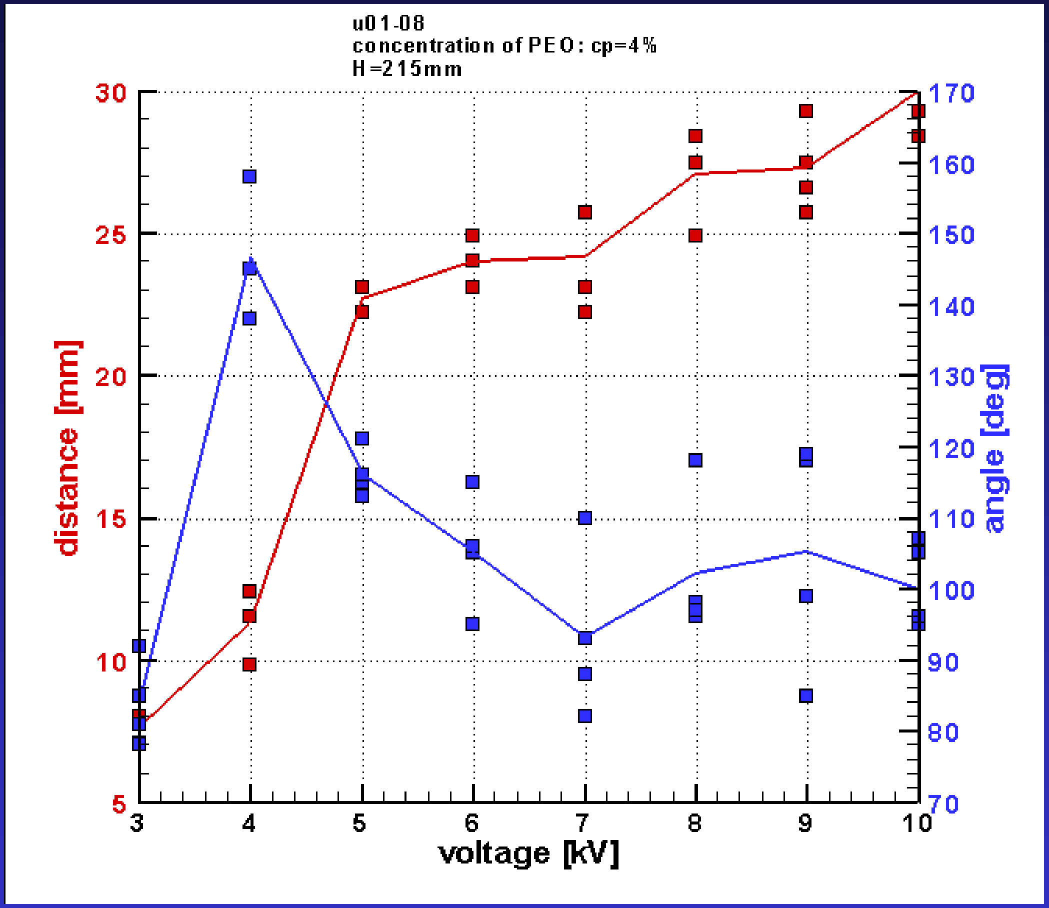


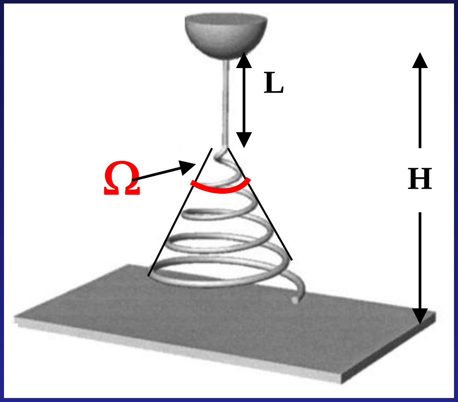


- Polymer: PEO
- Concentration: c=3%
- Solvent: 40% water-ethanol solution
- H=215mm
- V=8kV

➤ L (t) – instability of length of the rectilinear part

Parametric study

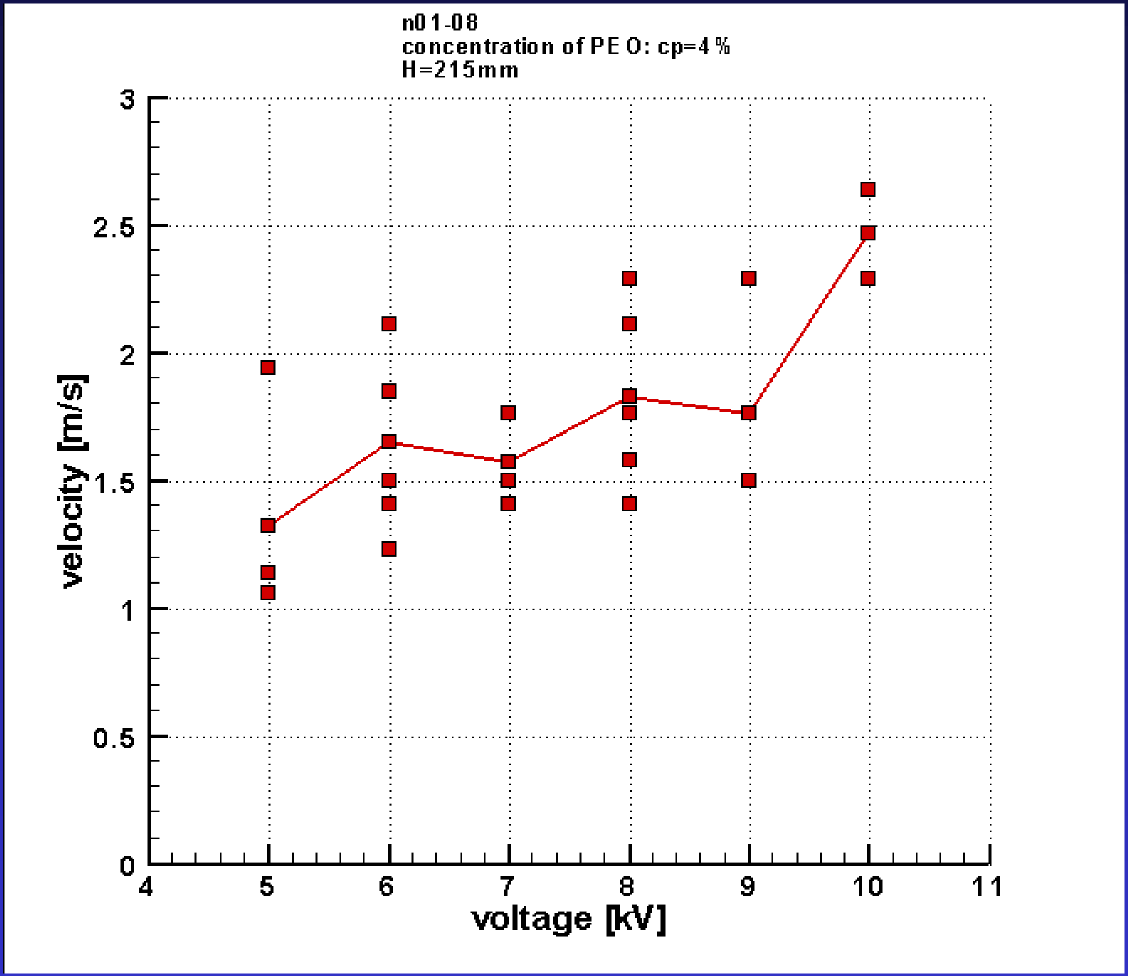


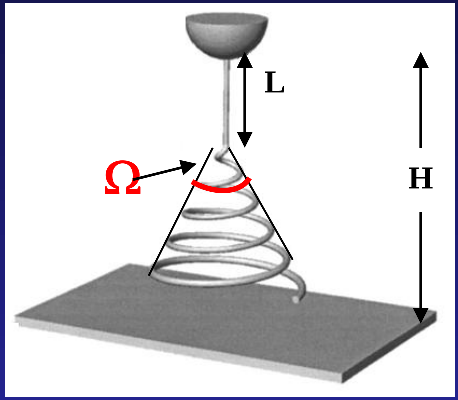


- Polymer: PEO
- Concentration: c=4%
- Solvent: 40% water-ethanol solution
- H=215mm

