DAAD Short-term grant Application

November 28, 2017

Applicant: Lic. Kevin Speyer

1 Previous Research Work

The candidate, Kevin Speyer, holds years of experience performing research in polymer physics and Soft Matter by computer simulations. He published two papers in international peer-reviewed journals. His main working subjects are Polymer Brushes, composed of semiflexible chains anchored to the walls of a nano-channel, and the interactions between this soft substrate and liquid flow in nano-fluidic systems. A wide range of physical quantities are measured in these systems, from the molecular degrees of freedom to thermodynamic or rheological properties. The work is performed by means of Molecular Dynamics simulations, in the context of Statistical Mechanics theory. The applicant hold PhD CONICET scholarship working in the Theory and Simulation of Soft Matter Group of the National Atomic Energy Commission (CAC-CNEA) in Argentina. The group has a history of collaboration with the Soft Matter Theory Group of Prof. Dr. Marcus Müller in Göttingen. The applicant's supervisor, Dr. Claudio Pastorino, has a vast experience in polymer physics theory and simulation, and is now a researcher in CNEA and CONICET at CAC-CNEA

In his Diploma Thesis (MS equivalent), entitled "Simulation of simple liquids confined in soft channels", the candidate studied a nanochannel with confining surfaces coated with grafted polymers. In this work, the interaction between the liquid and the grafted polymers was analyzed in equilibrium and in flow conditions. This first study was focused on the influence of the bending rigidity of the semiflexible polymers on the static and dynamical properties of the system. The interaction between the soft substrate and the liquid is hydrophobic, giving rise to a Cassie–Baxter state. Equilibrium properties such as brush height and bending energy were measured, varying the grafting density (number of chains per surface area) and the stiffness of the polymers. The characteristics of the brush–liquid interface and the morphology of the polymer chains supporting the liquid were studied for different bending rigidities. Non-equilibrium simulations were performed, moving the walls of the channel in opposite directions at constant speed, obtaining a Couette velocity profile in the bulk liquid. The molecular degrees of freedom of the polymers are studied as a function of the shear rate. The violation of the no-slip boundary condition and the slip properties were analyzed as a function of the shear rate, grafting density and bending stiffness. At high grafting densities, a finite slip length independent of the shear rate or bending constant was found, while at low grafting densities a very interesting non-monotonic dependence on the bending constant is observed. This work was published in the journal *Soft Matter*[22].

In another study, the candidate analyzed a system composed of a liquid droplet in a nanochannel, coated with semiflexible hydrophobic polymers by means of non-equilibrium molecular dynamics simulations. The studied system is then a moving droplet in a slit-like channel, coexisting with its vapor phase. The polymer chains, grafted by the terminal bead to the confining walls, are described by a coarse-grained model that accounts for chain connectivity, excluded volume interactions and local chain stiffness. The rheological, frictional and dynamical properties of the brush are explored over a wide range of persistence lengths. A rich behavior of polymer conformations and concomitant changes in the friction properties are found over the wide range of studied polymer stiffnesses. A rapid decrease in the droplet velocity was observed as the rigidity of the chains is increased for polymers whose persistence length is smaller than their contour

length. A strong relation between the internal dynamics of the brush and the droplet transport properties is found, which could be used to tailor flow properties by surface functionalization. The monomers of the brush layer, under the droplet, present a collective "treadmill belt" like dynamics which can only be present due the existence of grafted chains. The changes in spatial extension upon variations of polymer stiffness are described, with bidimensional velocity and density profiles. The deformation of the polymer brushes due to the presence of the droplet is analyzed in detail. Lastly, the droplet−gas interaction is studied by varying the liquid to gas ratio, observing a speed increase for droplets that flow close to each other, compared to a train of droplets that present a large gap between consecutive droplets. These results were recently published in *Langmuir[23]* journal.

The candidate works on a daily basis on large computation clusters, running coarse grain simulations in compiled languages, and performing post-processing statistical analysis with scripting languages (python, awk). He is familiar with various visualization tools for 3D atom dynamics (Visual Molecular Dynamics), color plots and data visualization (python, Xmgrace, gnuplot). He has experience in High Performance Computing, parallelizing code in non-trivial processes.

2 Working Project

Using large-scale computer simulation of coarse-grained polymer models we propose the study of non-equilibrium behavior of active polymer brushes. This soft-matter system mimics active biological systems capable of directed transport. The system also exhibits an intricate, non-equilibrium single-chain dynamics ("tumbling motion"), and our simulation study will elucidate to what extent the individual molecular motions are coupled and synchronized (spatiotemporal correlations) and how the molecular motion interacts and dictates the collective structure and flow field. The project takes advantage also of the strong experience of the applicant in semi-flexible polymer brushes, by adding the important element of chain activeness. A given energy per unit time will be injected in each grafted polymer to obtain a self-sustained oscillation of the polymers, which will give raise to a collective behavior depending on chain-stifness, grafting density and the properties of the liquid. The student will have the opportunity to learn about modern concepts of non-equilibrium statistical mechanics and state-of-the-art simulation techniques on clusters of CPUs and GPUs.

