

**LOMONOSOV MOSCOW STATE UNIVERSITY**

# **Theory and Simulations of Polyelectrolytes**

**International Summer School**

**Abstracts and Schedule**

**Moscow, Russia  
June 23 – 25, 2016**

# International Summer School

## Theory and Simulations of Polyelectrolytes

June 23–25 2016, Lomonosov Moscow State University

### Topics:

- Scaling principles in polymer science
- Implementation of long-range interactions
- Mean-field theory of polyelectrolytes
- SCFT with charged groups
- MD force-fields for electrostatics
- Multiscale simulations in organic electronics
- LBL, surfaces and layers
- Gels and capsules
- DNA and proteins
- Batteries and photovoltaics

### Program committee

Alexei Khokhlov (chairman)  
Alexander Chertovich (secretary)  
Viktor Ivanov  
Igor Potemkin  
Elena Kramarenko

### Local organizing team

Alexander Chertovich  
Pavel Kos  
Artem Sergeev  
Vladimir Rudyak  
Olga Bogomolova

## PARTNERS



# Schedule

All lectures will be held in Shuvalovsky building, Auditorium **B2**

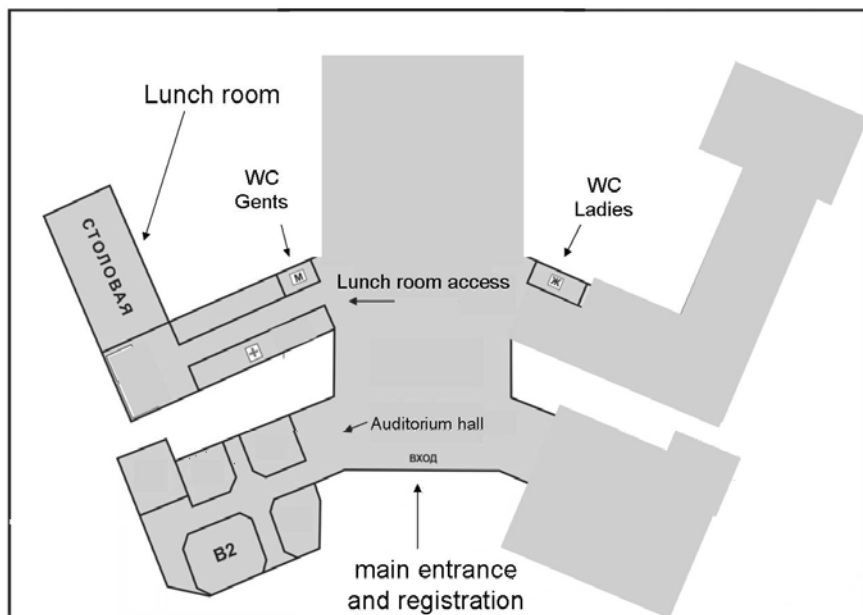
Student posters are welcome for discussion throughout the School in the Auditorium Hall (upper floor)

**Thursday, June 23 9.00 – 9.30 – REGISTRATION (Shuvalovsky bld.)**

<b>Thursday, June 23</b>	
09.30–09.40	<b><i>OPENING of the International Summer School</i></b>
09.40–10.40	<b><u>M. Tamm</u></b> , Introduction to polymer science
10.50–11.50	<b><u>I. Erukhimovich</u></b> , The key milestones in understanding the fluctuation effects and phase transitions in weakly charged polyelectrolytes
12.00–13.30	<i>Lunch</i>
13.30–14.30	<b><u>I. Potemkin</u></b> , Polyelectrolyte gels and microgels
14.40–15.40	<b><u>A. Shaytan</u></b> , Natural polyelectrolytes
15.50–16.50	<i>Coffee break and student posters</i>
16.50–17.20	<b><u>N. Brilliantov</u></b> , Strong collapse of single polyelectrolyte chain
17.30–18.00	<b><u>V. Ivanov</u></b> , Multiscale simulations in organic electronics
<b>Friday, June 24</b>	
09.30–10.30	<b><u>M. Rubinstein</u></b> , Scaling in polyelectrolyte solutions
10.40–11.40	<b><u>F. Leermakers</u></b> , Polyelectrolytes at interfaces and in the bulk
12.00–13.30	<i>Lunch</i>
13.30–14.30	<b><u>O. Borisov</u></b> , Solution properties of branched polyelectrolytes
14.40–15.40	<b><u>M. Muthukumar</u></b> , Collective dynamics of polyelectrolyte solutions
15.50–16.50	<i>Coffee break and student posters</i>
16.50–17.20	<b><u>F. Leermakers</u></b> , SCFT equations
17.30–18.00	<b><u>A. Rumyantsev</u></b> , Counterion association regimes