- L (V) – length of the rectilinear part
- Ω (V) – angle of the envelope cone

Parametric study



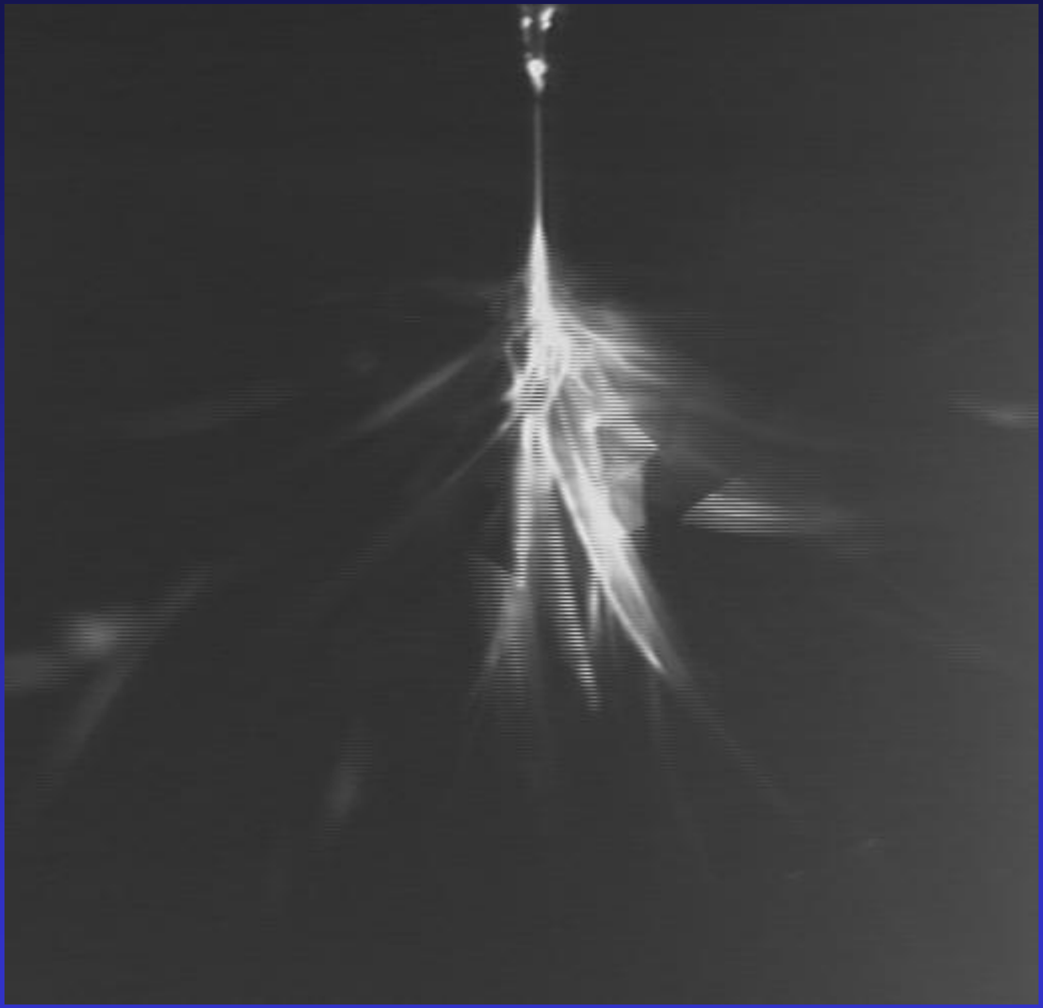


- <u>Polymer: PEO</u>
- Concentration: c=4%
- Solvent: 40% water-ethanol solution
- H=215mm

➢ U(V) – velocity of the fibre at the rectilinear part

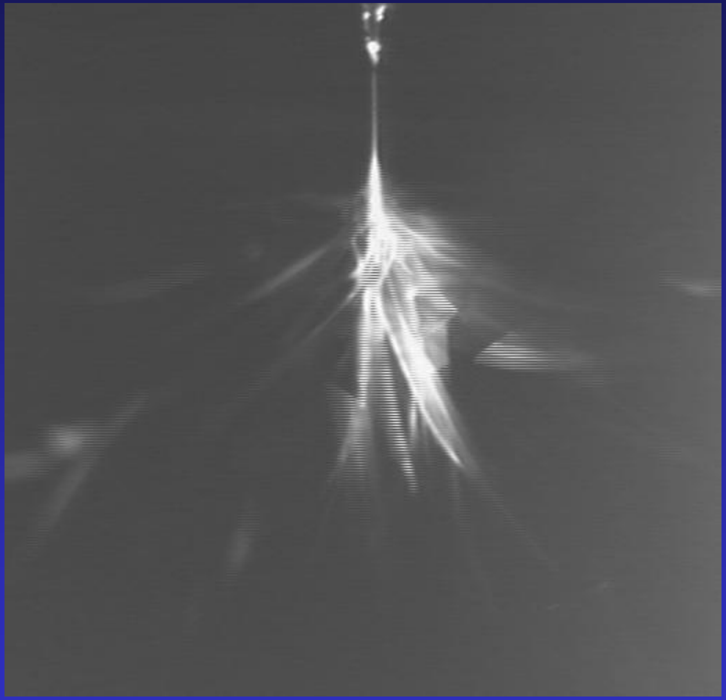
Electrospinning observed at 25fps

12 cm



- <u>Polymer: DBC</u>
- Concentration: c=9%
- Solvent: ethanol
- H=215mm
- V=6kV

Different structure of spinning fibres for DBC polymer

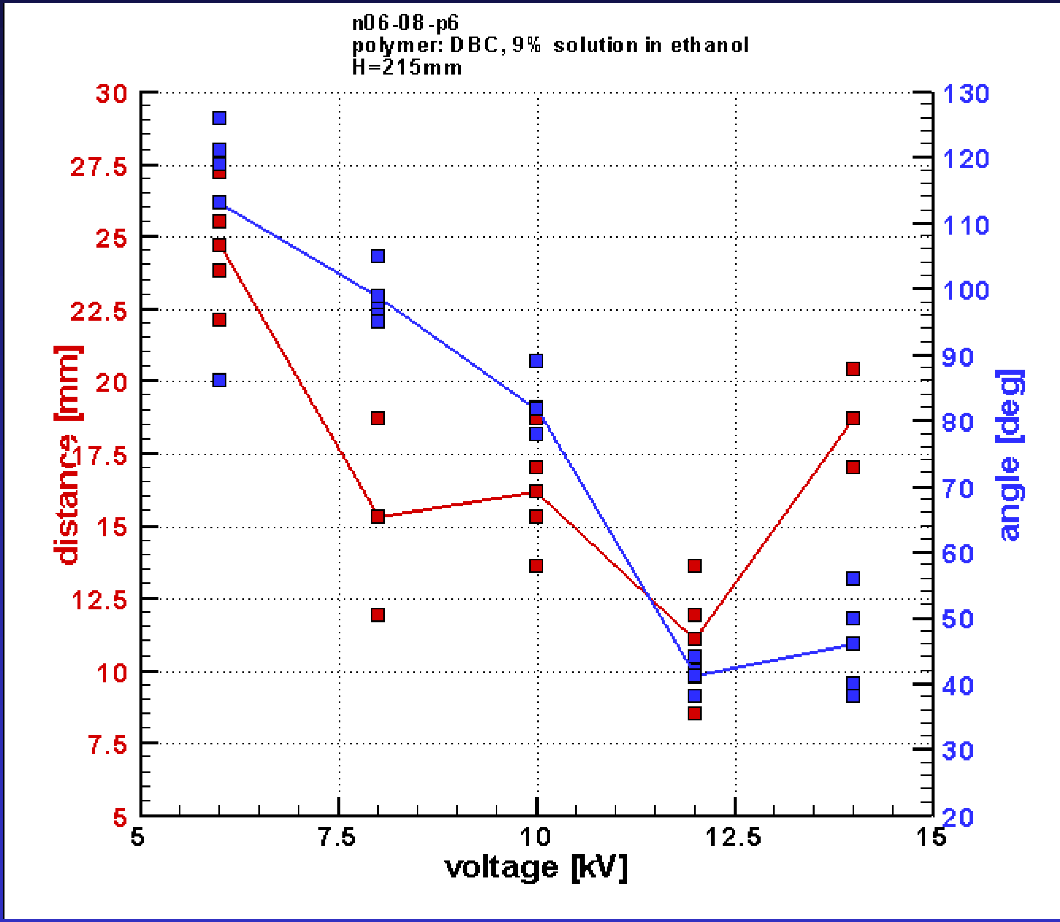


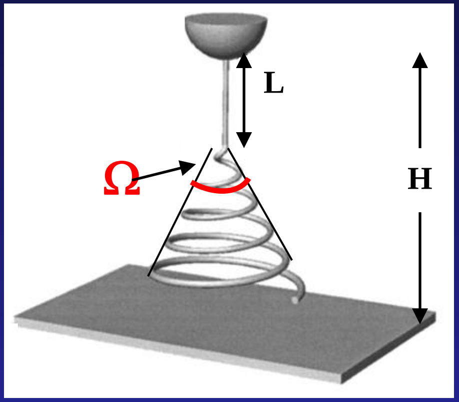
U=6kV

U=12kV

DBC: c=9% H=215mm

Parametric study





- Polymer: DBC
- Concentration: c=9%
- Solvent: ethanol
- H=215mm

- L (V) – length of the rectilinear part
- Ω (V) – angle of the envelope cone

Electrospinning observed at 25fps

12 cm

- Polymer: PAN
- Concentration: c=15%
- Solvent: DMF
- H=215mm
- V=13kV

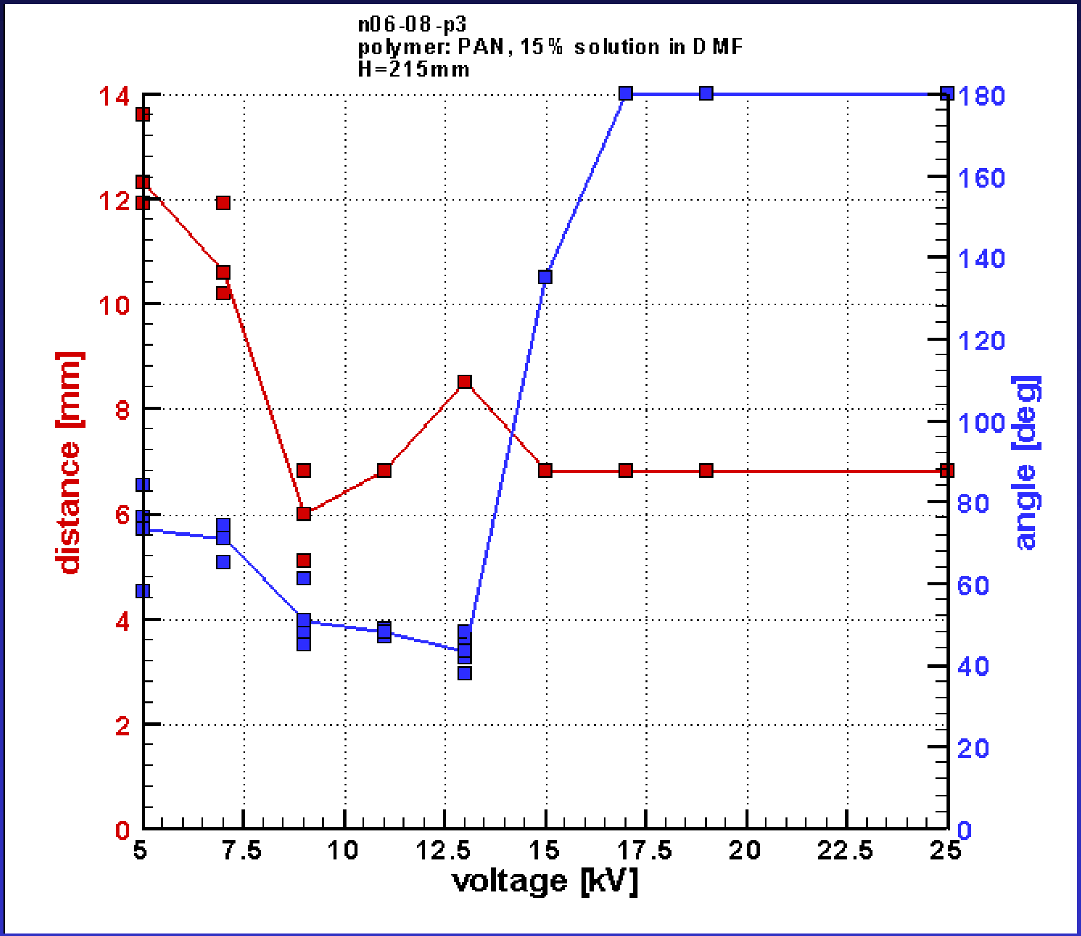
Different structure of spinning fibres for PAN polymer

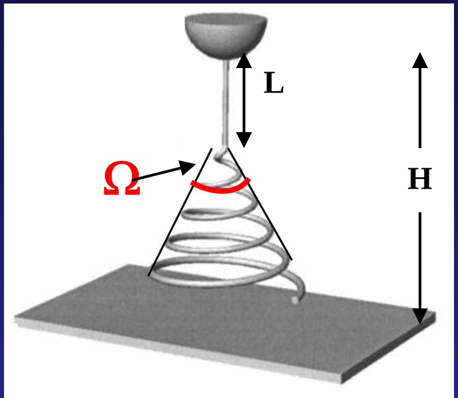
U=13kV

U=19kV

PAN: c=15% H=215mm

Parametric study





- <u>Polymer: PAN</u>
- Concentration: c=15%
- Solvent: DMF
- H=215mm

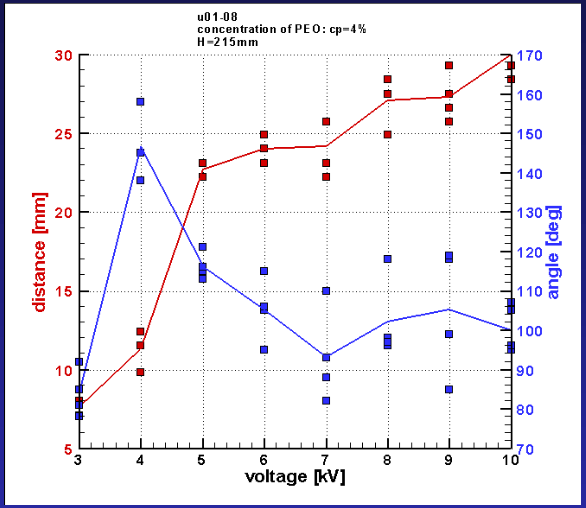
- L (V) – length of the rectilinear part
- Ω (V) – angle of the envelope cone

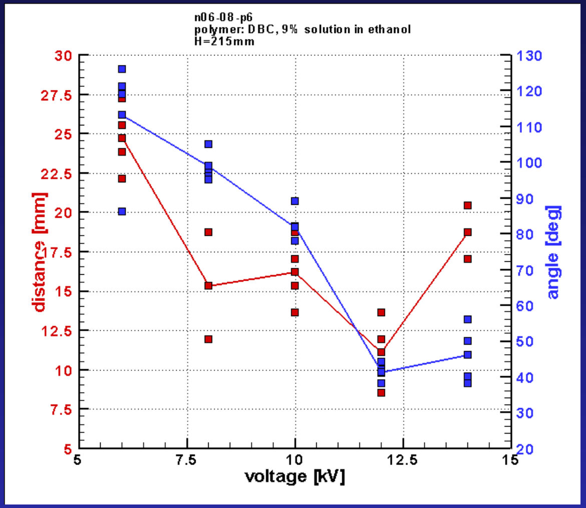
Electrospinning of Glycerol

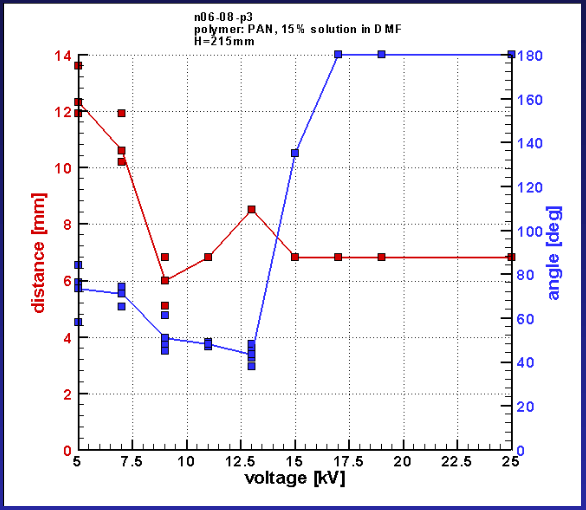
12 cm

- **<u>Glycerol</u>**
- **Concentration: c=88%**
- **Solvent: water**
- **H=215mm**
- **V=20kV**

Comparison of PEO & DBC &PAN polymers







PEO **DBC** **PAN**

- **L (V) – length of the rectilinear part**
- **Ω (V) – angle of the envelope cone**

Numerical model
Main assumptions

- *The electric field created by the generator is considered static and is approximated using a sphere-plate capacitor configuration*

- *The fibre is a perfect insulator with a constant electric charge density distributed over its surface*

- *The melt is viscoelastic and has constant elastic modulus, viscosity and surface tension*

Numerical model

2. Governing equations

- ***Mass conservation:***

$$\frac{D}{Dt}\left(\lambda\pi a^2\right) = 0$$

- ***Stress balance***

$$\frac{\partial\sigma}{\partial t} = G\frac{1}{\lambda}\frac{\partial\lambda}{\partial t} - \frac{G}{\mu}\sigma$$

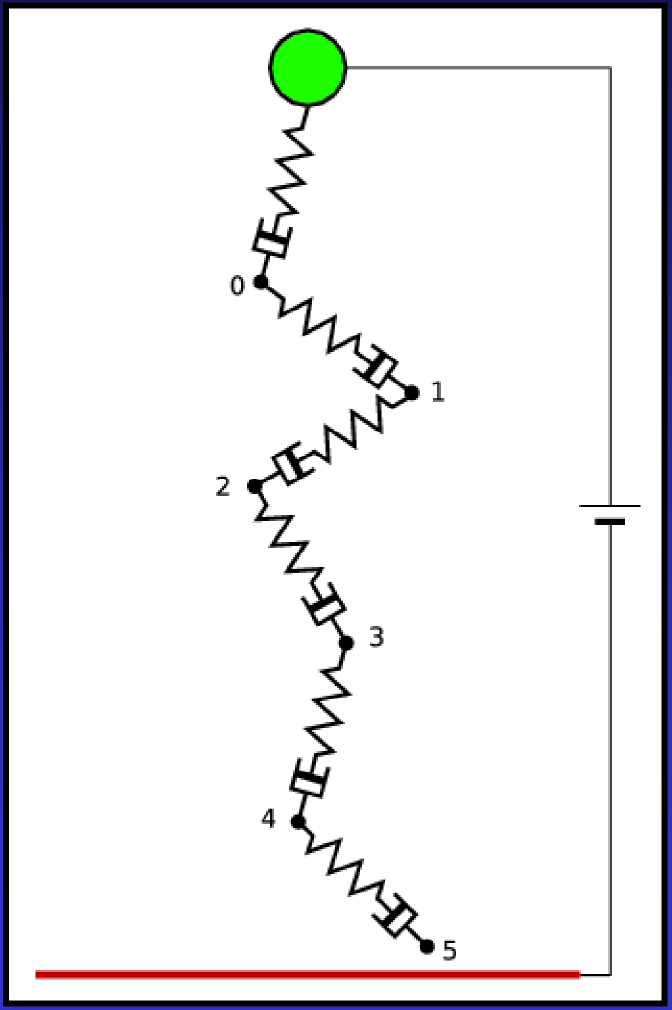
- ***Momentum balance***

$$\rho\lambda\pi a^2\frac{D\mathbf{V}}{Dt} = \lambda\pi a^2\int q^2\lambda(s^*)\,\pi a^2(s^*)\,C\left(\frac{a}{|\mathbf{r}-\mathbf{r}(s^*)|}\right)\frac{\mathbf{r}-\mathbf{r}(s^*)}{|\mathbf{r}-\mathbf{r}(s^*)|^3}ds^* + \lambda\pi a^2 q\mathbf{E} + \frac{\partial}{\partial s}\left(\pi a^2\sigma\mathbf{u}\right) + \frac{\partial}{\partial s}\left(\pi a\alpha\mathbf{u}\right)$$

α – ***surface tension***
λ – ***stretching parameter (relative elongation)***
μ – ***viscosity***
ρ – ***density***
σ – ***longitudinal stress***
a – ***radius of the fiber***
C – ***short-range E-field cutoff factor***
$\mathbf{E}$ – ***electric field***
G – ***elastic modulus***
q – ***charge per unit length***
$\mathbf{r}$ – ***coordinate vector***
s – ***Lagrangian curvilinear coordinate***
$\mathbf{u}$ – ***unit vector along the fiber***
$\mathbf{V}$ – ***velocity vector***

Numerical model

3. Discretized equations



- ***Mass conservation:***

$$\frac{d}{dt}\left(\pi\left|\mathbf{r}_i-\mathbf{r}_{i+1}\right|a_{i,i+1}^2\right) = 0$$

- ***Stress balance***

$$\frac{d\sigma_{i,i+1}}{dt} = G\frac{\left(\mathbf{r}_{i+1}-\mathbf{r}_i\right)\left(\mathbf{V}_{i+1}-\mathbf{V}_i\right)}{\left(\mathbf{r}_{i+1}-\mathbf{r}_i\right)^2}-\frac{G}{\mu}\sigma_{i,i+1}$$

- ***Momentum balance***

$$\begin{aligned}m_i\frac{d\mathbf{V}_i}{dt} &= q_i\sum_{j\neq i}q_jC_{i,j}\frac{\mathbf{r}_i-\mathbf{r}_j}{\left|\mathbf{r}_i-\mathbf{r}_j\right|^3}+q_i\mathbf{E}\\ &+\pi a_{i,i+1}^2\sigma_{i,i+1}\frac{\mathbf{r}_{i+1}-\mathbf{r}_i}{\left|\mathbf{r}_{i+1}-\mathbf{r}_i\right|}-\pi a_{i-1,i}^2\sigma_{i-1,i}\frac{\mathbf{r}_i-\mathbf{r}_{i-1}}{\left|\mathbf{r}_i-\mathbf{r}_{i-1}\right|}\\ &+\pi a_{i,i+1}\alpha\frac{\mathbf{r}_{i+1}-\mathbf{r}_i}{\left|\mathbf{r}_{i+1}-\mathbf{r}_i\right|}-\pi a_{i-1,i}\alpha\frac{\mathbf{r}_i-\mathbf{r}_{i-1}}{\left|\mathbf{r}_i-\mathbf{r}_{i-1}\right|}\end{aligned}$$

Numerical model

4. Boundary conditions

The last particle introduced at the tips keeps a constant velocity until the distance to the tip exceeds the initial bead length l_0:

$$\mathbf{V}_0 == -\frac{Q}{\pi a_0^2}\mathbf{z} \qquad \text{for } |\mathbf{r}_0 - \mathbf{r}_{\rm tip}| \le l_0$$

l_0 – ***initial bead length*** **[input]**
Q – ***volume flow rate*** **[input]**

A small perturbation is added to the position of each new particle introduced near the tip:

$$\begin{aligned} x_0 &= x_{\rm tip} + \epsilon \sin\varphi \\ y_0 &= y_{\rm tip} + \epsilon \cos\varphi \end{aligned}$$

ε – ***distance to the main axis*** **[input]**
φ – ***random phase***

Particles that reach the collector are considered neutralized and are removed from the fibre.

Numerical model

5. Parametric simulations

Reference case:

α = 0.07 N/m
Φ = 5000 V
μ = 10 Pa.s
$G = 10^5$ Pa

$\rho = 1000$ kg/m^3
a_0 = 150 µm
H = 20 cm
l_0 = 1 µm
$q = 200$ C/m^3
$Q = 3.6$ cm^3/h

Case	α	Φ	μ	G
1	3			
2	/3			
3		x2		
4			x5	
5				x2
6				/2

Numerical model

α = 0.07 N/m
Φ = 5000 V
μ = 10 Pa.s
$G = 10^5$ Pa
$\rho = 1000$ kg/m^3
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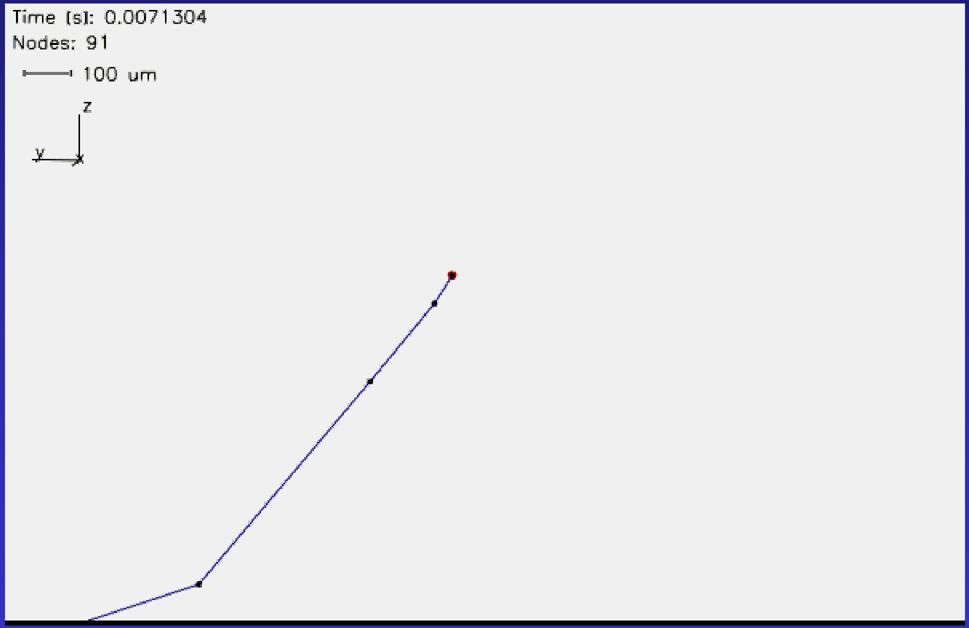
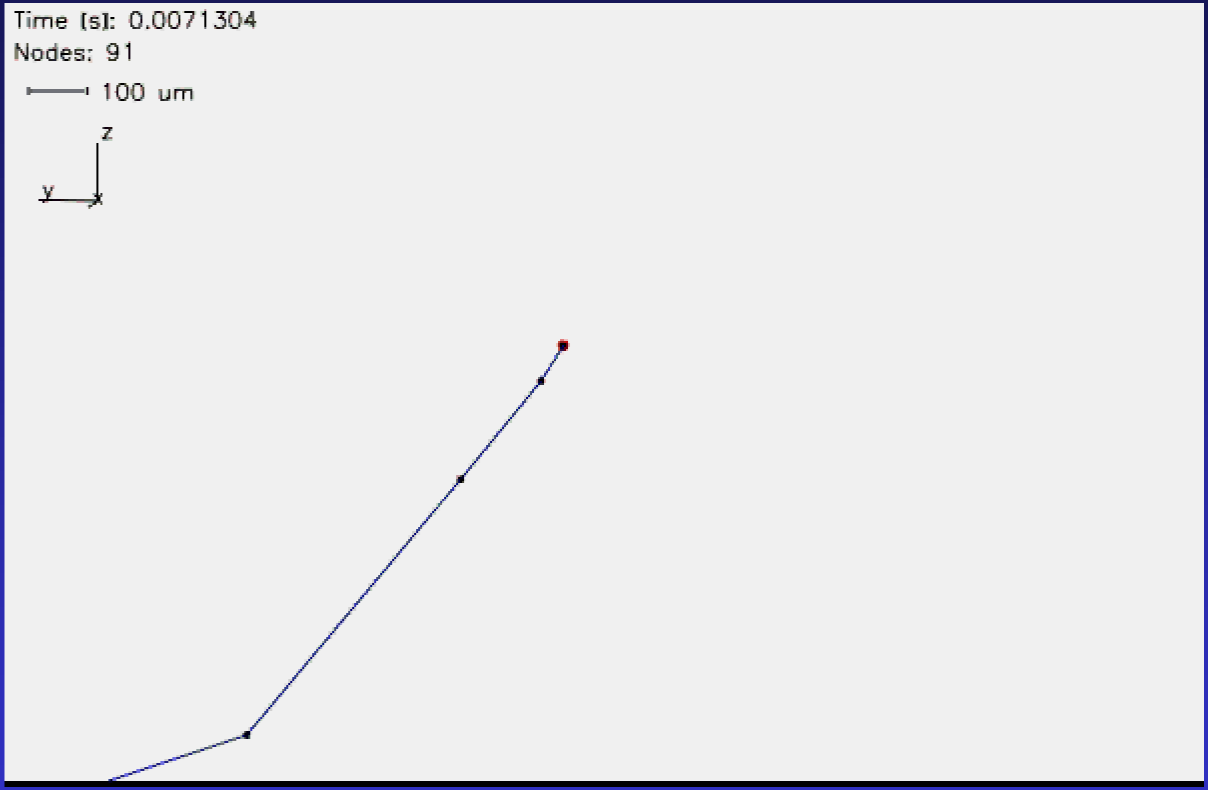


