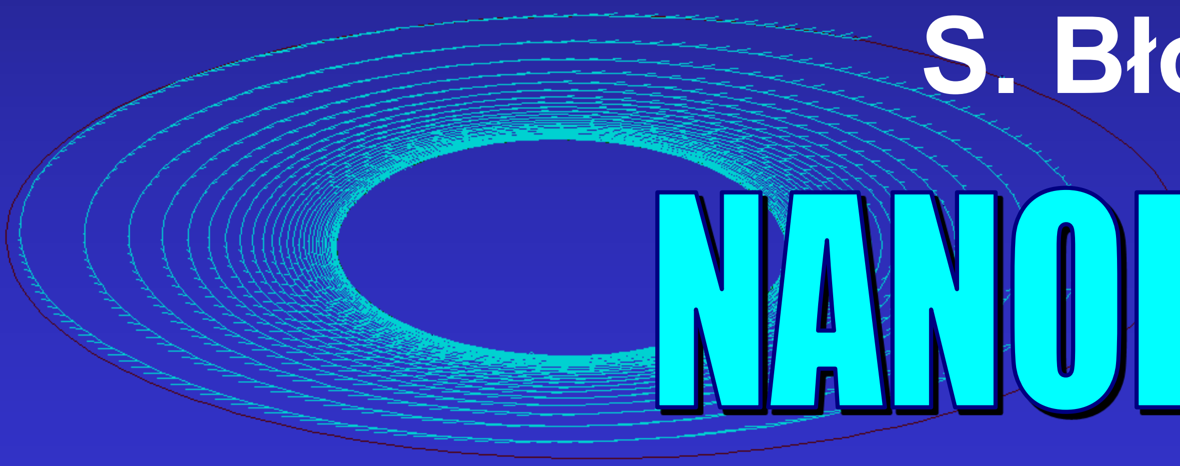
Institute of Fundamental Technological Research
Polish Academy of Sciences
&
Department of Mechanical Engineering
Technion - Israel Institute of Technology

T. A. Kowalewski
A. L. Yarin
S. Błoński



NANOFIBRES

by electro-spinning of polymer solution

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

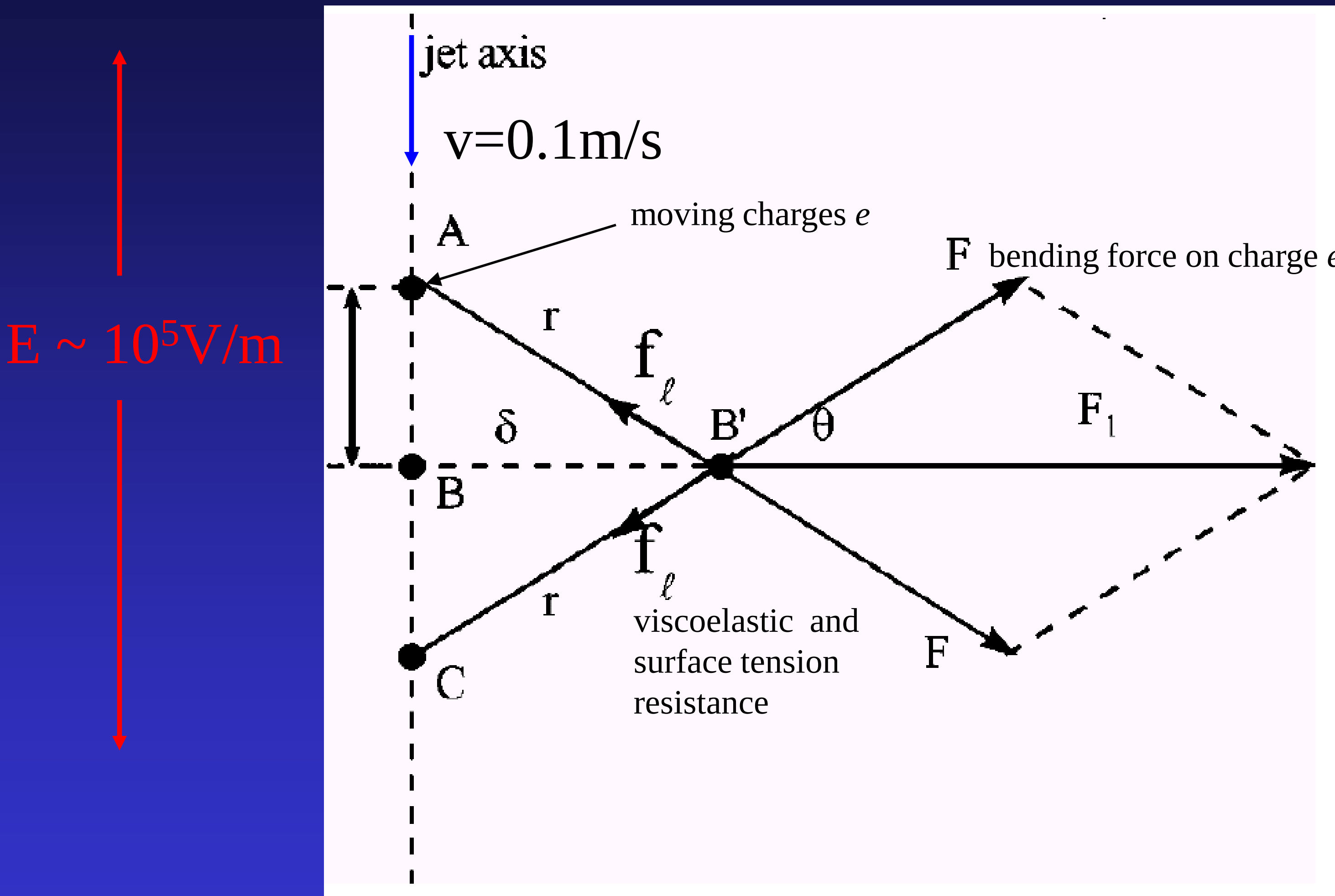
Orifice – 0.1mm

Primary jet diameter ~ 0.2mm

Micro-jet diameter ~ 0.005mm

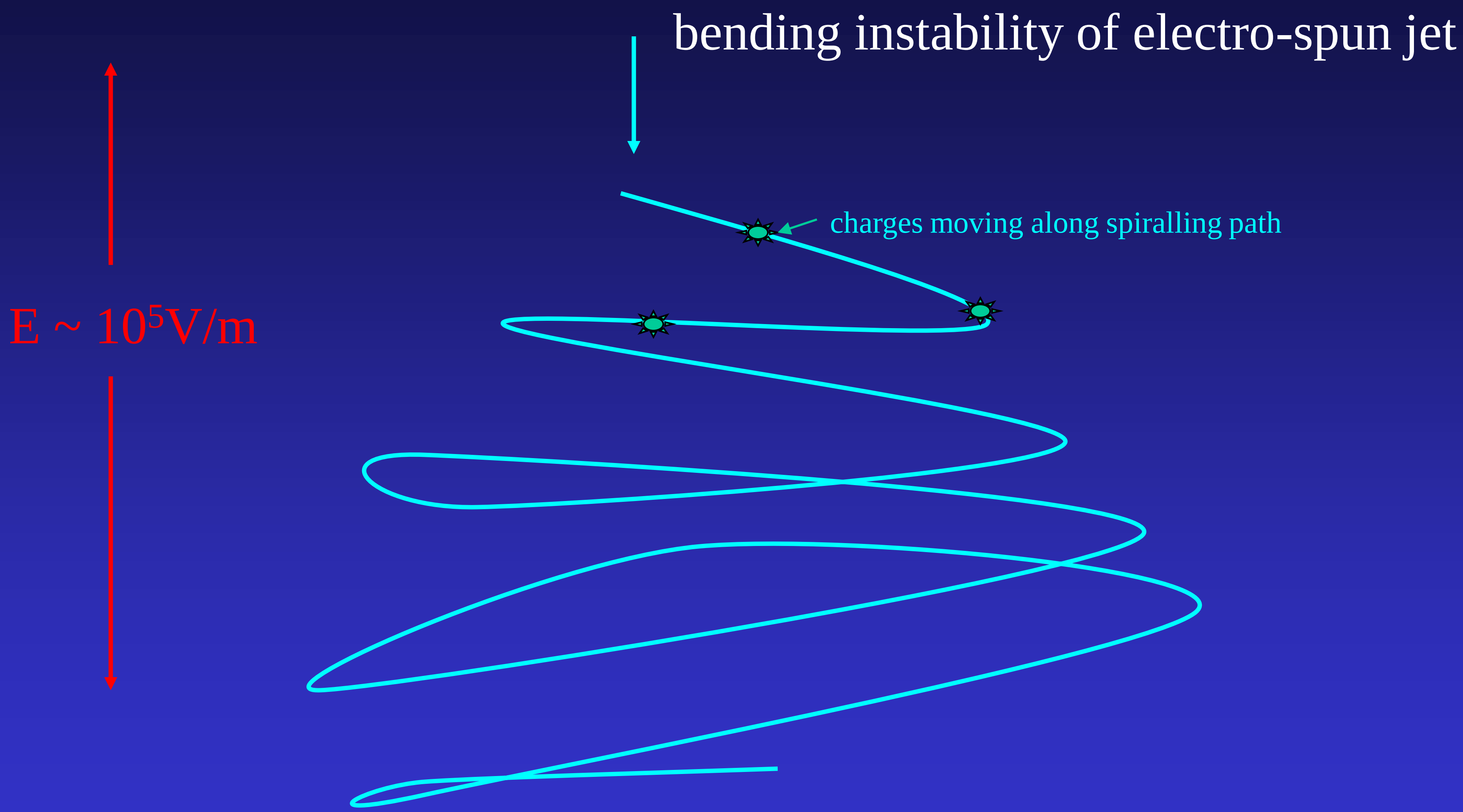
- Gravitational, mechanical or electrostatic pulling limited to l/d ~ 1000 by capillary instability
- To reach nano-range:
  - jet thinning ~10^{-3}
  - draw ratio ~10^{6} !

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

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

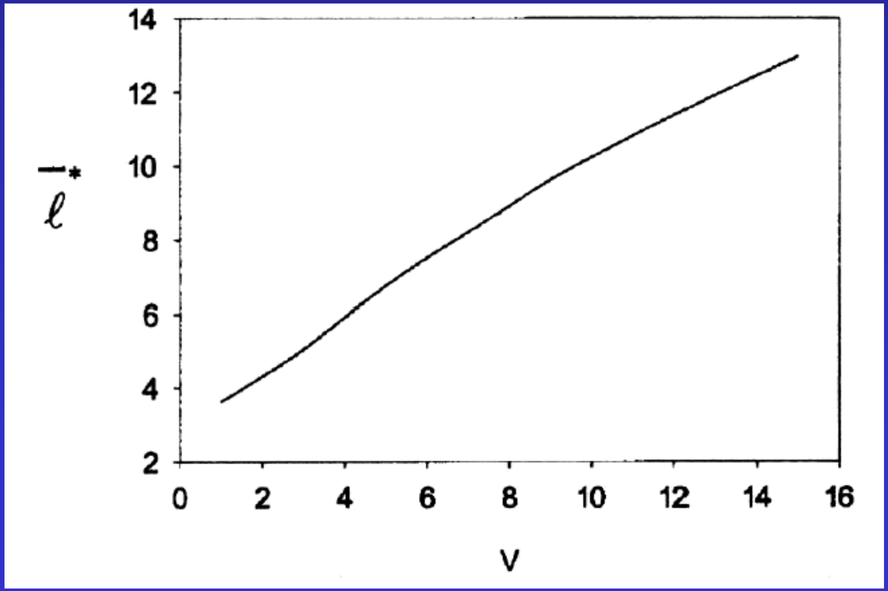
Stress balance: *μ - viscosity, G – elastic modulus stress, σ stress tensor, dl/dt – thread elongation*

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

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

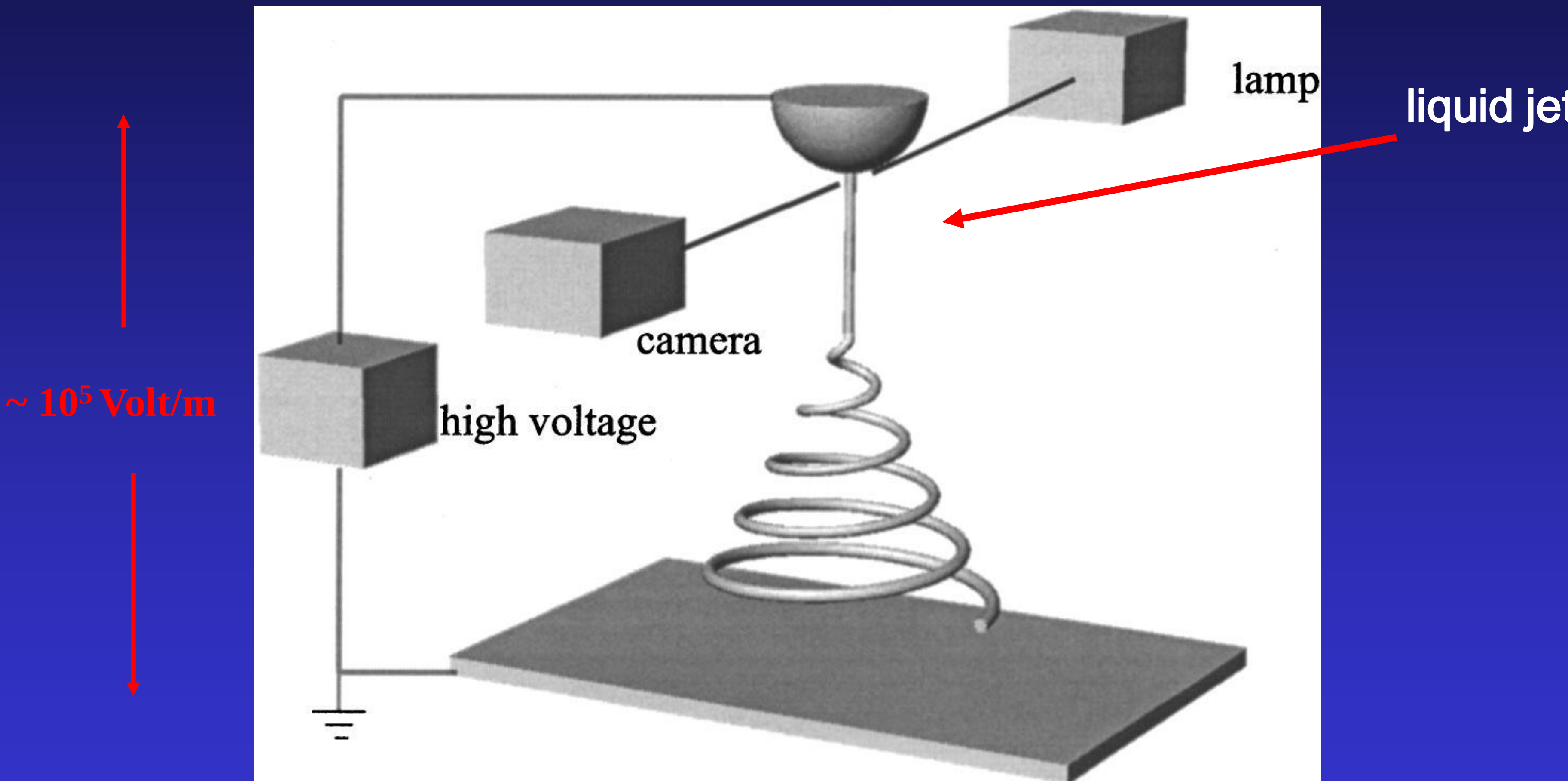
$$\frac{d\ell}{dt} = -v,$$

Kinematic condition for thread velocity v



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

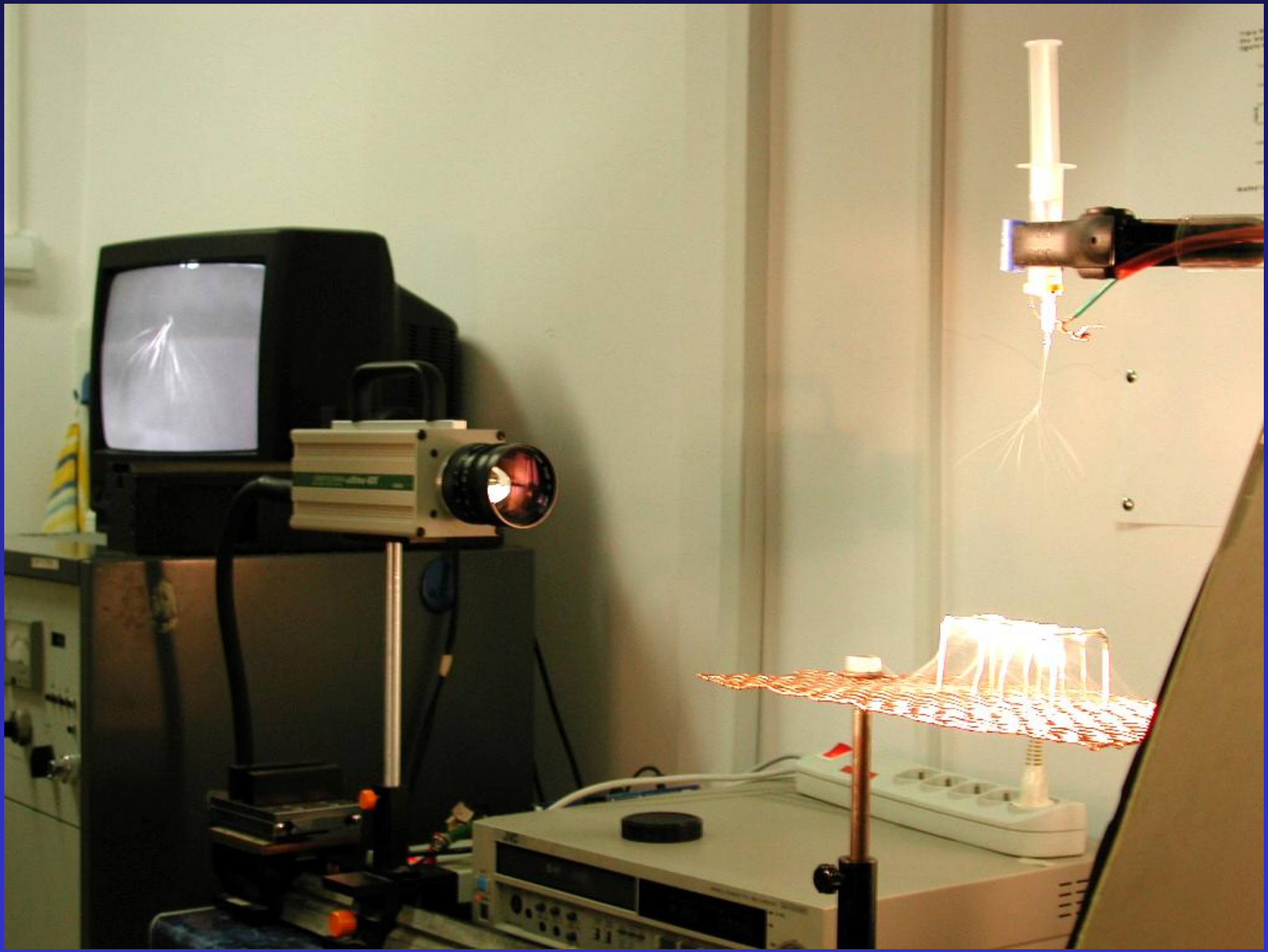
Nanofibres – basic setup



Nanofibres – howto?