<b>Saturday, June 25</b>	
09.30–10.30	<b><u>K. Kremer</u></b> , Molecular dynamics of polyelectrolytes
10.40–11.40	<b><u>E. Zhulina</u></b> , Block-copolymer polyelectrolytes in solution
12.00–13.20	<i>Lunch and student posters</i>
13.30–14.30	<b><u>R. Netz</u></b> , Fundamentals of dielectric effects and dielectric spectroscopy of electrolyte and polyelectrolyte solutions
14.40–15.40	<b><u>M. Olvera de la Cruz</u></b> , Assembly of anisotropic functionalized particles
15.50–16.20	<b><u>A. Gavrilov</u></b> , DPD simulation of charged systems
16.30–18.00	Closing Event (Lunch room)

### Shuvalovsky building



**June 23, 09.40-10.40**

## **INTRODUCTION TO POLYMER SCIENCE**

Mikhail Tamm

*Lomonosov Moscow State University, Russia*

Polymer physics is the field of physics that studies polymers, their fluctuations, mechanical properties, etc. While it focuses on the perspective of condensed matter physics, polymer physics is originally a branch of statistical physics. The statistical approach for polymer physics is based on an analogy between a polymer and a Brownian motion. The simplest possible polymer model is the so-called "ideal chain", corresponding to a simple random walk. In this lecture the basic set of simple models and qualitative ideas about the physical properties of polymers at a molecular level will be presented. All these concepts have been used successfully both in physical chemistry and in molecular biology.

June 23, 10.50-11.50

## **THE KEY MILESTONES IN UNDERSTANDING THE FLUCTUATION EFFECTS AND PHASE TRANSITIONS IN WEAKLY CHARGED POLYELECTROLYTES**

Igor Erukhimovich

*A.N.Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, Russia*

The purpose of the lecture is to demonstrate a variety of scenarios according to which the confrontation between the long-range Coulomb and short-range van der Waals interactions in polyelectrolytes results in destroying the homogeneous (disordered) state and formation of ordered phases and complexes. The basic issues to be discussed in the lecture are as follows.

1. Polyelectrolytes are the area of fluctuation effects: if the fluctuations were absent the total charge profile would be zero (due to electroneutrality) and, thus, electrostatic energy would equal zero either.
2. The electrostatic blob notion and distinction between the weakly and strongly charged polyelectrolytes (the blob is big in weakly charged ones).
3. Screening by non-point-like objects and different types of screening in polyelectrolytes (conventional screening, recharging and oscillating screening).
4. Polyelectrolytes in poor solvent: microphase vs macrophase separation. Phase diagrams.
5. Macrophase separation in polyelectrolyte solutions and polyelectrolyte complexes as the minimal droplets of the condensed phase.
6. Why could be the Debye-Hückel estimate of the electrostatic energy not always correct. The necessary extension.
7. Polyelectrolyte complexes and ordered polyelectrolyte complexes. Phase diagrams.
8. The polydispersity effects and charge fractionation. Why and how the polyelectrolyte polydispersity with respect to the linear charge density leads to the fact that the microphase separation is accompanied by the macrophase separation into the stronger and weaker charged polyelectrolyte chains (with the corresponding counterion densities).
9. Necklace model and microphase separation.

High swelling of polyelectrolytes (PEs) in comparison with neutral counterparts in aqueous media is usually ascribed to the presence of ionic groups capable of dissociation. In macroscopic polymer gels counterions are trapped within the network interior and create exerting osmotic pressure providing high gel swelling. Single chains in dilute solutions obtain non-zero charge owing to release of counterions, and

their extended conformations are the consequence of Coulomb repulsion of ionic groups. