

Insight into Electrospinning via Molecular Simulations

Jan Jirsák,^{†,‡} Filip Moučka,[†] and Ivo Nezbeda^{*,†,‡}

[†]Faculty of Science, J. E. Purkinje University in Ústí nad Labem, České mládeže 8, 400 96 Ústí nad Labem, Czech Republic

[‡]Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, Rozvojová 1, 165 02 Praha 6, Czech Republic

ABSTRACT: Monte Carlo and molecular dynamics simulations on pure water and aqueous electrolyte solutions exposed to a strong external electric field were used to model the electrospinning process from the free liquid surface, with the goal of assessing their potential to gain insight into the molecular-level mechanisms underlying the process. Three regimes involved in the electrospinning process—the free liquid surface, the apex of the Taylor cone, and the erupting jet—were selected for simulation using three different strategies. All simulations provide the same qualitative picture and exhibit scenarios consistent with experimental observations. It is found that ions play only a rather secondary role, in the sense that the process is driven by the water molecules. The strong electric field near the tip of the Taylor cone initially arranges the water molecules, creating an embryo of a jet into which the ions subsequently enter. At high concentrations, the ions can destabilize the jet, leading to electrospraying. At low electrolyte concentration, the embryo grows, leading to a stable jet and potentially to generation of a meso-/macroscopic fiber.

1. INTRODUCTION

Since their advent, molecular simulations¹ have become an indispensable tool for molecular physicists and chemists. First, they have provided a necessary pseudoexperimental tool, enabling them to study both simple and realistic molecular models to test/verify hypotheses concerning the molecular mechanisms governing the behavior of macroscopic fluid systems and to test various approximations and theories. Second, they have made it possible to develop and test the appropriateness and accuracy of the underlying molecular models. A primary output of molecular simulations have typically been thermophysical properties (equation of state, heat capacity, viscosity, etc.), entering macroscopic theories of the studied systems and their relation to various kinds of underlying intermolecular interactions.

With the advance of computer technology and the development of efficient simulation techniques, molecular simulation methodology has made it possible to study increasingly complex problems and this approach has become commonplace in many such fields, including mechanical engineering and material design, biology, and even medicine, often shedding light on problems that are inaccessible by other methods. Examples include the rheology of lubricants^{2,3} or protein self-assembly, potentially related to Alzheimer's and Parkinson's diseases.⁴ In these applications, the simulations need not necessarily yield numerical values of physical quantities, but they may help to *qualitatively* understand and explain the underlying molecular mechanism of the observed phenomena. This latter aspect is the motivation of this paper, with respect to the electrospinning (ES) process, which is not yet fully understood on the microscopic scale. Such molecular-level understanding might prove particularly useful in the particular case of needleless electrospinning (NLES) which is much more efficient than the common capillary spinning but technologically more difficult to optimize.

ES is an electrohydrodynamic phenomenon in which a thin (polymeric) filament is ejected from the surface of a polymer solution destabilized by the influence of a strong external electric field of intensity exceeding a certain critical threshold value. From the scientific point of view, electrospinning represents the problem of the behavior of liquid interfaces exposed to electric fields. From the engineering point of view, it is one of the electrodeposition methods by which nanofibers are produced from polymer solutions or melts. The setup of a common capillary/needle electrospinning (CES) process consists of a syringe needle connected to a high voltage power supply and a counter-electrode collector.⁵ The NLES process differs from the CES in that it does not use any capillary/needle, and the jet originates from the free liquid surface; NanoSpider technology⁶ is an example.

The ES process has four distinct regimes,⁷ which occur in different physical regions, see Figure 1: the base (B), which is a tapered structure called the Taylor cone, formed on the liquid surface (either free or on the tip of the needle/capillary); the jet (J) region, occurring beyond the base, where the polymer liquid driven by the high electrical potential forms a jet; the whipping region (W), where a single jet loses stability; and the collection (C) region, where the jets stop and fibers are collected. An early patent on electrospinning of polymer fibers was issued to Formhals as early as in 1934⁸ and further development and modifications of this technology have continued to the present time.⁹ The NLES process is a recently developed technology with the first patent issued in 2005.¹⁰

The above-described scenario corresponds to the situation when fibers are actually produced. However, this need not always occur. Two other possible behaviors also may occur,

Received: December 17, 2013

Revised: April 2, 2014

Accepted: April 22, 2014

Published: April 23, 2014

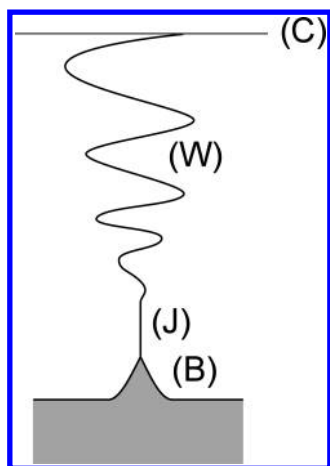


Figure 1. Schematic representation of the electrospinning process regimes: base (B), linear stable jet (J), whipping instability (W), collection of fibers (C).

which involve only spray of droplets or when a stream of solution emanates from the surface. The former spraying behavior is also important for its use in mass spectrometers, microreactors, and propulsion systems for satellites. Several factors affect which scenario takes place, the most important of which are the properties of the solution, the operating conditions (applied electric field, collecting distance), and the environmental conditions (temperature, humidity). The CES seems simpler to tune and optimize for it has two important parameters that can be adjusted to manipulate the outcome: the capillary diameter and the flow rate. NLES lacks such simple control parameters, and it is therefore more difficult to locate an operation window where nanofiber production takes place and the process runs efficiently. However, once such a window is found, NLES achieves much higher production rates compared to the more conventional CES process, which makes NLES very appealing.

For further development of ES technologies and improving their efficiency, the process must be better understood, and the relations between the various factors affecting them must be elucidated. Within the framework of electrohydrodynamics, the basic principles for dealing with electrified fluids were laid down by Taylor.^{11,12} With further development of the ES technology, phenomenological models relating various macroscopic properties have been developed. Hohman et al.¹³ proposed a method for quantitatively predicting the parameter ranges for the CES to occur, which was further simplified by Feng et al.¹⁴ Angammana and Jayaram¹⁵ recently formulated a model based on an existing viscoelastic electrospinning model and solved it using a finite element method. Regarding NLES (for a review of various setups see ref 16), only one theoretical model describing the initial stage of the process has thus far been developed.¹⁷ It is a one-dimensional model in which the capillary waves present on the surface increase their amplitude up to a certain critical stage where they lose stability and form the Taylor cone with a jet erupting from its apex (cone–jet mode).

All the phenomenological theories describe the ES process in terms of certain macroscopic parameters but are not able, in principle, to explain the underlying molecular basis. To understand the mechanism by which the molecules are drawn up from the bulk liquid it is necessary to study the process at the molecular level. Modern experimental techniques are able

to record processes at nano/meso scales and tell us what is occurring but existing explanations of the underlying molecular mechanism have often been based on intuition and speculation which may be misleading. For example, it is usually assumed⁷ that free charges move in response to the electric field and carry along the (neutral) polymer molecules. However, this intuitive picture is questionable because it is known that it is possible to jet even almost pure dielectric liquid, e.g., deionized water or glycerol.^{18,19}

On the other hand, molecular simulation makes it possible to bypass the unnecessary micro-/macroscale crossover step, which involves the use of macroscopic parameters, by studying directly how microscopic properties pertaining to the chemical nature of solution components directly influence the process.

At the molecular level, a relatively large number of simulation studies have previously dealt with problems related to ES. The behavior of drops (droplets) in a uniform electric field has been the focus of such studies, and typical problems addressed have been their deformation potentially ending as fiber, their fission or disintegration,^{20–22} or the location of ions within the drop.²³ Collisions of droplets with air molecules²⁴ and the process of vaporization of the bulk fluid have also been investigated.²⁵ Another group of studies has focused on the chemical properties of the final product and, primarily, on their relation to the composition of the spinning solution, see, e.g., refs 26 and 27. However, to the best of our knowledge we are unaware of any study simulating the ES process itself at the atomistic level. The only related studies have been simulation of an ionic liquid in an electric field²⁸ and a mesoscale dissipative particle dynamics simulation of the spinning of the polymer melt.²⁹

ES is a complex process, rapid and far from equilibrium, and spanning many length and time scales. Due to these different scales it is not possible to simultaneously model all features of the entire process by simulations. Proposing three different methodologies, we thus conduct a feasibility study to assess the potential of such technique to capture its essential features by focusing on three small selected regions which we believe are readily accessible to investigation by simulations. Furthermore, since there are indications that the polymer molecules play, at least in some cases, only a passive role, we consider here only the simplest systems underlying the ES process: pure water and dilute solutions of NaCl in an electric field of varying strengths under ambient conditions.

The paper is organized as follows. In the next section we briefly describe the simulation methodologies employed and their potential use for different stages of the ES process, along with the necessary technical details. In section 3 we then describe and analyze in detail the simulation results. Conclusions and an outline of suggested further research comprise section 4.

2. SIMULATION METHODOLOGY

2.1. General Considerations. Monte Carlo (MC) and molecular dynamics (MD) techniques are the two primary molecular simulation methodologies. The former method is best suited to study equilibrium system states, whereas the latter is well-suited to study time-dependent phenomena.

In Figure 2 we show the selected regions of the NLES process which are subjected to investigation in this study. Region (I) is the free surface, and simulations (both MC and MD) carried out at different “subcritical” strengths of the electrostatic field may reveal changes on the surface taking place while the geometrical arrangement of the layer remains

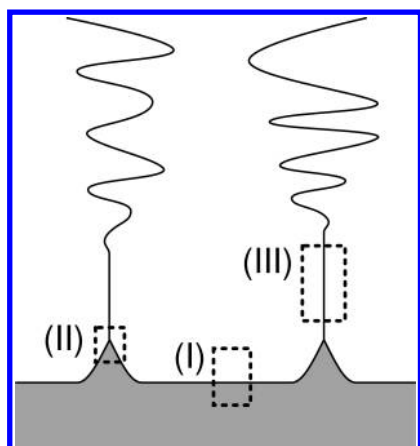


Figure 2. Schematic representation of the regions selected for simulation: Free surface (I), apex of the Taylor cone (II), and stable jet (III).

stable against perturbation by the field. MD simulation of this region makes it possible to study further dynamical processes on the liquid surface including the transformation of the liquid layer into a new stable structure when the initial arrangement loses stability. Region (II) refers to the apex of the Taylor cone and the emerging part of the jet. Formation of the jet is studied by MD simulations. Finally, region (III) may be regarded as a stable jet, whose properties may be studied by both MC (with caution) and MD simulations. However, it is also necessary to distinguish between aqueous electrolyte solutions and neat water. In the latter case an equilibrium state can be reached and studied by MC simulation, whereas in the former case there will always be a flow of particles (ionic conduction) and the MD methodology must be used.

The above-defined zones also require different methodologies to model by molecular simulation, differing in its use of boundary conditions. We consider the following scheme: Region (I), the planar interface, is modeled in a slab geometry with either complete 3D periodic boundary conditions (PBC) or 2D PBC with a soft impenetrable wall parallel to the liquid surface; region (II), the apex of the Taylor cone, is modeled with either 2D PBC with a wall or without periodic dimensions using a solid supporting plate; and finally, region (III), a segment of a jet, is modeled with full 3D PBC. Further details are discussed in the following section 3.

The driving force of the ES process is the electric field, created by a fixed voltage supply connected to electrodes. We model this using simulations involving a uniform electrostatic field parallel to one of the edges of the simulation box. This is an approximation based on the assumption that the instantaneous electric field in the studied region, which is a sum of the external field generated by electrodes and the field created by the particles outside the simulation box, is constant and uniform within the length and time scale of the simulated process. The strength of the external electric field employed in the simulation box cannot be thus directly related to the voltage applied between the electrodes in the experiments. The field used in our simulations went up to 2.5 V/nm.

Although the above-given strength of the field may seem unusually high, it is fully consistent with other studies, starting with a study of Svishchev and Kusalik,³⁰ who induced water to freeze at the field of 1 V/nm. A total alignment of the water molecules was observed, in simulations, in the field strength of 40 V/nm.³¹ Practically all other studies of water and other

liquids used the field strength of this order. As for real ES experiments, the usual voltage applied is between 10 and 30 kV. A very strong electric field is thus expected around the apex of the Taylor cone. The exact strength depends on the electrode separation and the geometry of the apex. Using typical experimental values, then for a sphere-shaped apex we get for a rough estimate of the range of the strength of the field values between 1 and 100 V/nm (for details see, e.g., ref 32). We also note that when water is subjected to strong electric fields in the order of 100 MV/m, the dielectric breakdown phenomenon is observed, see, e.g., the work of Joshi et al.³³ The electric fields applied in our simulations are up to 25 times stronger; therefore, a question may arise why this phenomenon is not considered in the simulations. According to the study of Sklarczyk et al.,³⁴ the breakdown occurs when electrons are injected from a metal electrode to the conduction band of the water molecules which occurs at sufficiently high electric fields on the surface of the electrode. In our simulations, we apply the strong electric field only to the apex of the Taylor cone where no electrode is present and we consider the field on the surface of the electrode (not simulated) by several orders of magnitude weaker; therefore, electrons are not injected to water and the breakdown does not occur. Furthermore, as regards real experiments, the breakdown in water is manifested by luminous lines called streamers passing sporadically between electrodes, which however are not observed in the ES experiments.

2.2. Simulation Details. All simulations were performed using nonpolarizable rigid interaction-site models. Water was modeled by three-site potentials (TIP3P³⁵ or SPC/E³⁶), i.e., a rigid molecule with three centers representing the oxygen and two hydrogen atoms. The oxygen atoms interact via the Lennard-Jones potential and bear a point charge whereas the hydrogen sites bear only point charges. Ions are modeled in a similar way, as Lennard-Jones sites bearing a charge. The interaction energy between particles (molecules or ions) i and j assumes thus the form

$$u_{ij}(q_i, q_j) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{R_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{R_{ij}} \right)^6 \right] + \frac{1}{4\pi\epsilon_0} \sum_{\alpha, \beta} \frac{Q_\alpha Q_\beta}{r_{\alpha\beta}} \quad (1)$$

where q_k represents the generalized coordinates of particle k , R_{ij} denotes the distance between the Lennard-Jones sites, Q_γ is the electrostatic charge of site γ , $r_{\alpha\beta}$ denotes the distance between Coulombic site α of particle i and site β of particle j , and the summation runs over all possible Coulombic interactions between particles i and j . The resulting three-site models are computationally feasible for large-scale simulations while reproducing simultaneously many structural and thermodynamic properties of liquid water reasonably well.³⁷ We use force fields compatible with the employed water force field developed by Joung and Cheatham.³⁸ For further details of the models and values of the potential parameters, we refer the reader to the original papers. For the cross nonelectrostatic interaction between the water molecule and ion or between counterions, the standard Lorentz–Berthelot combining rules were applied, i.e.,

$$\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj}) \quad \text{and} \quad \epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}} \quad (2)$$

Monte Carlo simulations were performed in a canonical (NVT) ensemble using in-house software. The SPC/E water

force field and associated Joung and Cheatham ionic force fields were employed. The Ewald summation method was used to treat the electrostatic forces. The temperature was set to 298.15 K. Typically, the simulated systems reached equilibrium after 1.5×10^{10} trial moves comprising either translations or rotations of single molecules, and 2×10^{11} such trial moves were generated during each MC simulation in total. The parameters of the trial moves were adjusted to yield acceptance ratios between 0.2 and 0.4.

Molecular dynamics simulations were performed using the GROMACS package (version 4.5.5).^{39,40} A leapfrog integrator⁴¹ with time step 1 or 2 fs was employed. The TIP3P water force field and associated Joung–Cheatham ionic force fields were used. To account for the long-ranged electrostatic interactions beyond the cutoff distance the particle-mesh Ewald method^{42,43} was used. Typical simulation protocols involved long equilibration period (≥ 1 ns) with a thermostat (usually set to 298.15 K), shorter equilibration (50 ps) in the microcanonical ensemble, and a production run (>100 ps) in a uniform electric field with intensity of the order of 1 V/nm.

Simulations with a reduced number of periodic dimensions involved the use of solid underlays: an endless smooth impenetrable wall or a finite-size supporting platelet. The smooth wall is realized by a 9–3 type potential, and the plate by a rigid square grid of LJ centers. The parameter values in both cases are arbitrary and are not specifically adjusted to represent any real solid material, as the role of solid underlay is only to substitute the nonsimulated part of the liquid.

3. RESULTS AND DISCUSSION

Each set of simulations using a specific type of boundary conditions represents an independent study, and it is therefore convenient to arrange the results according to the number of periodic dimensions, i.e., 3, 2, and 0, corresponding to subsections 3.1, 3.2, and 3.3 in the following.

3.1. Full Periodic Boundary Conditions. **3.1.1. Thin Liquid Film.** The simulation of region (I) does not pose any severe problems and is qualitatively similar to the simulation of the vapor–liquid equilibrium with an explicit interface. Below a certain magnitude of the electric field intensity, the liquid surface remains stable and no dynamical processes as, e.g., pulling fibers (molecules) out of the solution occur. We carried out both MC and MD simulations. The schematic Figure 3 gives a caricature of a potential realization of the simulation of this region.

The basic simulation cell is surrounded by its identical replicas due to PBC in all directions. Molecules form an endless horizontal liquid layer indicated by the shadowed rectangle. The thickness of the layer in the simulation must be sufficiently large to allow for neglecting the mutual interaction of the surfaces. An implementation of this type of simulation with the electric field originally perpendicular to the liquid surface and parallel to one of the simulation cell edges is shown in Figure 4 for an aqueous solution of NaCl of molality $m = 0.524$ mol/kg and external field $E = 0.1$ V/nm.

At these conditions no liquid surface instability was observed and various physical quantities may be evaluated for use in phenomenological theories and for intuitive explanations and understanding. These include, e.g., the surface tension or the dependence of the solution composition on the distance from the surface. A series of such simulations at different field strengths provides the dependence of the quantities on the strength of the applied field and this dependence may

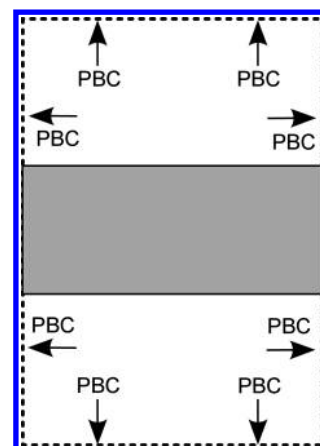


Figure 3. Schematic representation of the simulation of the thin liquid layer.

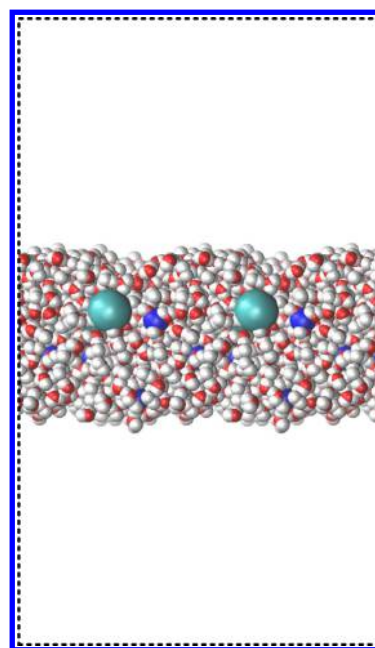


Figure 4. Snapshot of a typical configuration obtained by the Monte Carlo simulation of a thin liquid layer. NaCl aqueous solution at molality $m = 0.524$ mol/kg and the external field $E = 0.1$ V/nm. Colored spheres represent atoms and ions as follows: red–oxygen, white–hydrogen, blue–sodium cation, and cyan–chloride anion.

contribute to qualitative understanding. As an example of a possible output, we show in Figure 5 the dependence of density of different species along the cross-section of the slab.

When a series of such simulations with gradually increasing field strength is carried out, we observe that at sufficiently strong fields the liquid surface loses its stability. Very pronounced structures resembling swaying “tentacles” appear at stronger electric fields. Eventually, the liquid becomes rearranged into a cylindrical structure with its axis parallel to the field. Due to the PBC, the cylinder represents an endless fiber. An implementation of such a simulation is demonstrated in Figure 6 by a series of snapshots of the aqueous solution of NaCl at the applied electric field $E = 1.5$ V/nm.

3.1.2. Segment of a Jet. One may relate the simulated endless cylinder to a jet created during electrospinning, i.e., stage (J), but this relation is not as simple as in the case of the simulation of the surface. In reality, the jet is subject to changes

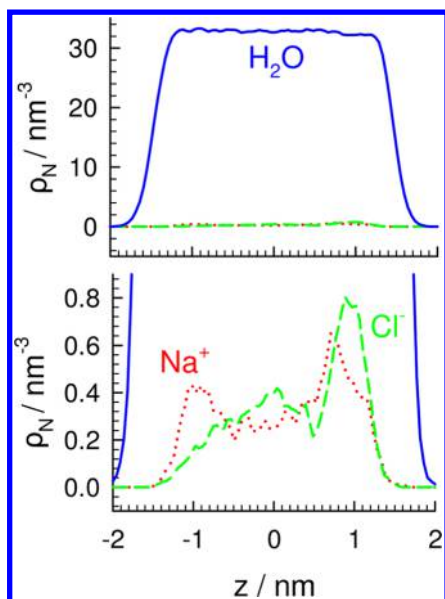


Figure 5. Number density profiles of different components along the cross-section of the thin liquid layer obtained by the Monte Carlo simulation of NaCl solution at molality $m = 0.524$ mol/kg and the external field $E = 0.1$ V/nm.

caused by evaporation, collisions with molecules of air, etc. This type of simulation must be therefore carried out with care and under the assumption that the mentioned effects and processes do not qualitatively affect the properties of the fiber jet. An example of the properties one can investigate, at least qualitatively, is the distribution and orientation of the molecules within the fiber jet as a function of the specified conditions.

3.2. 2D Periodic Boundary Conditions. The 2D PBC can be used for studying both regions (I) and (II). In the former case, they complement the full 3D PBC arrangement with no considerable difference between the two methods. On the other hand, the 2D PBC (combined with a wall) methodology

appears to be truly beneficial in the investigation of the apex of the Taylor cone, i. e., region (II) of Figure 2, which can be conducted according to the scheme depicted in Figure 7.

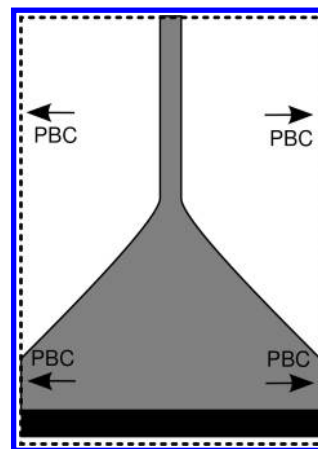


Figure 7. Schematic representation of the simulation of the apex of the Taylor cone and the initial part of the jet using periodic boundary conditions. The black rectangle represents an infinite solid wall.

Since with this choice of simulation cell the cone crosses several simulation cell walls it is convenient to apply the PBC in directions perpendicular to the external electric field. The remaining part of the cone may be replaced by a solid wall repeating itself due to the periodic conditions, represented by the black rectangle in Figure 7. The initial configuration can be generated by the simulation of a liquid layer, similarly to the simulation of the stable liquid surface discussed in subsection 3.1. The applied electric field brings about a deformation of the surface, which results in the formation of a number of protruding structures suggestive of the embryos of the macroscopic jets observed in electrospinning, cf. Figure 6a. This evolution is similar to the situation discussed in the preceding subsection, but in this case only a single liquid

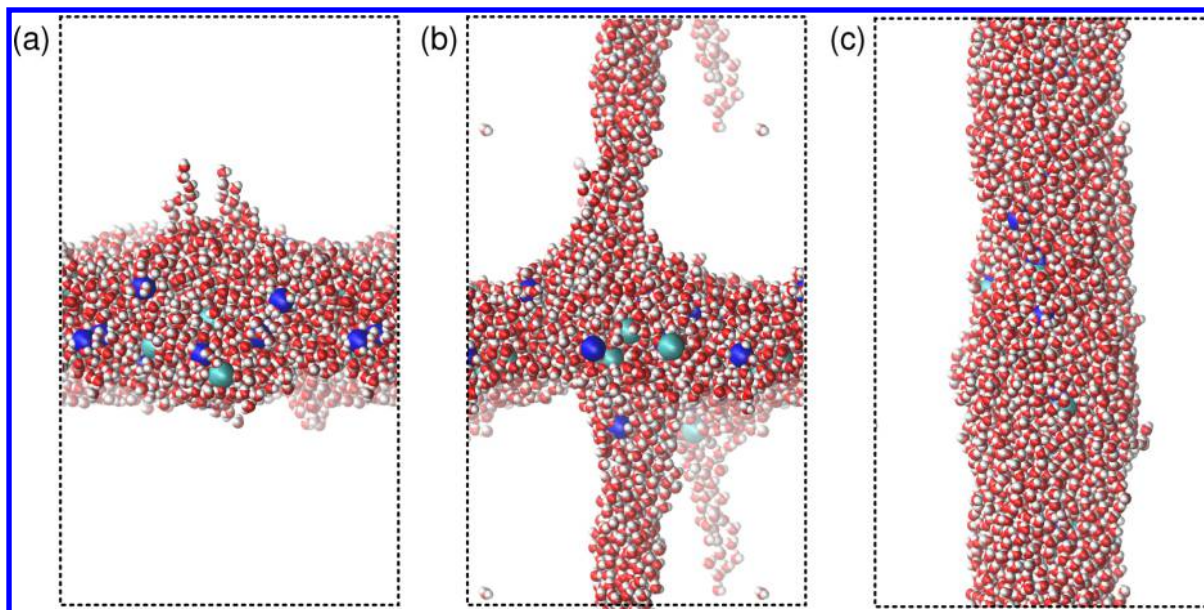


Figure 6. Time sequence of snapshots for the NaCl solution at the applied electric field $E = 1.5$ V/nm showing transformation of a liquid layer to a cylindrical structure. (a) System soon after the field is applied, at $t = 15$ ps; (b) column of water formed from the layer, $t = 48$ ps; (c) final cylindrical structure, $t = 185$ ps. For the meaning of the colored spheres, see the caption for Figure 4

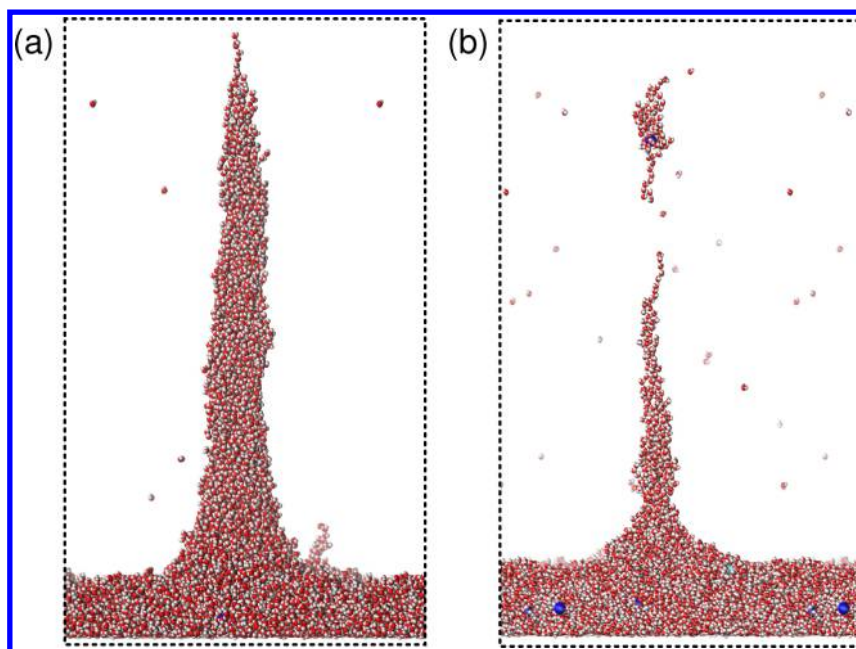


Figure 8. Snapshots of configurations obtained for NaCl aqueous solutions of different concentration at the applied field $E = 1.5$ V/nm. (a) Low concentrated solution ($t = 101$ ps) and (b) solution of a higher concentration when the instability of the jet is observed ($t = 356$ ps). For the meaning of the colored spheres, see the caption for Figure 4

surface is exposed and thus able to form protrusions. This is certainly a more appropriate model for the real situation during electrospinning. Some of the embryos keep growing whereas other vanish. In most cases we can observe the formation of one dominant and growing conical structure developing into a jet.

A typical implementation of such a simulation for the aqueous solution of NaCl is demonstrated by snapshots in Figure 8 where we compare the development for two solutions of different concentrations. In Figure 8a, a dilute solution was simulated, which resulted in the formation of the stable jet, whereas in the case of a concentrated solution we observed disintegration of the jet into droplets; see Figure 8b.

3.3. Nonperiodic Boundary Conditions. Region (II) may be also simulated according to the scheme depicted in Figure 9. Such a simulation is similar to that depicted in Figure 7. The apex of the cone from which the jet originates is included in the

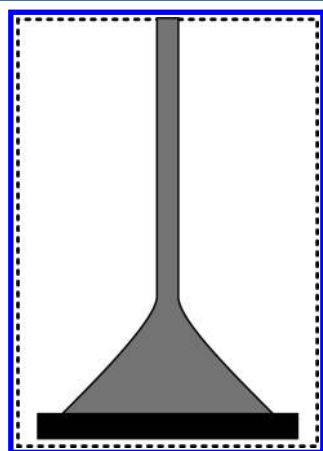


Figure 9. Schematic representation of the simulation of the apex of the Taylor cone and the initial part of the jet without the use of periodic boundary conditions. The black rectangle represents a solid underlay.

simulation and the remaining part of the Taylor cone is also approximated by a solid wall. However, no periodicity is considered in this scheme. It is convenient to start the simulation in this geometry by placing a condensed sample of the water molecules on an underlay, with subsequent equilibration without the external electric field. It is then possible to claim that the droplet obtained in this way represents the apex of the Taylor cone before the instant when the jet occurs. After switching on the electric field the droplet becomes deformed—elongates in the direction of the field—and one may observe instability resulting either in a pointed jet or a spray of droplets. An advantage of this type of simulation is the absence of the periodic images, which in the previous cases caused an increased computational cost and possibly also unphysical effects on the development of the jet. An example of the implementation of this simulation is demonstrated in Figure 10 showing pure water in a series of snapshots at different times.

4. CONCLUSIONS

We have used molecular simulations to model selected parts of the needleless process of spinning from a free liquid surface under the effect of a strong external electric field to examine to what extent they can contribute to the molecular level understanding of the process. For simplicity, we have considered in this feasibility study only pure water and a dilute solution of sodium chloride. Three different methodologies have been used to investigate the electrospinning process, using both Monte Carlo and molecular dynamics methods. All the simulations provided mutually consistent results in qualitative agreement with experiment demonstrating the potential of simulations to provide understanding of the selected parts of the actual electrospinning process from the molecular point of view. The present study thus opens the way for further systematic research on the electrospinning process considering more realistic models incorporating also polymers and involving detailed structural analysis.

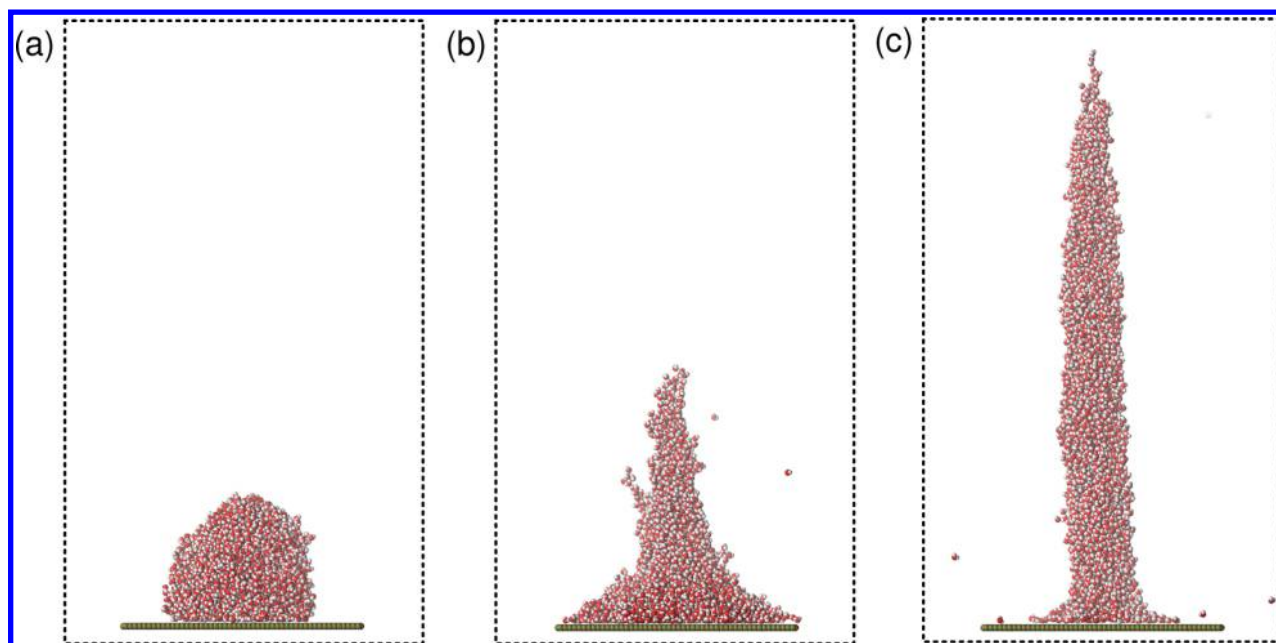


Figure 10. Sequence of snapshots showing the transformation of a droplet on the wall—modeling the apex of the Taylor cone—to a jet. Water is subjected to the external electric field $E = 1.5$ V/nm. (a) System before the field was applied, (b) the instant soon after the field was applied, $t = 17$ ps, and (c) a later instant when the droplet is transformed to the jet, $t = 144$ ps. For the meaning of the colored spheres, see the caption for Figure 4

The simulations showed how a sufficiently strong external field can lead to destabilization of the liquid surface, resulting in the protrusion of pointed structures resembling macroscopic jets observed in electrospinning. There are two potential subsequent scenarios: The structure (i) keeps growing, which may be identified with the embryos of fibers or (ii) disintegrates into droplets, which may be identified with electrospraying. Whereas in the case of pure water only scenario (i) is observed, in the case of aqueous NaCl solutions both (i) and (ii) occur depending on the electrolyte concentration. The latter case reveals the role of ions and points to a balance between the strength of the external field and ion concentration as primary factors affecting the process.

AUTHOR INFORMATION

Corresponding Author

*E-mail: ivonez@icpf.cas.cz.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was 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 program “Projects of Large Infrastructure for Research, Development, and Innovations” (LM2010005), is highly appreciated. Valuable discussions with W. R. Smith, University of Ontario Institute of Technology, are also greatly acknowledged.

REFERENCES

- (1) Frenkel, D.; Smit, B. *Understanding Molecular Simulation: From Algorithms to Applications*, 2nd ed.; Academic Press: London, 2002.
- (2) Jabbarzadeh, A.; Tanner, R. I. Molecular dynamics simulation and its application to nano-rheology. *Rheology Rev.* **2006**, 165–216.
- (3) McCabe, C.; Cui, S.; Cummings, P. T.; Gordon, P. A.; Saeger, R. B. Examining the rheology of 9-octylheptadecane to giga-pascal pressures. *J. Chem. Phys.* **2001**, 114, 1887–1891.
- (4) Hall, C. K. Thermodynamic and kinetic origins of Alzheimer’s and related diseases: A chemical engineer’s perspective. *AIChE J.* **2008**, 54, 1956–1962.
- (5) Wendorff, J. H.; Agarwal, S.; Geiner, A. *Electrospinning*; Wiley-VCH: Weinheim, 2012.
- (6) Elmarco. *Nanospider Electrospinning Technology*. <http://www.elmarco.com/electrospinning/electrospinning-technology> (accessed Dec 11, 2013).
- (7) Reneker, D.; Chun, I. Nanometre diameter fibres of polymer, produced by electrospinning. *Nanotechnology* **1996**, 7, 216–223.
- (8) Formhals, A. Process and apparatus for preparing artificial threads. US Patent 1975504, 1934.
- (9) Teo, W. E.; Ramakrishna, S. A review on electrospinning design and nanofibre assemblies. *Nanotechnology* **2006**, 17, R89–R106.
- (10) Jirsák, O.; Sanetrník, F.; Lukáš, D.; Kotek, K.; Martinová, L.; Chaloupek, J. A method of nanofibres production from a polymer solution using electrostatic spinning and a device for carrying out the method. US Patent WO 205024101, 2005.
- (11) Taylor, G. Disintegration of water drops in an electric field. *Proc. R. Soc. London, Series A* **1964**, 280, 383–397.
- (12) Taylor, G. Electrically driven jets. *Proc. R. Soc. London, Series A* **1969**, 313, 453–475.
- (13) Hohman, M.; Shin, M.; Rutledge, G.; Brenner, M. Electrospinning and electrically forced jets. I. Stability theory. *Phys. Fluids* **2001**, 13, 2201–2220.
- (14) Feng, J. The stretching of an electrified non-Newtonian jet: A model for electrospinning. *Phys. Fluids* **2002**, 14, 3912–3926.
- (15) Angammana, C. J.; Jayaram, S. H. A theoretical understanding of the physical mechanisms of electrospinning. *Proceedings of the ESA Annual Meeting on Electrostatics*, Cleveland, OH, 2001.
- (16) Niu, H.; Wang, X.; Lin, T. In *Nanofibers—production, properties and functional application*; Lin, T., Ed.; InTech, 2011.
- (17) Lukáš, D.; Sarkar, A.; Pokorný, P. Self-organization of jets in electrospinning from free liquid surface: A generalized approach. *J. Appl. Phys.* **2008**, 103, 084309.
- (18) López-Herrera, J. M.; Barrero, A.; Boucard, A.; Loscertales, I. G.; Márquez, M. An Experimental Study of the Electrospraying of Water

in Air at Atmospheric Pressure. *J. Am. Soc. Mass Spectrom.* **2004**, *15*, 253–259.

(19) Hohman, M.; Shin, M.; Rutledge, G.; Brenner, M. Electrospinning and electrically forced jets. II. Applications. *Phys. Fluids* **2001**, *13*, 2221–2236.