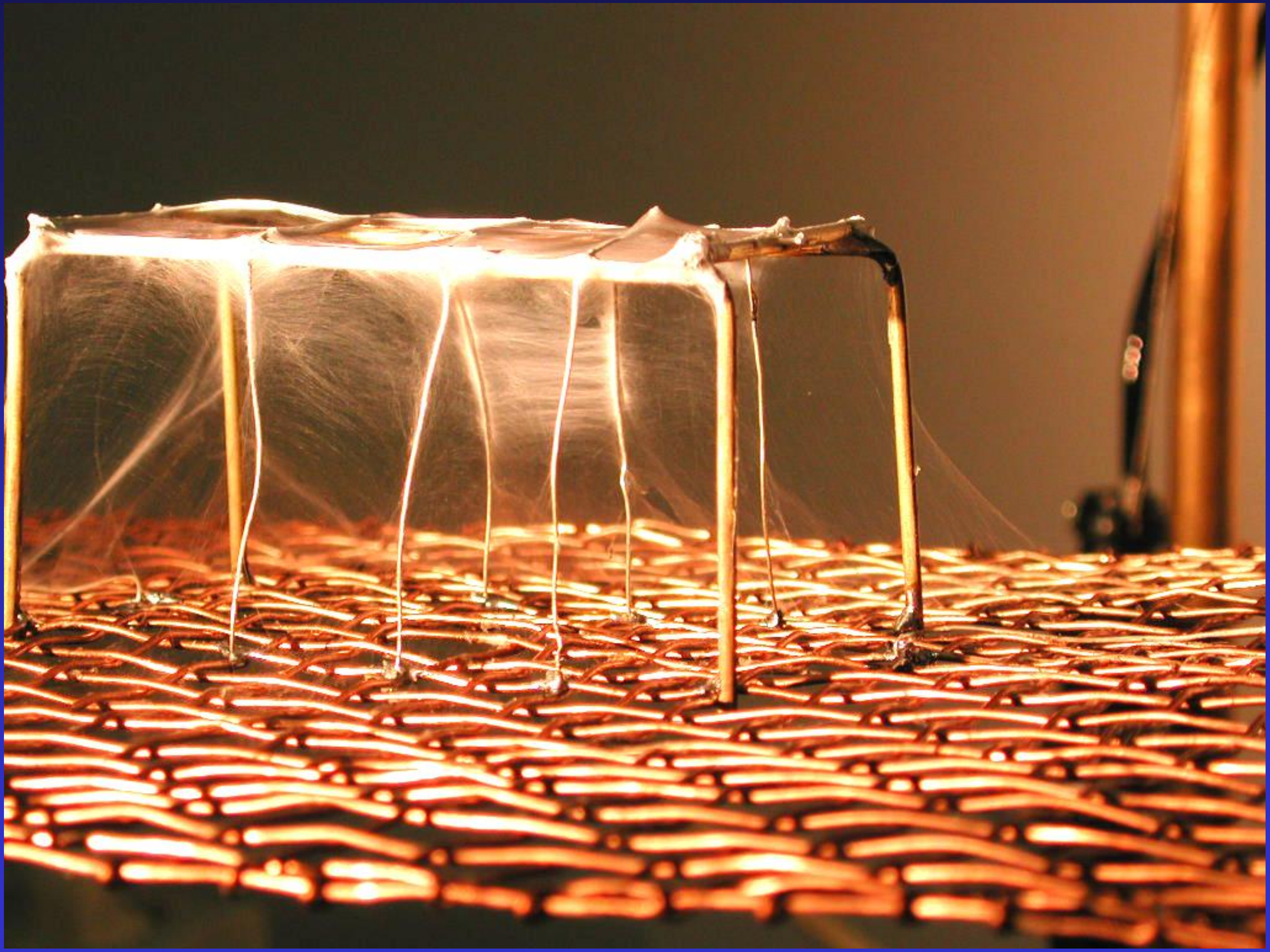
1. Viscoelastic fluid:
   - Dilute solution (4 – 6)% of polyethylene oxide (molar weight $4 \cdot 10^5$ g/mol), in 40% ethanol –water solvent
2. Electrostatic field
   - high voltage power supply (5-30kV)
   - plastic syringe
   - metal grid to collect fibres
3. Visualization
   - high speed camera (4000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

Nanofibres – basic setup



Nanofibres collection

Nanofibres collection

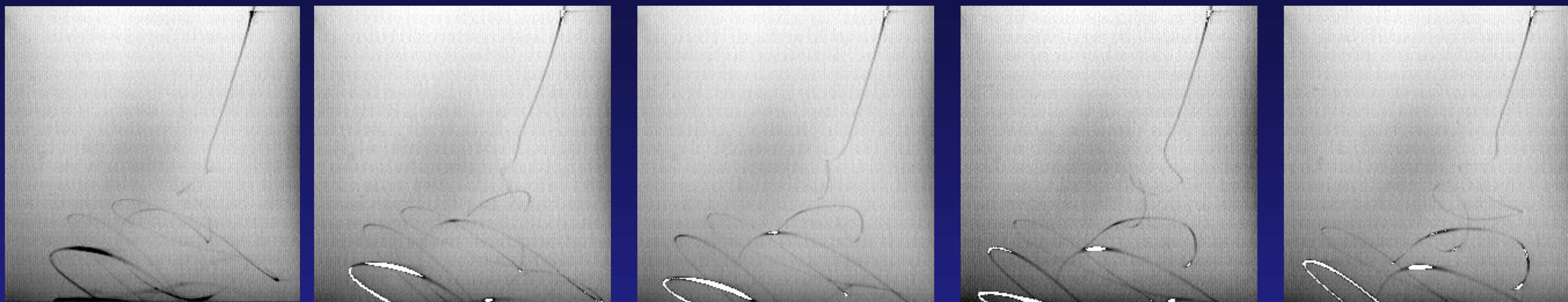


Electrospinning observed at 30fps

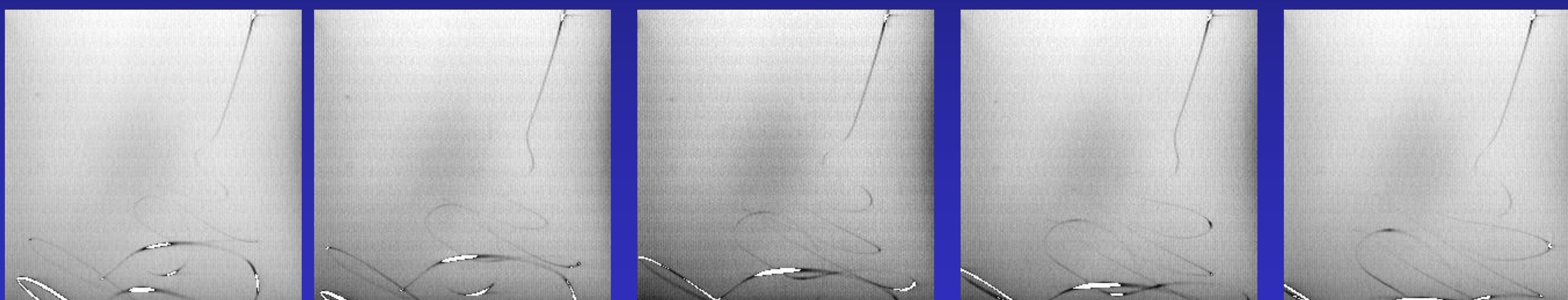
5 cm

Average velocity of the fibres: 2 m/s

Electrospinning observed at 4500fps



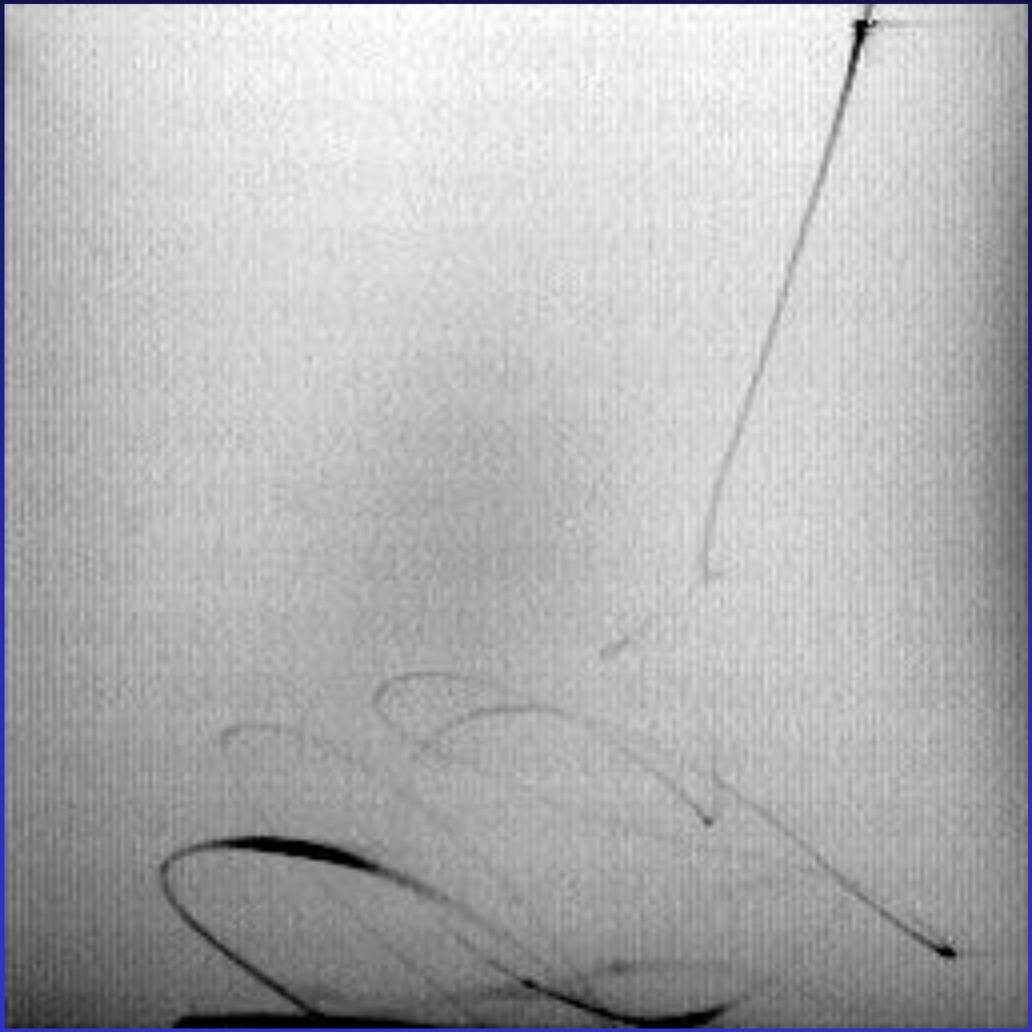
0.0 ms | 8.9 ms | 17.8 ms | 26.7 ms | 35.6 ms



44.4 ms | 53.3 ms | 62.2 ms | 71.1 ms | 80.0 ms

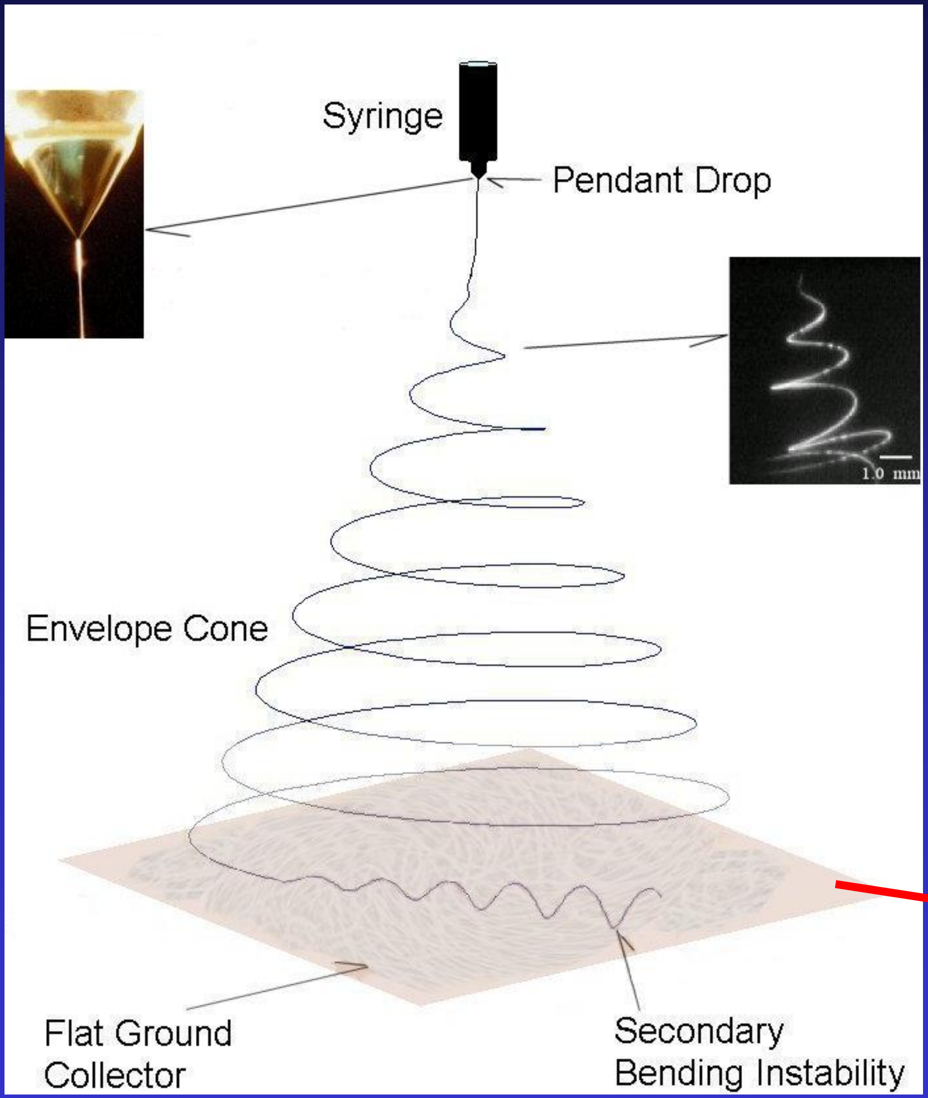
Electrospinning observed at 4500fps

5 cm

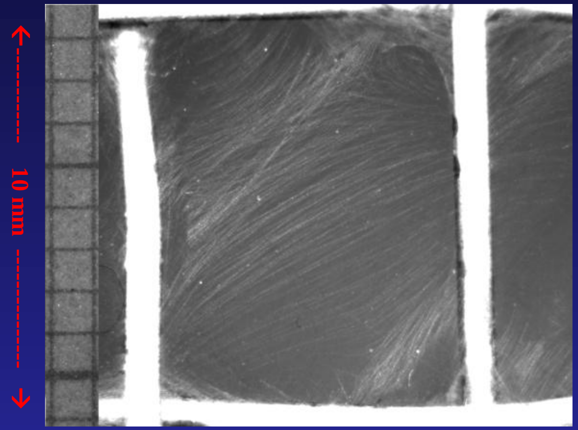


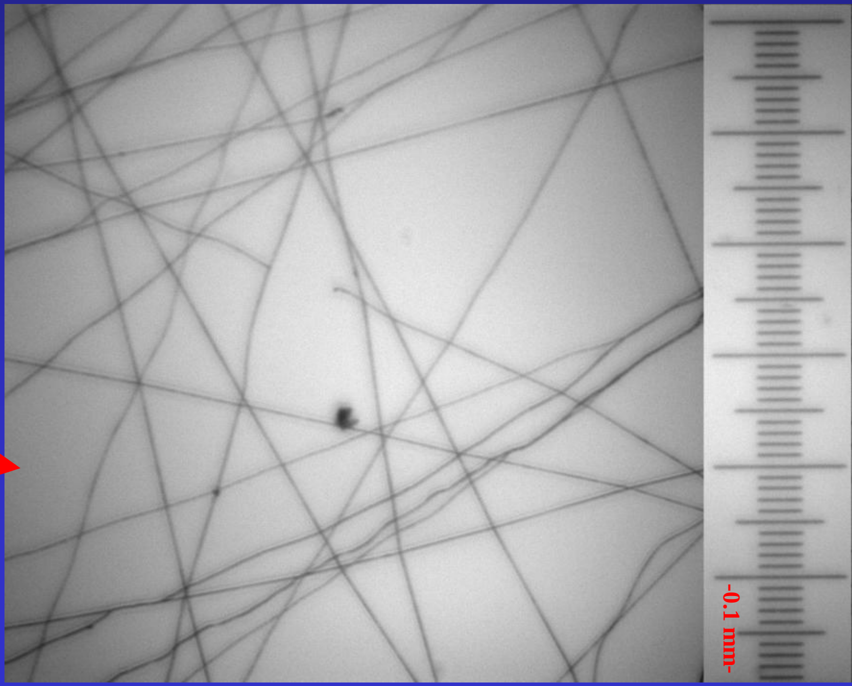
Average velocity of the fibre: 2 m/s

Electrospinning

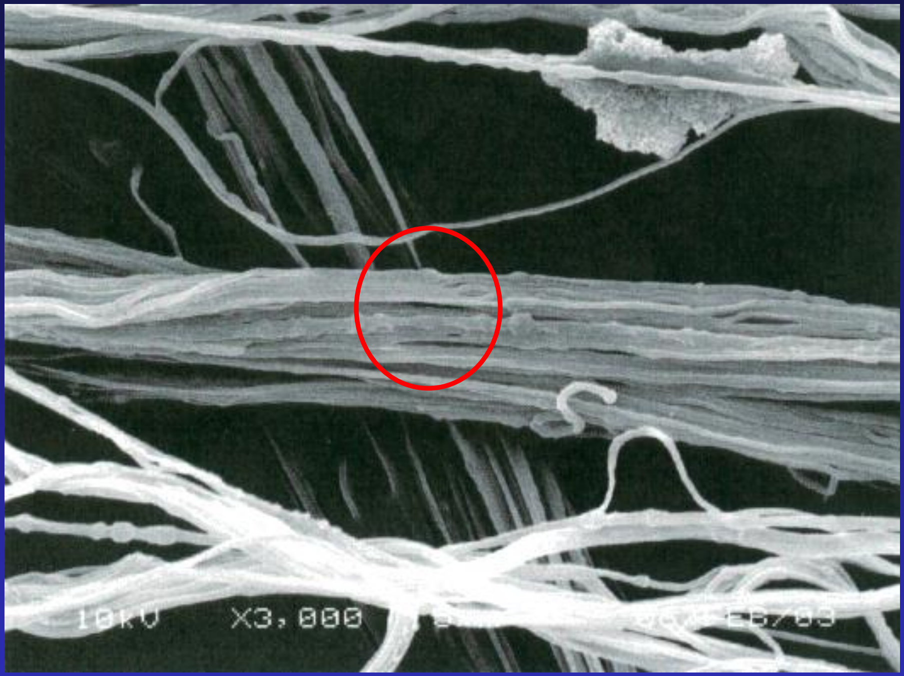


Collected nanofibres



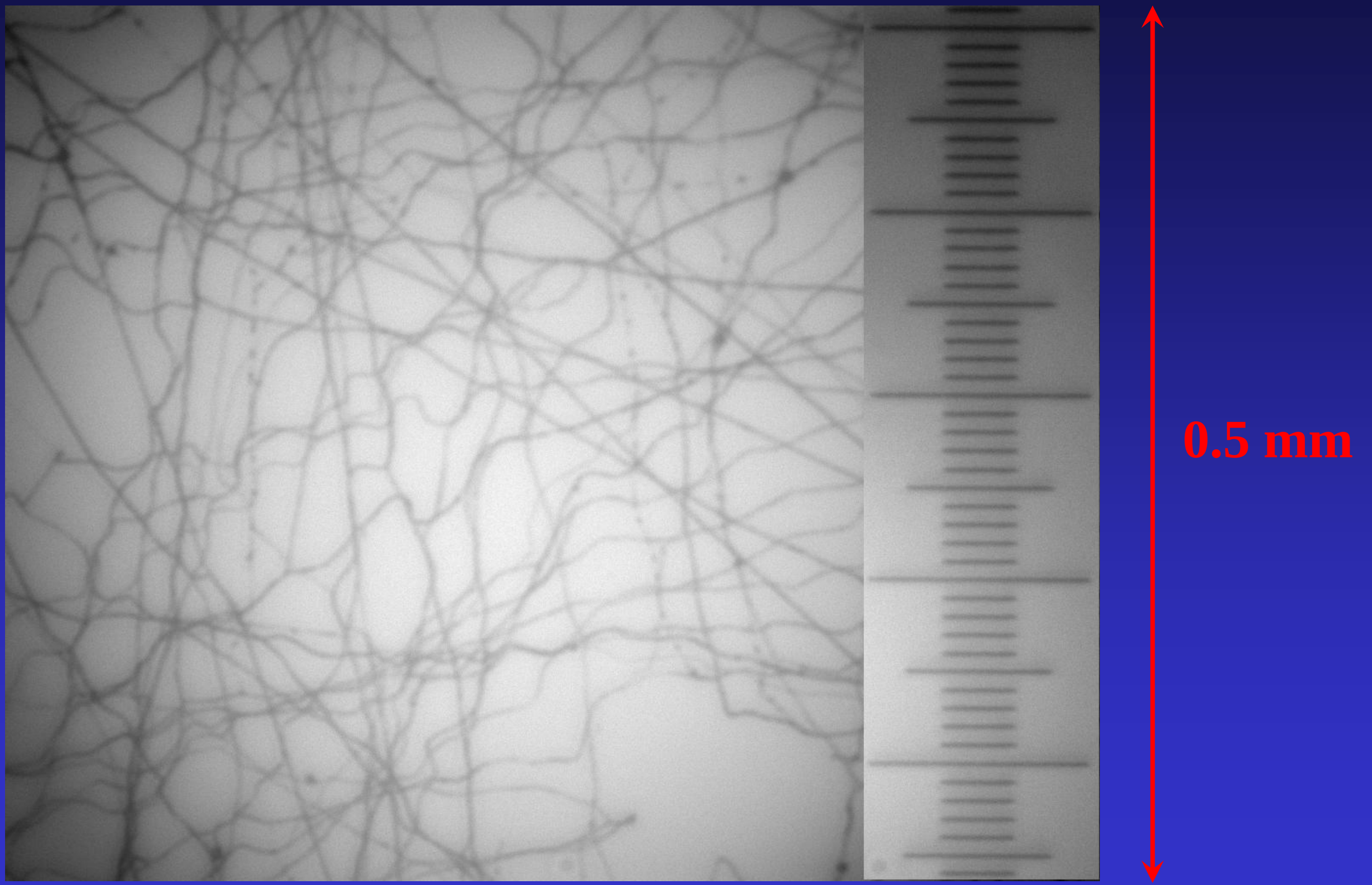


Electron microscopy



PEO nanofibres

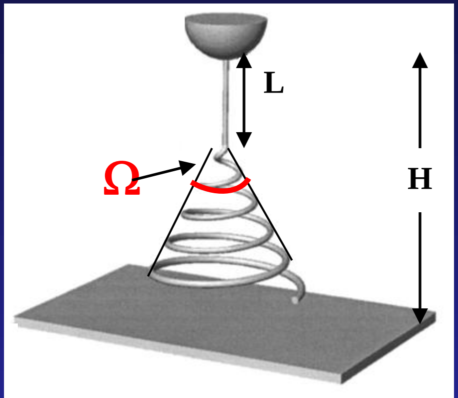
Failure modes



Parametric study

Model validation varying following parameters:

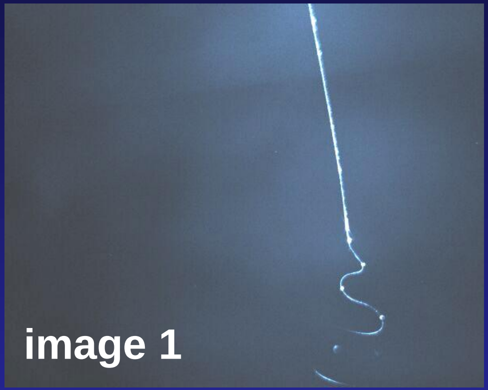
- L – length of the rectilinear part
- Ω – angle of the envelope cone (image analysis)
- U – velocity of the fibre by PIV method
- a – fibre diameter (image analysis)
- structure of collected woven (failure modes)
- elongation strength of single fibre measured by air jet



Effect of

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

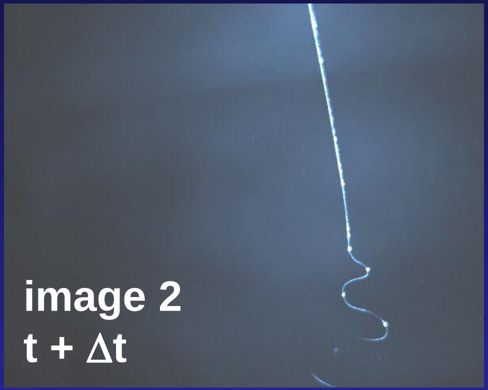
Parametric study



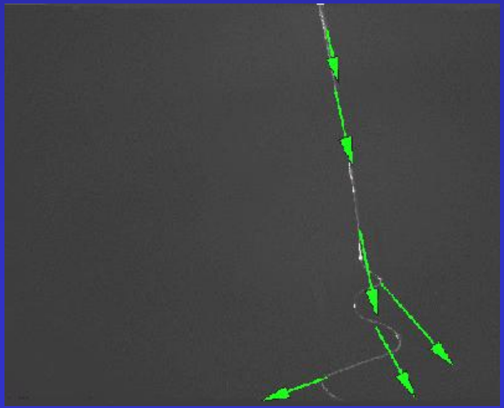
PIV

cross – correlation

$\Delta t = 500\ \mu s$



- 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



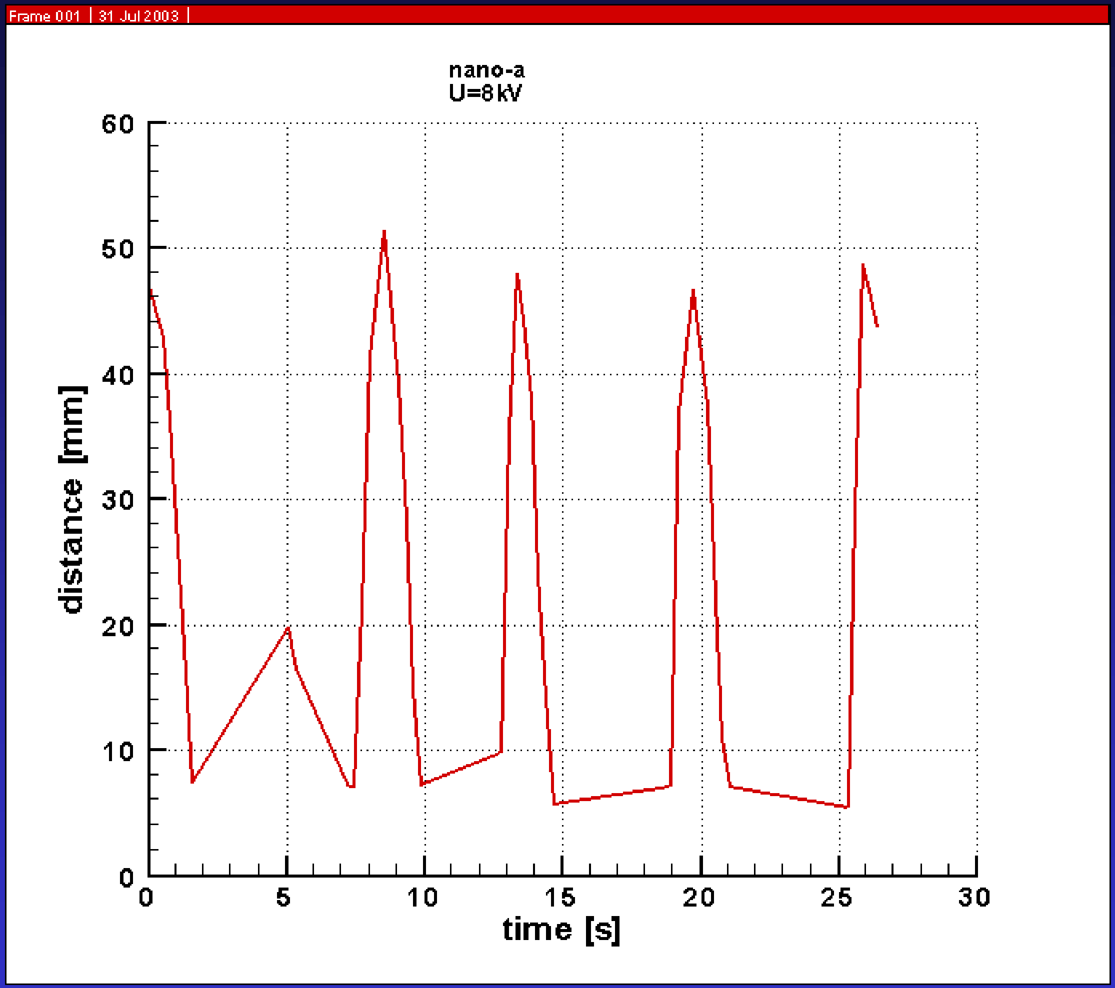
Average velocity of the fibres: 2 m/s

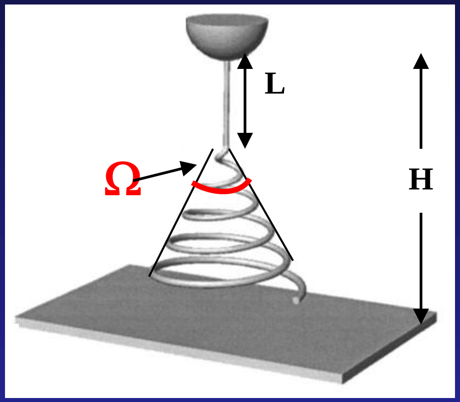
Tested polymers

Test	Polymer	Solvent	Concentration	Voltage [kV]	Electrospinning
I	**PEO** Polyethylene-oxide	40% water – ethanol solution	3 – 4 %	3 – 12	good and stable process for voltage up to 10kV
II	**DBC***	Ethanol	2-29%	6 – 16	fairly good
III	**TAC***	Ethanol	7-30 %	3 – 30	polymer too viscous
			1-7 %	10 – 30	difficult
IV	**PAN***	DMF	1-25 %	5 – 25	very good

[*]*Prepared at Technical University of Łódź by dr Anna Błasińska*

Parametric study

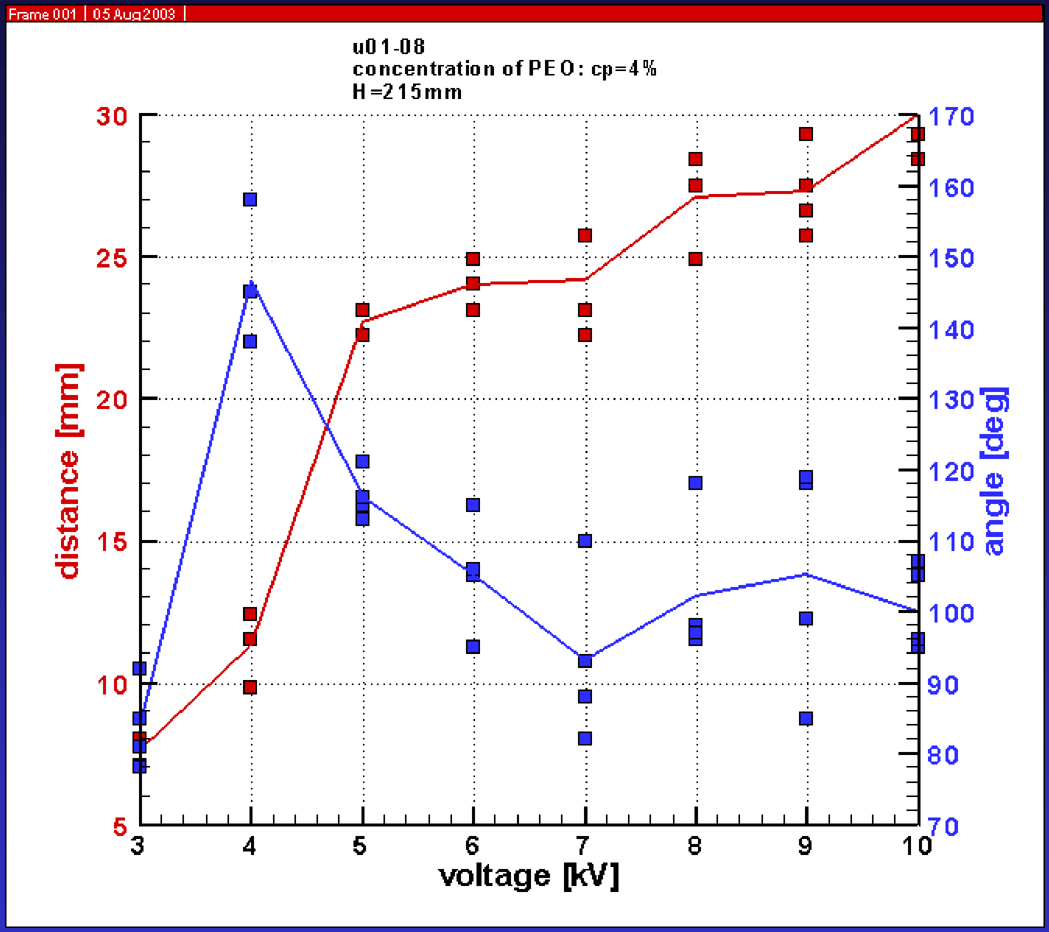


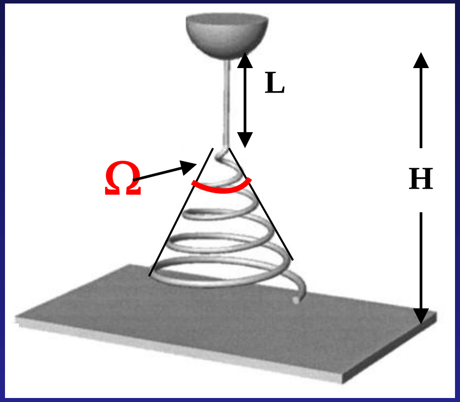


- <u>Polymer: PEO</u>
- Concentration: c=3%
- Solvent: 40% water-ethanol solution
- H=215mm
- V=8kV

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

Parametric study

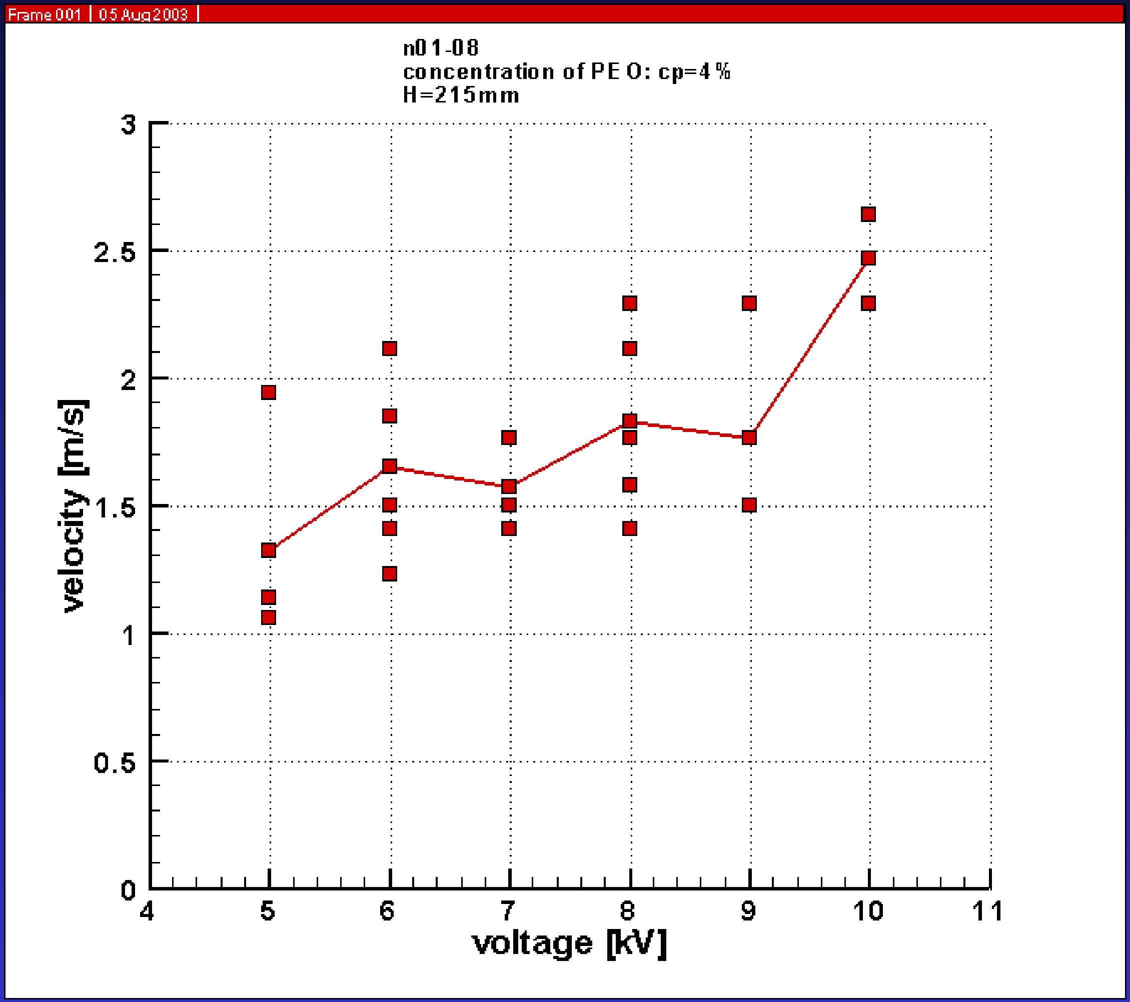


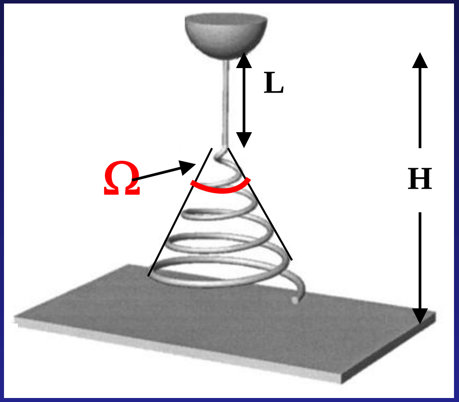


- **Polymer: PEO**
- **Concentration: c=4%**
- **Solvent: 40% water-ethanol solution**
- **H=215mm**

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

Parametric study



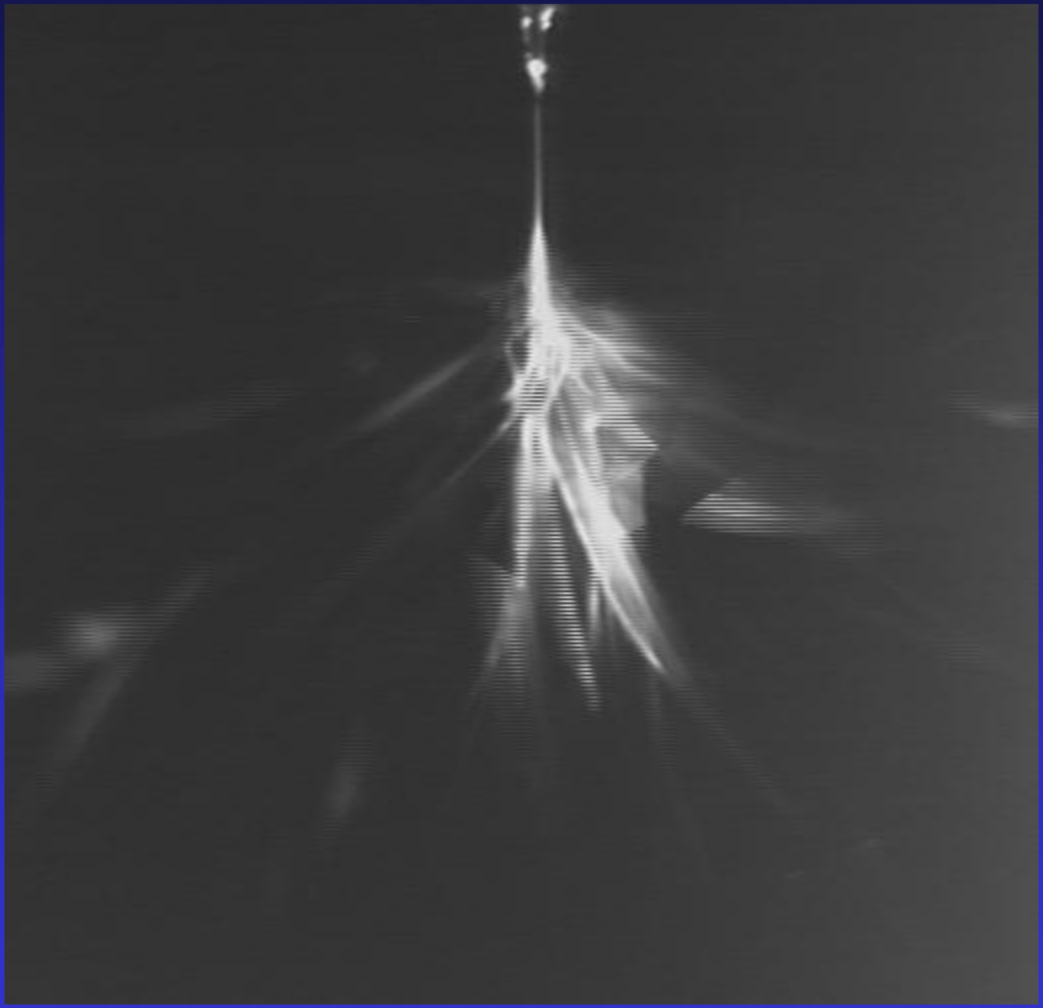


- Polymer: PEO
- Concentration: c=4%
- Solvent: 40% water-ethanol solution
- H=215mm

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

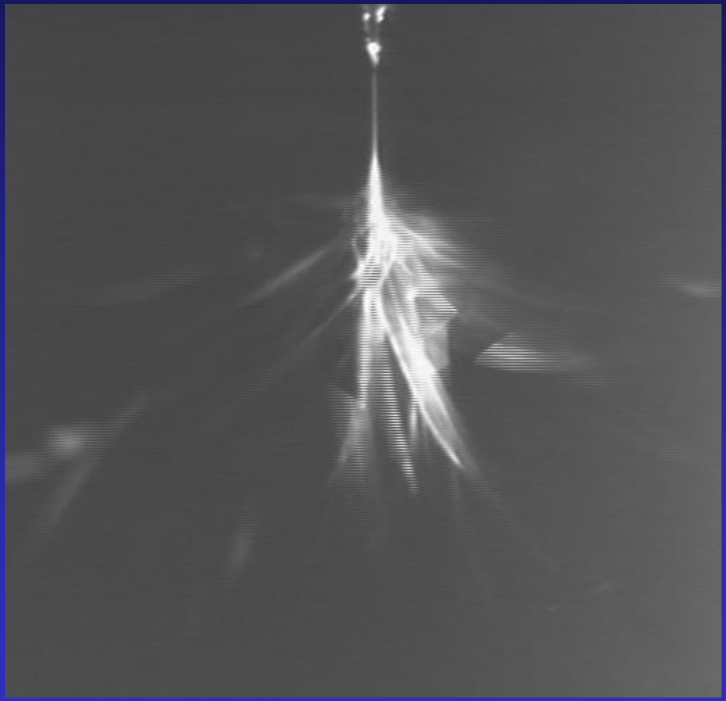
Electrospinning observed at 25fps

12 cm



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

Different structure of spinning fibres for DBC polymer

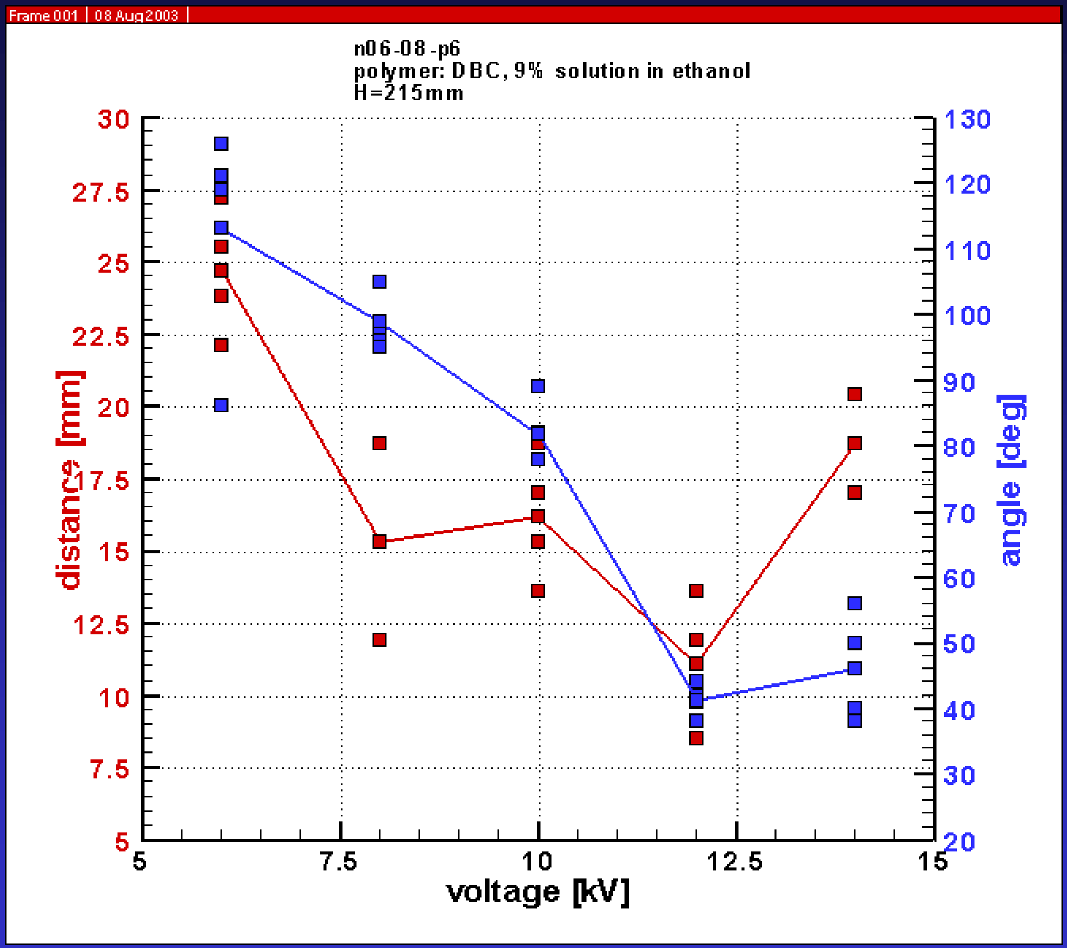


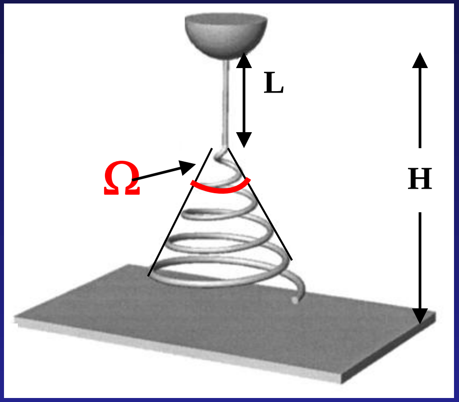
U=6kV

U=12kV

DBC: c=9% H=215mm

Parametric study





- <u>Polymer: DBC</u>
- 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

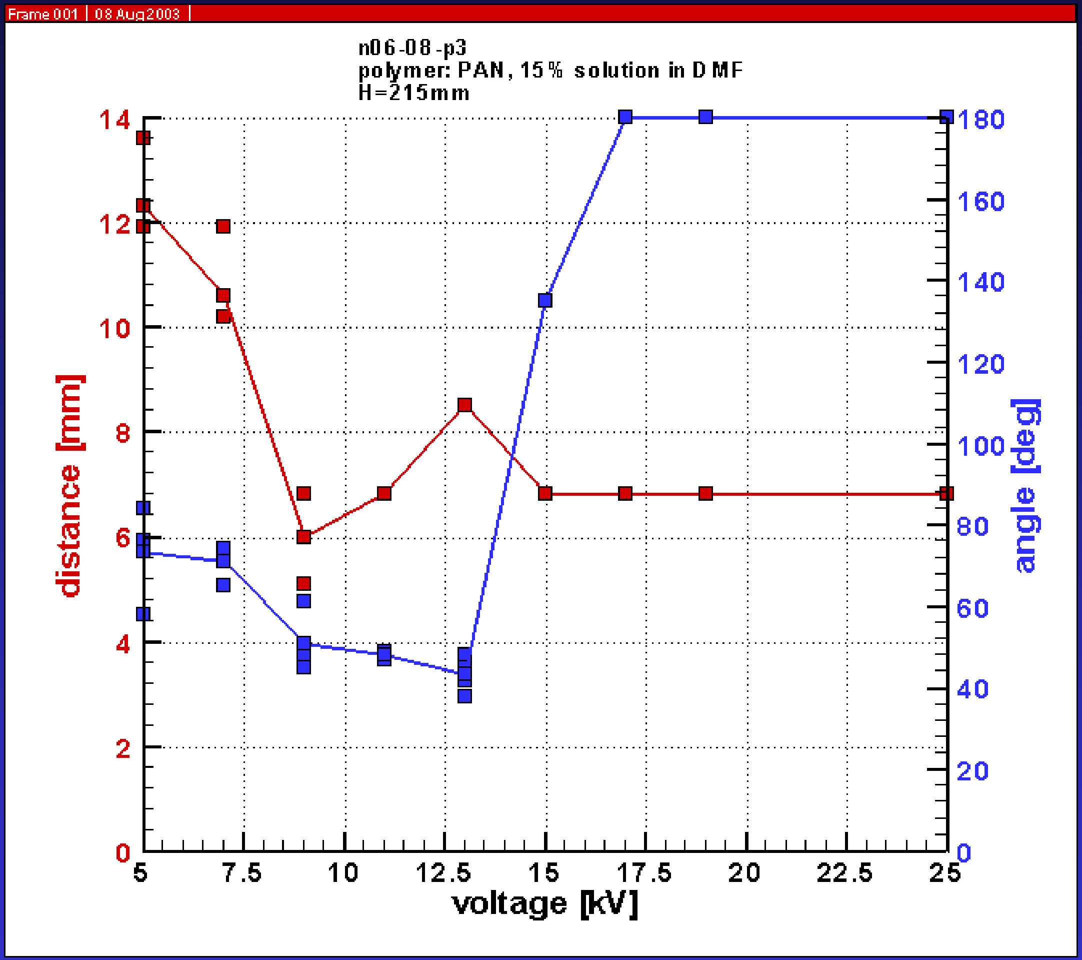
Different structure of spinning fibres for PAN polymer

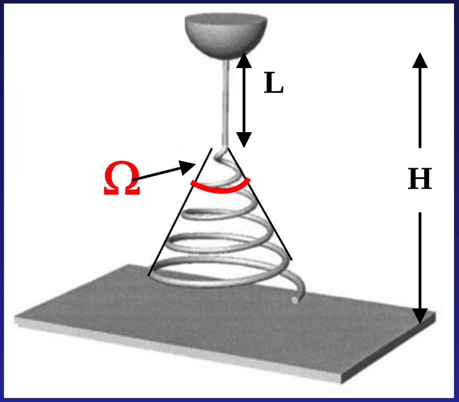
U=13kV

U=19kV

PAN: c=15% H=215mm

Parametric study

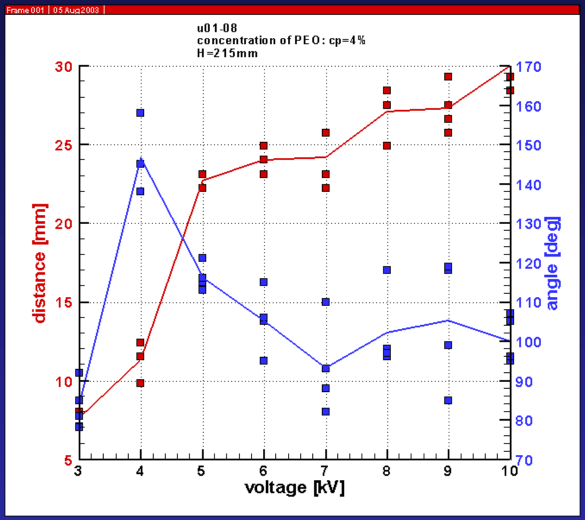


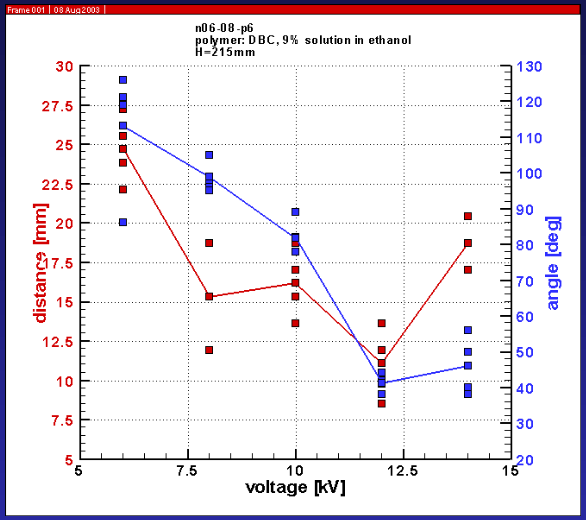


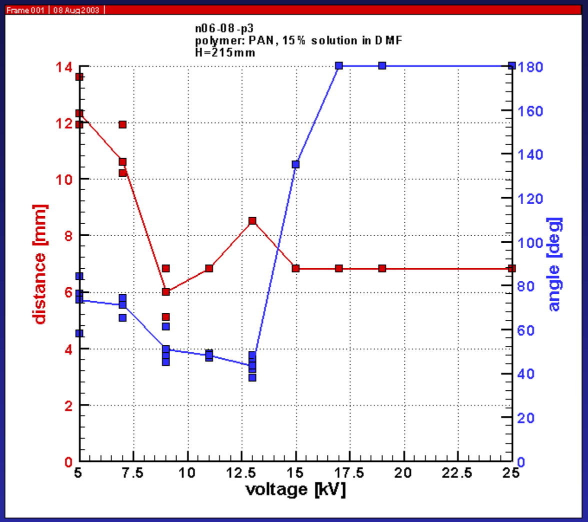
- <u>Polymer: PAN</u>
- Concentration: c=15%
- Solvent: DMF
- H=215mm

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

Comparison of PEO & DBC &PAN polymers







PEO

DBC

PAN

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

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
- ✓ Electrospinning of polymer solutions still lacks detailed mathematical model, necessary to perform process optimisation

Acknowledgements

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.

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