

MOLECULAR SIMULATION OF ELECTROSPINNING

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Abstract

Our recent attempts to apply standard molecular simulation techniques to the process of electrospinning are presented. We employ a molecular dynamics simulation to study phenomena involved in the electrospinning of polymer solutions, with particular attention to the formation of the Taylor cone and the development of a liquid jet. A molecular-based approach allows us to reveal the molecular structure and dynamics, which are inaccessible to continuum methods.

Keywords: Electrospinning; molecular simulation; fluids in electric field; polymer solutions

1. INTRODUCTION

Electrospinning [1] is an electrodeposition method for producing nanofibers. It involves a polymer solution or melt brought to a high-voltage electrode (tens of thousands volts). Under the strong electric field a Taylor cone forms on the surface of the liquid, and from the tip of the cone a thin jet is ejected. The jet flies towards the counter-electrode and solidifies on the way to land in the form of a fiber. Nanofibers collected on the electrode form a nonwoven fabric with unique properties.

In order to run the process efficiently and reproducibly, it is necessary to understand the underlying mechanisms, i.e., to find relations between a number of parameters affecting the electrospinning process and to link these relations to fundamental physical principles. Key parameters include: properties of the solution (composition, viscosity, surface tension), ambient conditions (pressure, temperature, humidity), and the nature and strength of the applied electric field.

In general, electrospinning can be studied by macroscopic theories treating fluid as a continuum or by microscopic methods taking fluid's molecular structure into account. Most researchers investigate spinning phenomena through purely macroscopic theories [2] without any reference to microscopic changes in the structure of the solution. However, no matter what macroscopic theories yield, all the observations have their origin in the properties of the molecules comprising the system and their specific arrangement in the investigated samples; moreover, the very definitions of some properties used in macroscopic theories may be questionable at the non-equilibrium and/or anisotropic conditions imposed by the field. Thus, despite all the effort invested, "[a] complete understanding of this mechanism remains to be elucidated and the factors that govern fiber formation are not well understood." [3]

Possibilities for a detailed experimental study of molecular structure in liquids are rather limited, thus researchers often employ computer simulations (pseudoexperiments) [4] on suitably chosen models to gain insight into the system at molecular scale and to determine characteristics which are difficult to obtain by other means. This is also the case of the ongoing effort of the present authors, who utilize molecular dynamics simulation to unravel microscopic background of electrospinning complementing the macroscopic phenomenology of the process.

Our group started to address the above task in a series of papers [5-7], first studying pure water and aqueous solutions of sodium chloride and then adding polymer chains. In our simulations it was observed that even pure water, without the presence of any ions, was capable of jetting caused by the tendency of dipoles to align in parallel with the field and to form head-to-tail chains. Added ions had only a minor effect on the initial stages of jet formation; nevertheless, their solvation shells disturbed the aligned structure of the dipoles and could

cause the breakup of the jet. It was found that with increasing ionic concentration the intensity of the electric field needed to maintain continuous jet also increased [6, 7]. First simulation studies on aqueous solutions of poly(ethylene glycol) (PEG) [7] found essentially the same mechanisms of jet formation as in the case of pure water or aqueous solutions of NaCl, and further showed conformational changes of the polymer chain in the jet.

In this contribution we continue our previous attempts [7] to study jetting of polymer solutions by molecular dynamics. We study two possible PEG chain lengths and calculate several structural properties. In the following, the used techniques and parameters are outlined; further, selected results are presented and discussed; and, finally, the paper is concluded by a short summary and a sketch of future perspectives.

2. METHODS

Standard molecular dynamics package, GROMACS (versions 4.5 and 4.6) [8], is employed to generate classical trajectories. A leap-frog integrator with a typical time step $\Delta t = 0.002$ ps is used. LINCS [9] algorithm is employed for constraining bond lengths in a polymer chain, SETTLE [10] is used to constrain water geometry. Whenever periodic boundary conditions (PBC) are applied, the particle-mesh Ewald method [11] is used to treat electrostatic forces.

Water is represented by a rigid three-site model, SPC [12], whereas ions and polymer are modeled using GROMOS parameter sets, which adopt a united-atom (UA) approach representing CH₃, CH₂, and CH groups by single interaction sites. Besides Lennard-Jones and Coulombic forces between sites at different molecules, also intramolecular interactions are incorporated in the case of polymer chain, i.e., bending, proper and improper dihedrals, and third-neighbor interactions. Bond lengths are kept fixed (except for the cases of difficult chain equilibration). Simulations with PEG chains presented here use GROMOS53A6_{OXY+D} force field [13] for all components (water is modeled by SPC, ions are Na⁺ and Cl⁻).

Simulations herein make use of a solid underlay made of Lennard-Jones sites with positions fixed in a rectangular grid. The underlay serves as a support on which a droplet of the electrospun solution resides. The parameters of the underlay sites have been tuned to maintain a reasonable contact angle of the droplet around 90°.

Typical simulation protocol involves a long (~ 10 ns) thermostated equilibration under PBC, a short (~ 1 ns) thermostated equilibration without PBC, and finally a production run (without thermostat and PBC) under a uniform electric field in a normal direction to the underlay plane (z-axis).

3. RESULTS AND DISCUSSION

In **Fig. 1** and **Fig. 2** we show the jet development from the PEG solution comprising 5.3kDa chains and 10.5kDa chains, respectively. Composition of the solution is specified in captions; we use hydroxyl-terminated PEG chains. One can see that the electric field deforms an initially spherical droplet to a conical shape. Further, we observe the change in the conformation of polymer molecules along with deformation of the droplet. Polymer chain uncoils when it is forced to enter the jet, which can be quantitatively monitored using the end-to-end distance (the distance of terminal hydrogens) or the radius of gyration, see **Fig. 3** and **Fig. 4**, respectively.

In aqueous solutions, an important characteristic of solvation processes is the number of hydrogen bonds (H-bonds). **Fig. 5** shows the development of the mean number of water-water hydrogen bonds in the two PEG solutions studied, whereas **Fig. 6** involves PEG-water hydrogen bonds. It seems, at least for the particular generated trajectories, that while water-water H-bond numbers diminish slightly, the PEG solvation shell remains basically intact. The decline in water-water H-bonds is probably caused mainly by the increasing surface area and the fragmentation of the liquid due to fast evaporation of water or the ejection of accelerated ions surrounded by a water cluster, both of which can be observed when visualizing the trajectories (see the

rightmost panel of **Fig. 2**). We used the following H-bond criterion: $\text{H-O}_d \cdots \text{O}_a$ angle less than 30° , $\text{O}_d \cdots \text{O}_a$ distance less than 0.35 nm (subscripts: d - donor, a - acceptor).

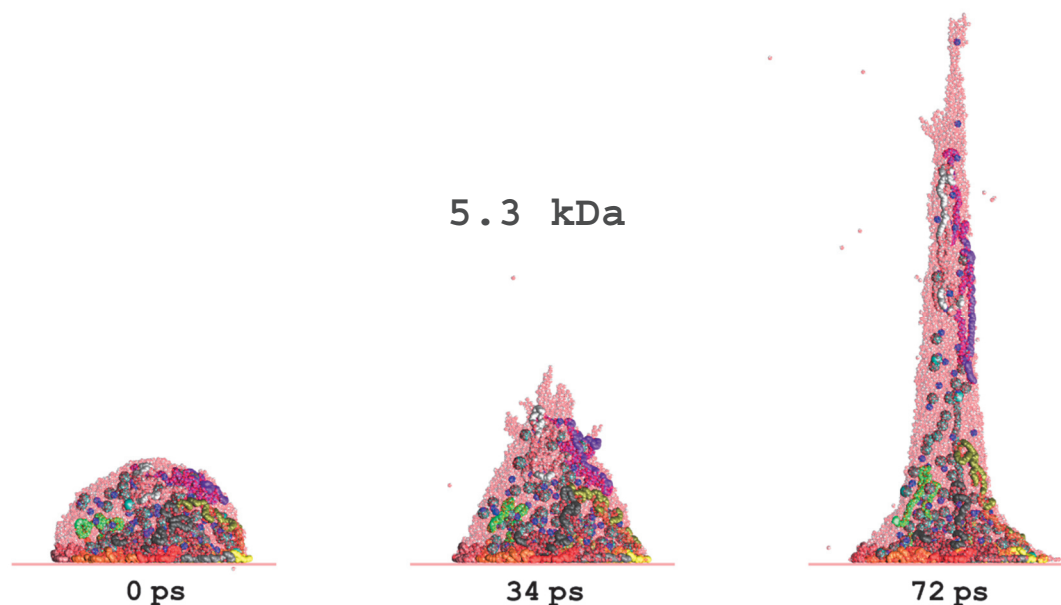


Fig. 1 Simulation snapshots for 5.3kDa PEG at different instants (0, 34 and 72 ps from turning the field on).

Transparent molecules - water; blue spheres - sodium cations; cyan spheres - chloride anions; pink bar - solid underlay; colored chains - PEG. Composition: 12 PEG chains (119 monomer units each), 23707 water molecules, 72 NaCl ion pairs. Graphics created using VMD [14]

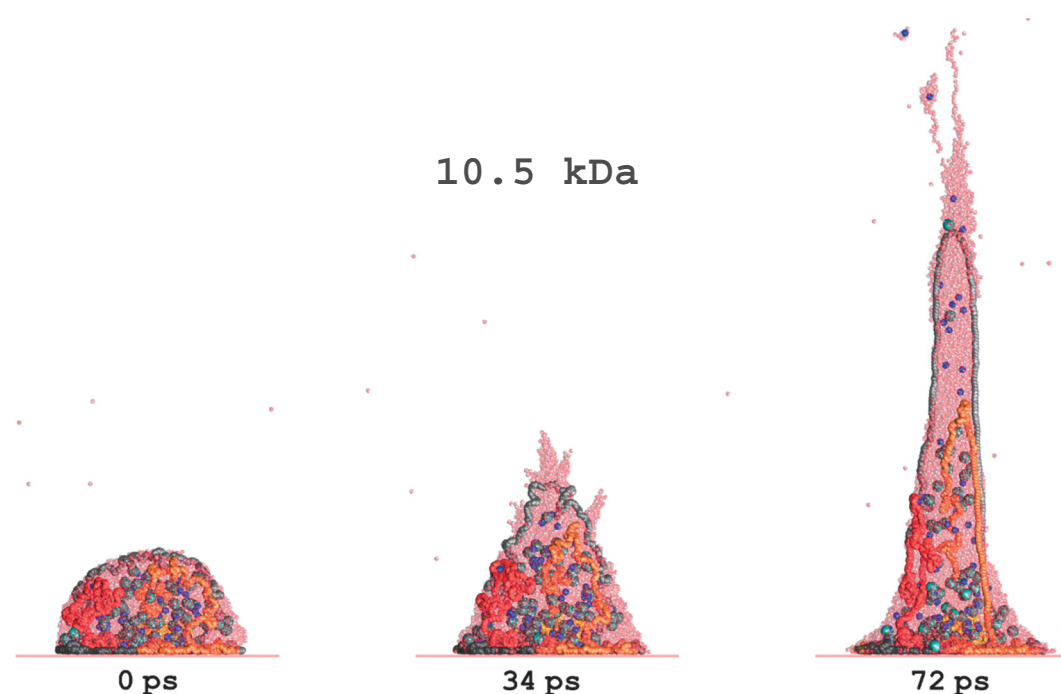


Fig. 2 Simulation snapshots for 10.5kDa PEG. For a legend see **Fig. 1**. Composition: 6 PEG chains (239 monomer units each), 23730 water molecules, 72 NaCl ion pairs. Graphics created using VMD [14]

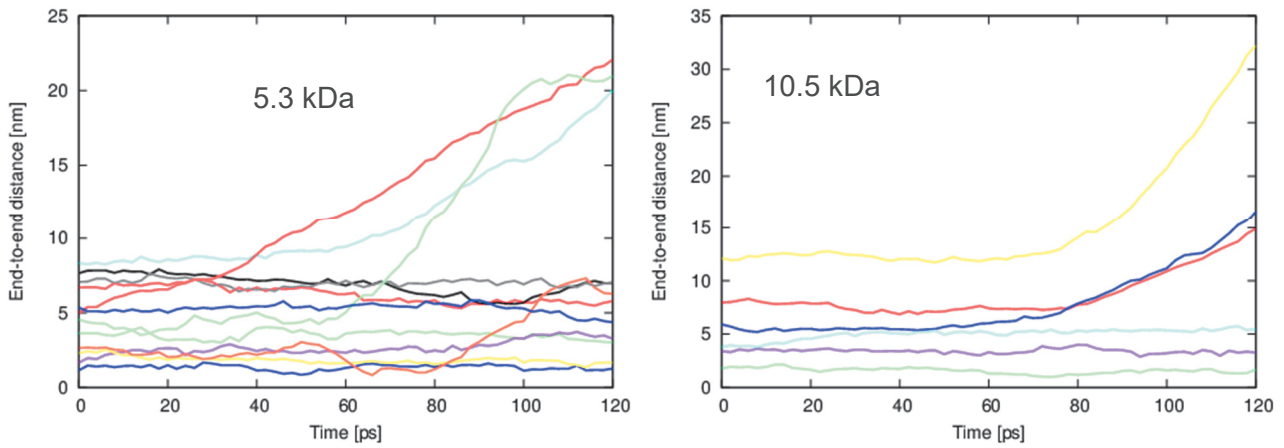


Fig. 3 End-to-end distance for individual PEG chains. Left - 5.3kDa PEG; right - 10.5kDa PEG.
All plots in this and subsequent figures made with gnuplot [15]

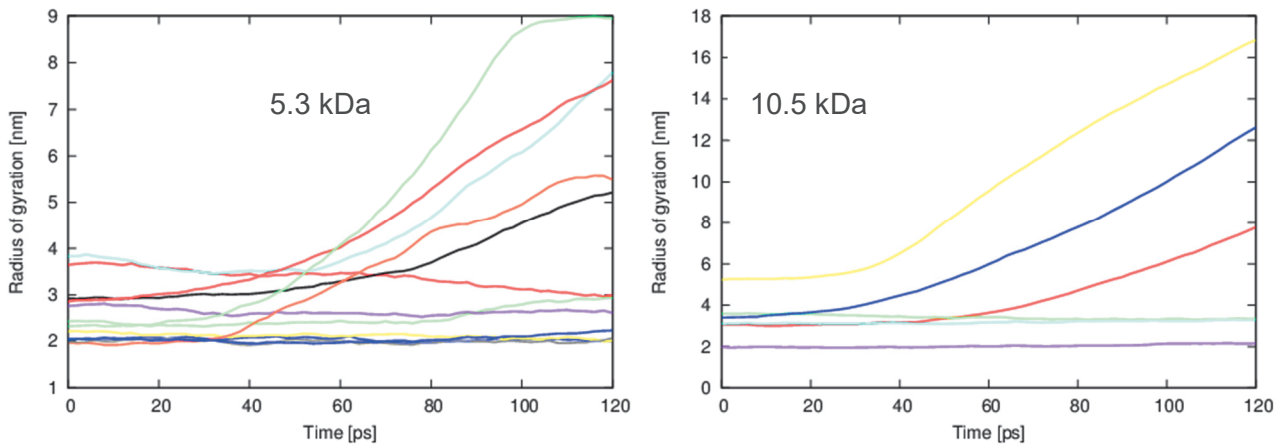


Fig. 4 Radius of gyration for individual PEG chains. Left - 5.3kDa PEG; right - 10.5kDa PEG