2.1 Goals

Polymers in flow have attracted abiding interest by experimental and theoretical researchers. By irreversibly grafting a polymer onto a solid substrate one fabricates brush coatings that are both, mechanically stable as well as versatile for tuning the wettability and friction of the coated surface.[27] In our previous collaboration we have developed and utilized coarse-grained computer simulations to study polymer brushes under flow,[16, 19, 17, 14] studied how the brush coating dictates the hydrodynamic boundary condition,[13, 11] and studied the tumbling motion of the individual grafted macromolecules and the concomitant reversal of the near-surface flow under shear.[12, 20]. We propose now to extend our study to collective phenomena in active polymer brushes, which exhibit collective, non-equilibrium phenomena.

The coating of the surfaces with tethered polymers alters the flow properties in the ultimate vicinity of the coated surface. These boundary effects become particular important in microfluidic devices that manipulate confined liquids at the pico-liter scale, electroosmotic flow, or vascular biological systems.[26] Much interest has focused on driving the liquid motion externally, e.g., by a pressure difference, shear of confining boundaries, or an electric field. Such conditions are particularly relevant for applications such as lab-on-chip devices,[24, 25] controlled drug delivery, functionalized surfaces and sensing at the nano-scale.

Active particles and polymers in biological context or active, synthetic realizations constitute an alternative driving mechanism that has attracted much attention recently. In these systems, the active entities possess internal degrees of freedom that enable them to take energy from the environment and perform mechanical work in the form of, e.g., systematic movements. Active systems under study range from

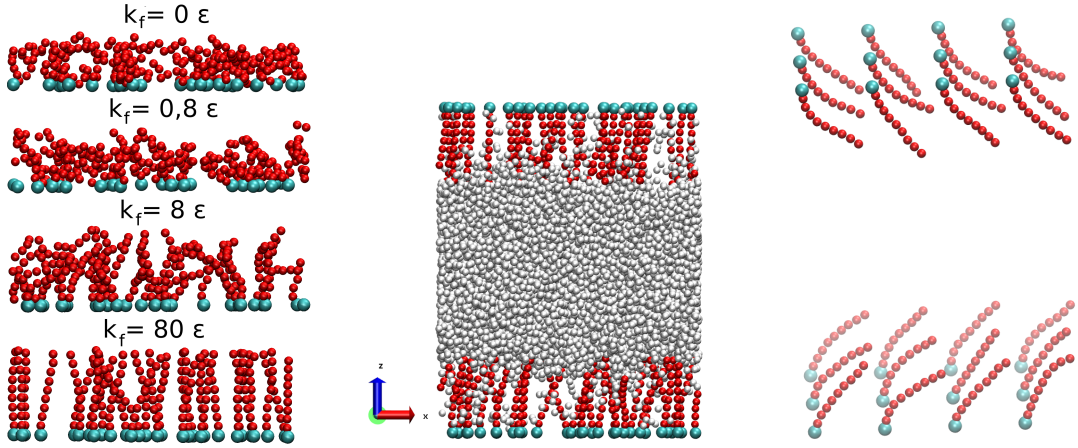

Figure 1: Left panel: Grafted polymer layers with increasing stiffness, which is parameterized by the bending constant k_f. Center panel: Planar channel filled with liquid confined between two stiff polymer brush layers with $k_f = 80$. Right panel: Illustration of an active brush oscillating with the same phase (phase-locked state, grafting points arranged on square lattice).

bacteria[21] or spermatozoa, to smaller functional units of cells and micro-organisms such as cilia, flagella and molecular motors.[3, 4] These last cases include also so-called micro-swimmers of biological origin, such as opalinas and chlamydomonas or synthetic experimental systems such as self-propelled droplets, catalytic Janus colloids or thermophoretic nano-particles.[4] Understanding the mechanisms how the coupling among active units results in directional motion [5, 10, 2, 1, 15] and the collective states of these active materials is of great current interest.

The coordinated motion of cilia, which are comprised of active, semiflexible filaments anchored to a surface, can give rise to directed motion of micro-organisms in nature or to pumping of fluids in certain tissues. For example, cilia in the human respiratory tract pump viscous fluids away from the lungs or propel dust particles out of the body. This amazing function and the efficiency of cilia transport has stimulated research groups to design synthetic analogues in order to regulate flow or particle motion in microfluidic devices.