(20) Luedtke, W. D.; Landman, U.; Chiu, Y.-H.; Levandier, D. J.; Dressler, R. A.; Sok, S.; Gordon, M. S. Nanojets, electrospray, and ion field evaporation: Molecular dynamics simulations and laboratory experiments. *J. Phys. Chem. A* **2008**, *112*, 9628–9649.

(21) Ahadi, E.; Konermann, L. Ejection of solvated ions from electrosprayed methanol/water nanodroplets studied by molecular dynamics simulations. *J. Am. Chem. Soc.* **2011**, *133*, 9354–9363.

(22) Znamenskyi, V. S.; Vertes, A. Molecular dynamics of ion formation from charged nanodroplets in electrospray ionization. *50th ASMS Conference on Mass Spectrometry and Allied Topics*, Orlando, FL, June 2–6, 2002.

(23) Ahadi, E.; Konermann, L. Surface charge of electrosprayed water nanodroplets: A molecular dynamics study. *J. Am. Chem. Soc.* **2010**, *132*, 11270–11277.

(24) Daub, C. D.; Cann, N. M. How are completely desolvated ions produced in electrospray ionization: Insights from molecular dynamics simulations. *Anal. Chem.* **2011**, *83*, 8372–8376.

(25) Okuno, Y.; Minagawa, M.; Matsumoto, H.; Tanioka, A. Simulation study on the influence of an electric field on water evaporation. *Theochem—J. Mol. Struct.* **2009**, *904*, 83–90.

(26) Lu, C.; Chen, P.; Li, J.; Zhang, Y. Computer simulation of electrospinning. Part I. Effect of solvent in electrospinning. *Polymer* **2006**, *47*, 915–921.

(27) Zhang, W.; Chen, M.; Zha, B.; Diao, G. Correlation of polymer-like solution behaviors with electrospun fiber formation of hydroxypropyl- β -cyclodextrin and the adsorption study on the fiber. *Phys. Chem. Chem. Phys.* **2012**, *14*, 9729–9737.

(28) Borner, A.; Li, Z.; Levin, D. A. Prediction of fundamental properties of ionic liquid electrospray thrusters using molecular dynamics. *J. Phys. Chem. B* **2013**, *117*, 6768–6781.

(29) Liu, Y.; Wang, X.; Yan, H.; Guan, C.; Yang, W. Dissipative particle dynamics simulation on the fiber dropping process of melt electrospinning. *J. Mater. Sci.* **2011**, *46*, 7877–7882.

(30) Svishchev, I. M.; Kusalik, P. G. Crystallization of liquid water in a molecular dynamics simulation. *Phys. Rev. Lett.* **1994**, *73*, 975–978.

(31) Sutmann, G. Structure formation and dynamics of water in strong external electric fields. *J. Electroanal. Chem.* **1998**, *450*, 289–302.

(32) Okuno, Y.; Minagawa, M.; Matsumoto, H.; Tanioka, A. Simulation study on the influence of an electric field on water evaporation. *J. Mol. Structure: THEOCHEM* **2009**, *904*, 83–90.

(33) Joshi, R. P.; Kolb, J. F.; Xiao, S.; Schoenbach, K. H. Aspects of plasma in water: Streamer physics and applications. *Plasma Process. Polym.* **2009**, *6*, 763–777.

(34) Szklarczyk, M.; Kainthla, R. C.; Bockris, J. O'M. On the dielectric breakdown of water: An electrochemical approach. *J. Electrochem. Soc.* **1989**, *136*, 2512–2521.

(35) Jorgensen, W. L.; Chandrasekhar, J.; Madura, J. D.; Impey, R. W.; Klein, M. L. Comparison of simple potential functions for simulating liquid water. *J. Chem. Phys.* **1983**, *79*, 926–935.

(36) Berendsen, H. J. C.; Grigera, J. R.; Straatsma, T. P. The missing term in effective pair potentials. *J. Phys. Chem.* **1987**, *91*, 6269–6271.

(37) Vega, C.; Abascal, J. L. F. Simulating water with rigid non-polarizable models: A general perspective. *Phys. Chem. Chem. Phys.* **2011**, *13*, 19663–19688.

(38) Joung, I. S.; Cheatham, T. E., III Determination of alkali and halide monovalent ion parameters for use in explicitly solvated biomolecular simulations. *J. Phys. Chem. B* **2008**, *112*, 9020–9041.

(39) Hess, B.; Kutzner, C.; van der Spoel, D.; Lindahl, E. GROMACS 4: Algorithms for highly efficient, load-balanced, and scalable molecular simulation. *J. Chem. Theory Comput.* **2008**, *4*, 435–447.

(40) van der Spoel, D.; Lindahl, E.; Hess, B.; van Buuren, A. R.; Apol, E.; Meulenhoff, P. J.; Tieleman, D. P.; Sijbers, A. L. T. M.; Feenstra, K.

A.; van Drunen, R.; Berendsen, H. J. C. *Gromacs User Manual*, version 4.5; The GROMACS development team, 2005.

(41) Hockney, R. W.; Goel, S. P.; Eastwood, J. Quiet high resolution computer models of a plasma. *J. Comput. Phys.* **1974**, *14*, 148–158.

(42) Daren, T.; York, D.; Pedersen, L. Particle mesh Ewald: An N-log(N) method for Ewald sums in large systems. *J. Chem. Phys.* **1993**, *98*, 10089–10092.

(43) Essmann, U.; Perera, L.; Berkowitz, M.; Darden, T.; Lee, H.; Pedersen, L. A smooth particle mesh Ewald method. *J. Chem. Phys.* **1995**, *103*, 8577–8593.