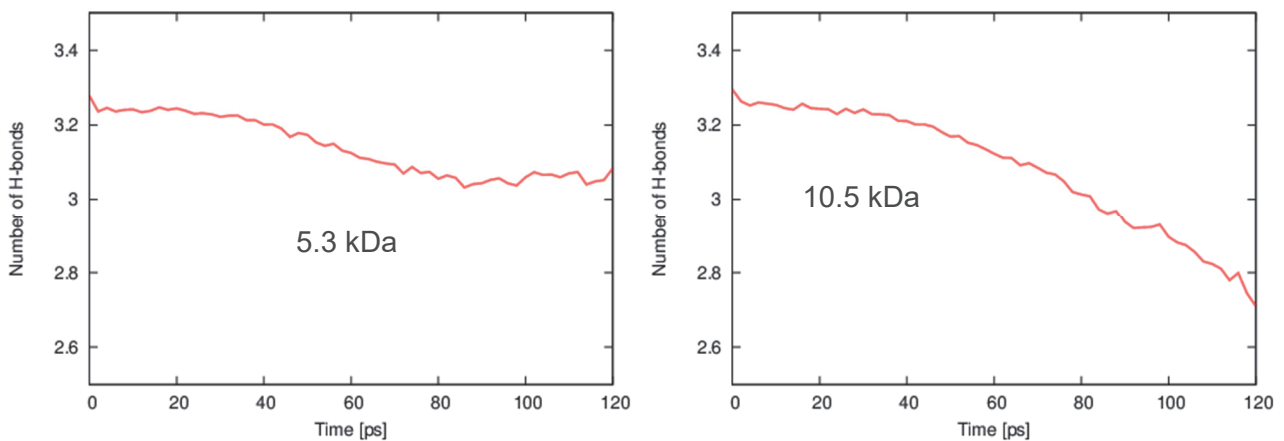


Fig. 5 Mean number of water-water H-bonds per water molecule. Left - 5.3kDa PEG; right - 10.5kDa PEG

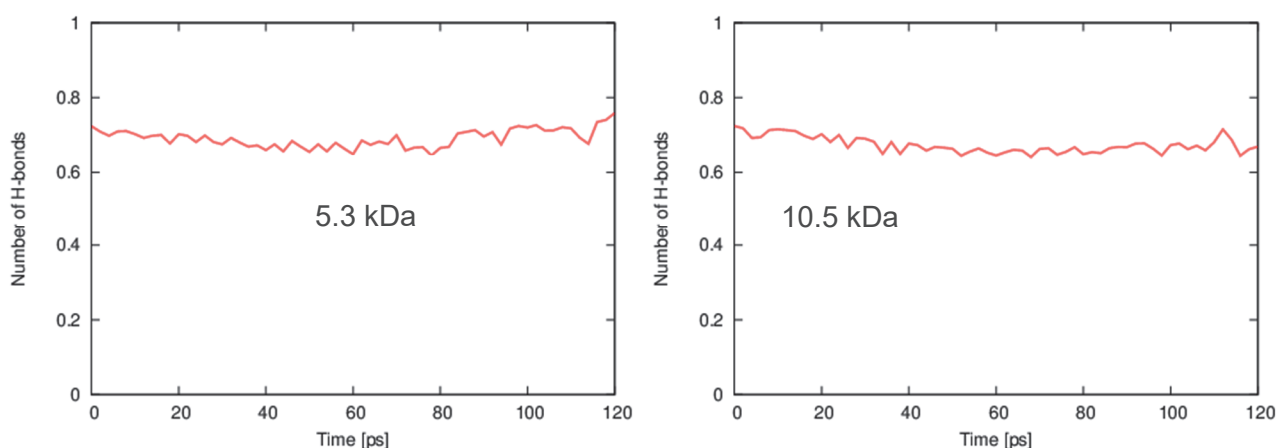


Fig. 6 Mean number of PEG-water H-bonds per PEG oxygen. Left - 5.3kDa PEG; right - 10.5kDa PEG

4. CONCLUSION

An account is given of an application of molecular simulations to electrospinning of polymer solutions. There is a number of studies dealing with electric-field-induced phenomena in liquids, but as regards electrospinning, molecular modeling studies are quite rare and have emerged only recently, partly due to the complex multi-scale nature of the process.

In the present contribution we use molecular dynamics simulation to investigate the jetting from a droplet of polymer solution. We have observed the formation of a nanoscale analogue of the Taylor cone and the subsequent ejection of the jet. We use PEG chains of two different lengths in aqueous solution containing sodium chloride. We have shown how the conformational structure of the polymer can be monitored. We have also observed that during the initial stages of the process the polymer remains well solvated.

Future work will be focused on the following tasks: (i) systematic study on solutions with varying concentrations of components and degrees of polymerization; (ii) averaging trajectories to obtain smooth and representative characteristics of process dynamics; (iii) using different polymers (PVA currently running) and/or solvents (or even solvent mixtures); (iv) simulation of later stages of jetting (solvent evaporation and fiber solidification); (v) upscaling the simulation to approach realistic scales.

ACKNOWLEDGEMENTS

This work has been supported by the Czech Science Foundation (Grant No. P208/12/0105). Access to computing and storage facilities owned by parties and projects contributing to the National Grid Infrastructure MetaCentrum, provided under the programme "Projects of Large Infrastructure for Research, Development, and Innovations" (LM2010005), is greatly appreciated.

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