We propose to study planar nano-channels coated by active polymers, end-grafted to the confining walls of a narrow slit channel. The system is a generalization of semi-flexible polymer brushes, which have been previously studied thoroughly by the applicant. For this project we add a protocol energy injection which gives raise to self-sustained movement. Fig. 1 presents preliminary examples of these systems. We have already developed a coarse-grained beating model for the individual chains that captures the essential features of the movement of typical active filaments, such as cilia or flagellae. A cilium filament, for example, presents a power stroke and a recovery stroke. In the former the cilium stretches out and moves rather fast in one direction. In the recovery stroke, in turn, the cilium bends and slowly retracts.[4] We reproduced this asymmetric beating pattern with our coarse-grained model. This motion results from an internal activity or is driven by coupling to an external, time-dependent field. A deep characterization of this model must be done in dry brushes, to study then the liquid transport due to the collective motion of active grafted polymers. Specifically, we propose two types of couplings between self-sustained polymer chains. The first one is given by the direct interaction between neighboring chains and the second one is an harmoning coupling of neighboring chains close to the grafting point.

The applicant will study the synchronization of the polymers of the active brush and their interaction with the liquid:

- What is the relative importance of mechanical/steric and hydrodynamic interactions in the collective dynamics of the polymer chains?
- How do synchronized, active brushes produce directed flow in a nano-channel?

- What are the effects of the interaction with the liquid on the local dynamics of active chains and synchronization, when the liquid is exposed to (external) shear?
- Methachronal waves are frequently observed in biological cilia, i.e., there are regions of perfect synchronization surrounded by disordered beating patterns. We want to address also the origin of these collective features and the relationship with the liquid flow in the channel.

2.2 Methodology

We will use coarse-grained molecular dynamics simulations of coarse-grained bead-spring models. The active polymer brushes are described by the Kremer-Grest model, [6, 9] where segments interact via a Lennard-Jones potential describing the harsh excluded volume of individual segments. A Finite Non-linear Extensively Elastic (FENE) potential accounts for the chain connectivity. We have used this model in our previous joint work on polymer brushes.[16, 17, 20] Additionally, we apply a harmonic bending potential between two consecutive bonds that connect a given monomer with its two nearest neighbors in order to tune the rigidity of the semi-flexible polymer chain.[22] The applicant has an important experience in the study of semi-flexible brushes under flow and has implemented the bending rigidity of the polymer chains.[22, 23] Importantly the combination of harsh excluded-volume interactions between segments and a maximal bond length guarantees that chain contours cannot cross through each other in the course of the simulation. These entanglement effects that dramatically alter the dynamics in dense melts of long polymers, may be important for the synchronization of the active polymers.

We are planning the use of molecular dynamics simulation with a DPD (or Lowe-Anderson) thermostat.[7, 8] This pairwise thermostat obeys translation invariance and locally conserves momentum, thereby duly accounting for hydrodynamic interactions that are mediated via the explicit solvent.[14, 19, 18] We have experience in using this simulation techniques to study isothermal flows in nano-channels. [12, 18, 20, 11]

The simulations of active brushes will be performed by a MPI-parallel simulation code that is well suited for computer clusters, but the applicant will learn the use and programing of a GPU-program that is based on the HOOMD code (see http://glotzerlab.engin.umich.edu/hoomd-blue), in his visit to Göttingen. The latter allows for large-scale simulations on clusters of GPUs that are available at the von-Neumann Institute for Computing in Jülich and the Argentinian group will strongly benefit of this knowledge.

2.3 Detailed work plan

- Channel with explicit solvent: synchronization and hydrodynamic coupling
  - An explicit solvent will be added to channel coated by active brushes, described by Lennard-Jones particles, to account for momentum conservation and the concomitant hydrodynamic interactions, taking advantage of the experience of the German group.
  - We will analyze the effect of solvent-mediated hydrodynamic coupling between active chains and characterize changes in the collective chain dynamics, as compared to the case of elastic coupling alone (in dry brushes).
- Liquid flow with synchronized chain dynamics
  - Imposing coordinated movement to the chains, mimicking typical cilia dynamics, we will study the flow generated in the solvent.
  - Upper and lower active brush layers of the slit channel will be studied as a function of polymer beating frequency, amplitude, and direction. Directed flow in the vicinity of the individual active brush layers can be achieved by choosing parameters that result in synchronization (obtained in the previous task using the "dry channel"), or by imposing a phase-locked dynamics with a time-dependent external force.

– Special interesting cases are in-phase movement of active upper and lower brushes and anti-phase movement of upper and lower grafted layers. If the polymers drive locally the fluid, the in-phase movement is expected to produce a plug flow, whereas the anti-phase movement results in shear flow.

– A parallelization scheme with GPU of some parts of the code will be studied and implemented by the applicant wiht the help of the Prof. Müller and his group.

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