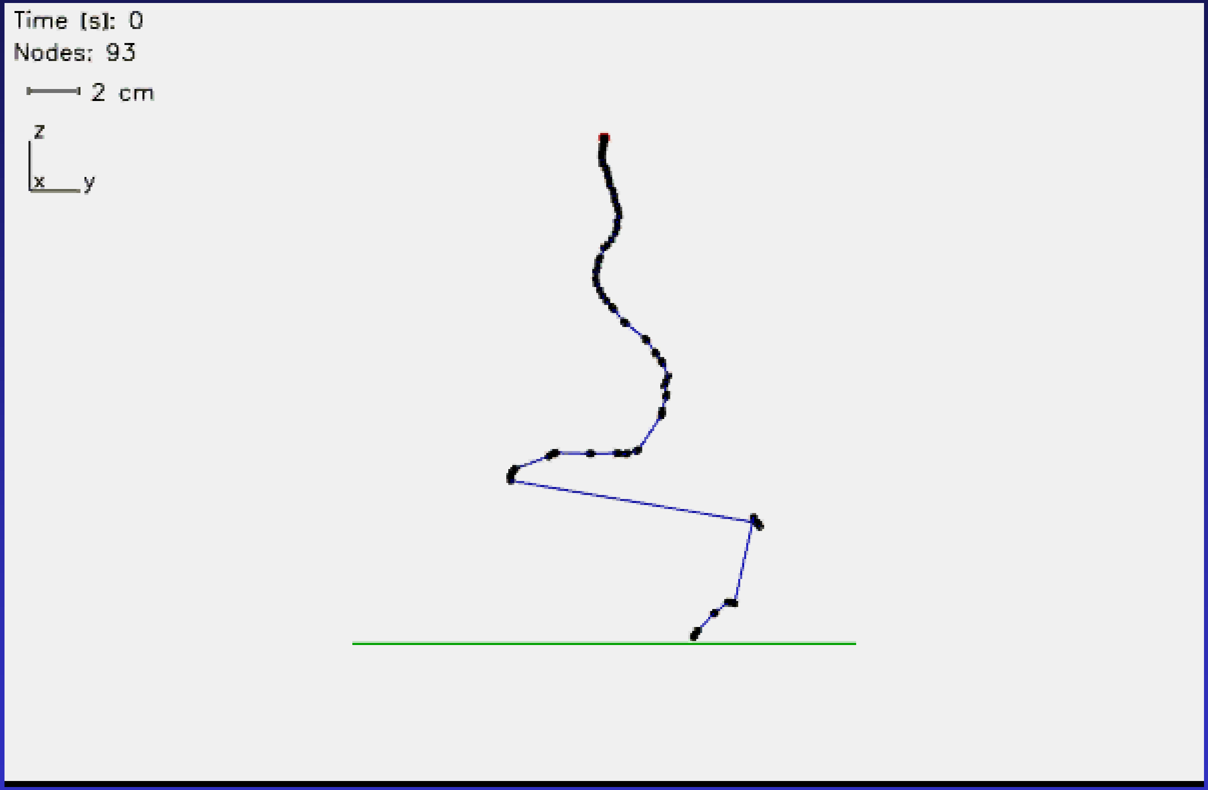
Numerical model

Reference case



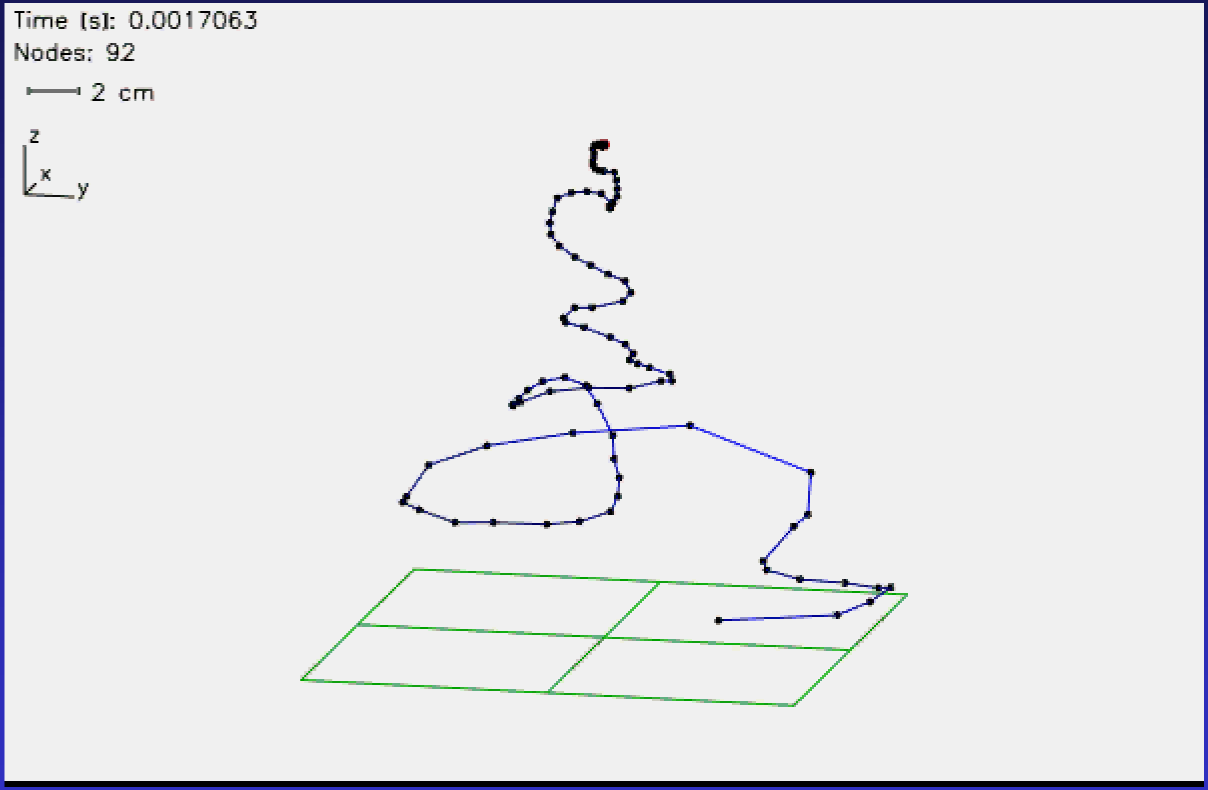
Numerical model

Triple surface tension



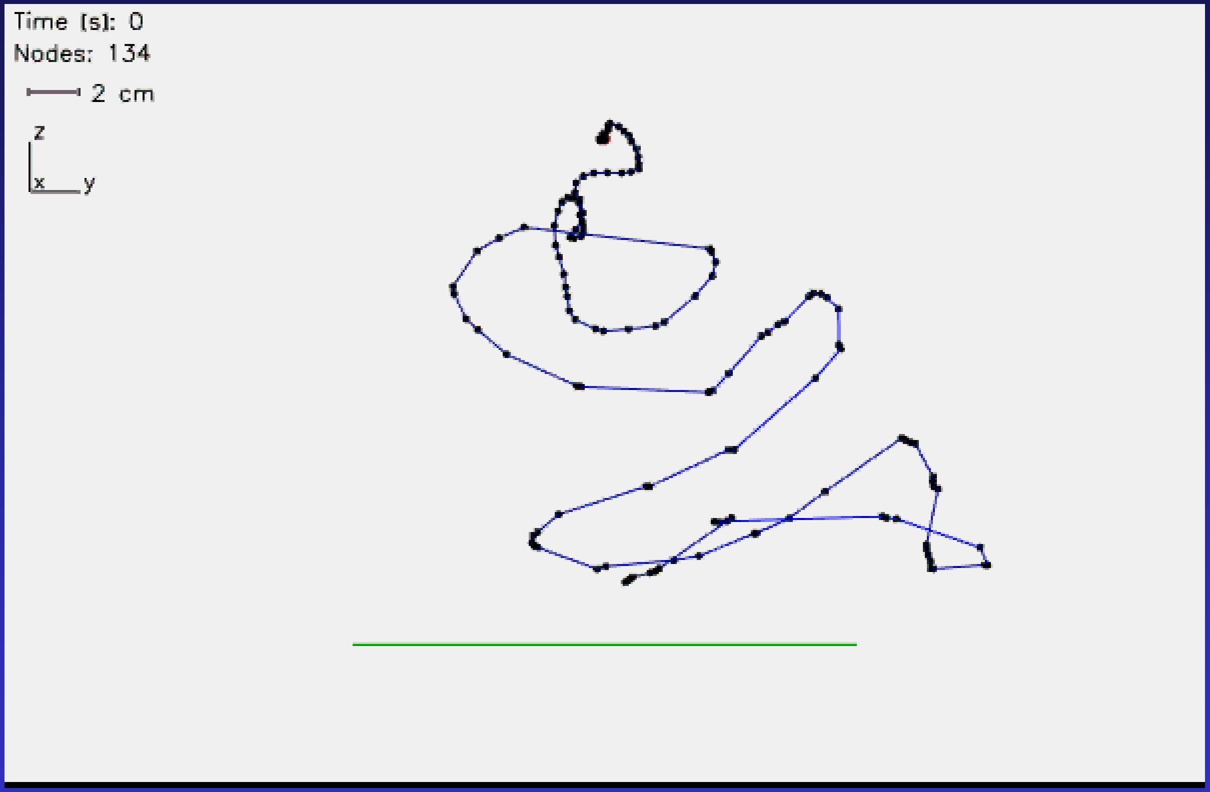
Numerical model

1/3 surface tension



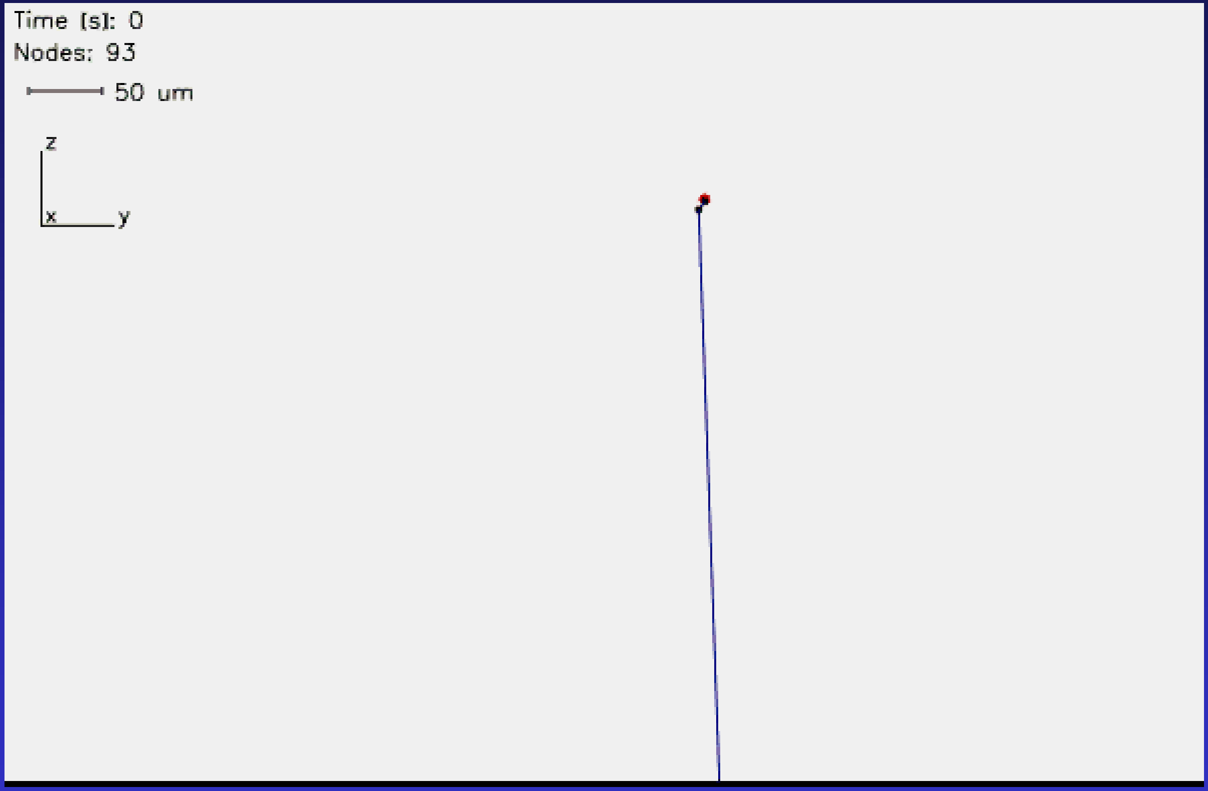
Numerical model

½ Voltage



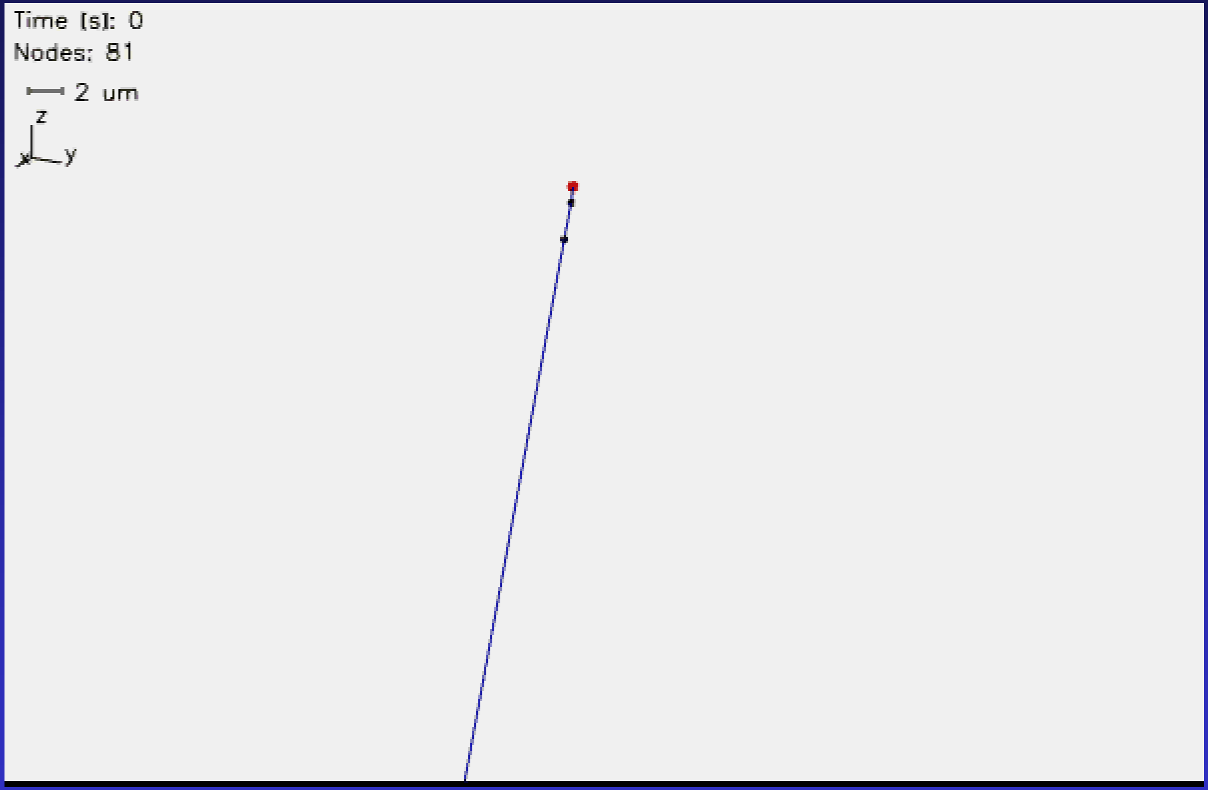
Numerical model

5 times higher viscosity



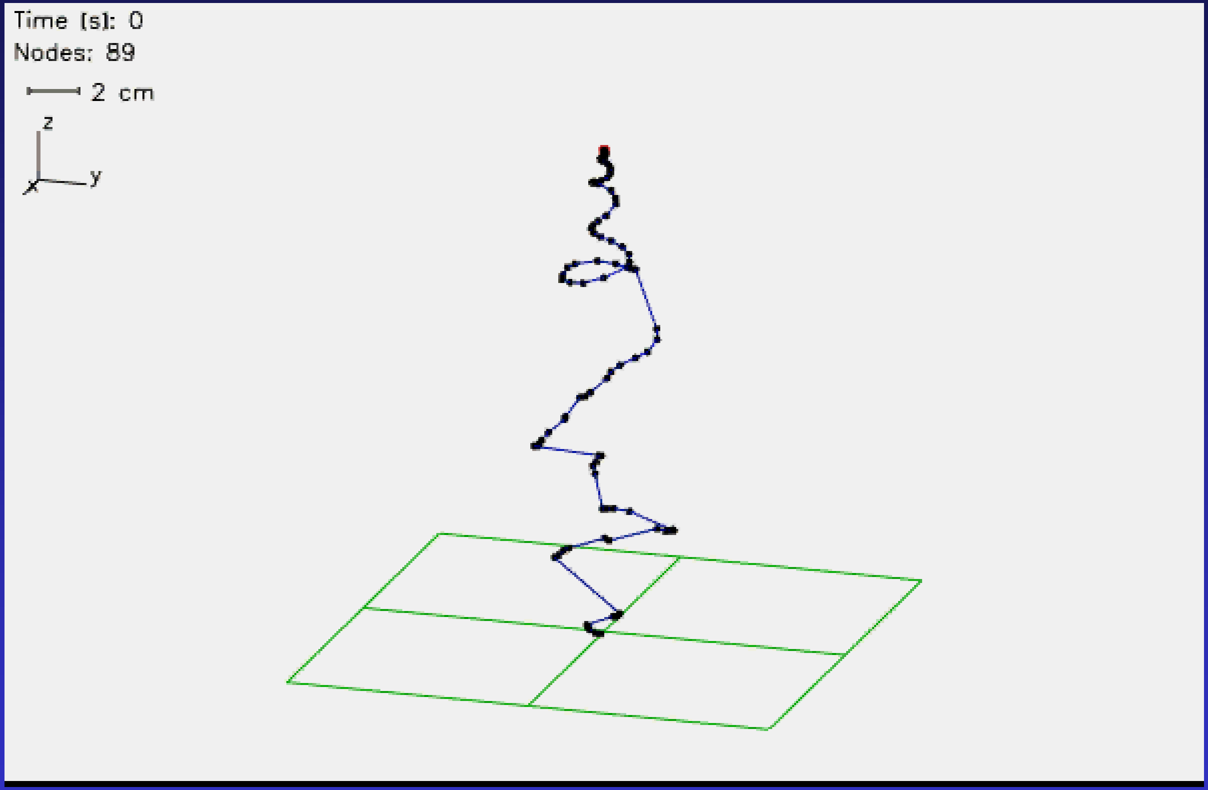
Numerical model

Double elastic modulus



Numerical model

Half elastic modulus



Numerical model

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$G = 10^5$ Pa

$\rho = 1000$ kg/m^3
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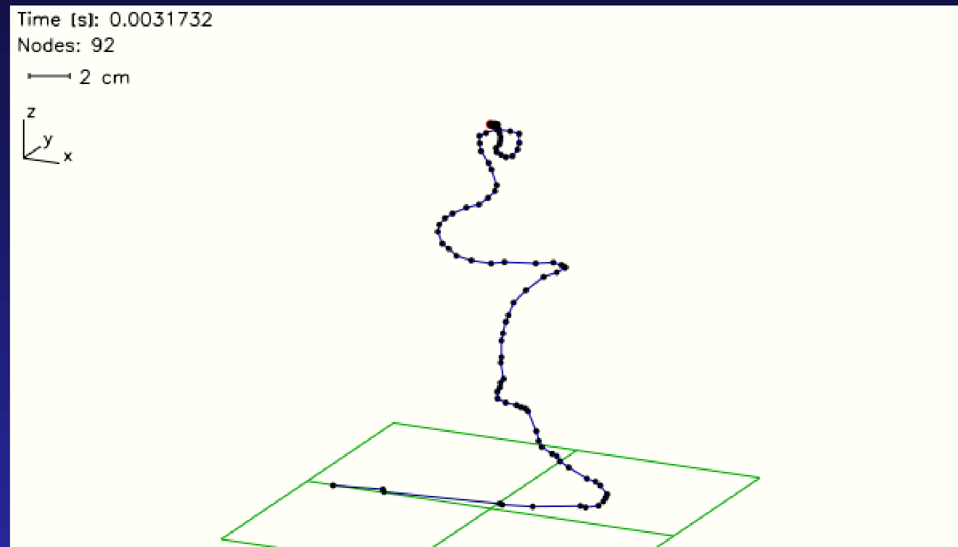
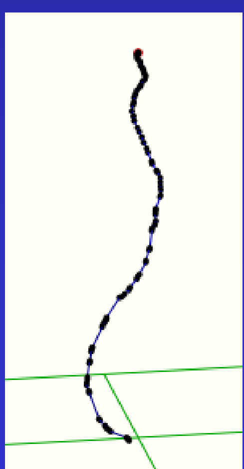
H = 20 cm
l_0 = 1 µm
$q = 200$ C/m^3
$Q = 3.6$ cm^3/h

Reference case:

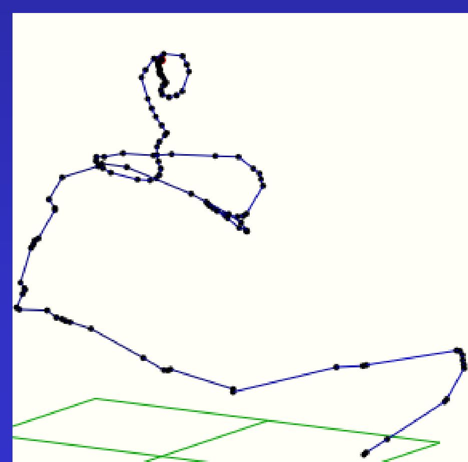


α = 0.21N/m

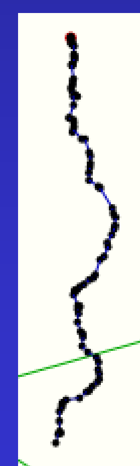


α = 0.023N/m

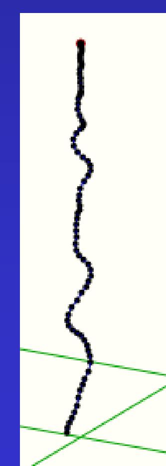
Φ = 2500V



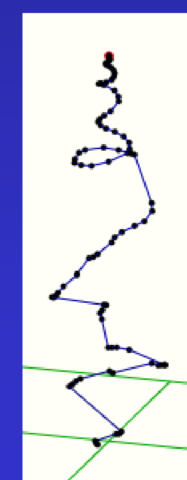
μ = 2 Pa.s



$G = 2{\cdot}10^5$ Pa



$G = 5{\cdot}10^4$ Pa



Conclusions

- ✓ Electrostatic elongation of polymer threads allows to produce relatively easily fibres in nano range diameters

- ✓ Collection of nano-woven of bio-active polymers, e.g.. chitin may have practical application for tissue growth

- ✓ Simulations recover some key physical phenomena but fail at modelling the straight jet portion

- ✓ The modeling of electrospun fibers is still embryonic. Improvements are required in many areas:
  - better physical description (evaporation, varying viscosity, ...)
  - checking of the mathematical correctness of the model (is the discrete charge model fully consistent?)
  - development of a fast algorithm for Coulomb interactions
  - ...

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We would like to acknowledge the valuable contribution of dr Anna Błasińska from TU of Łódź and Anna Blim from IPPT PAN in the work presented.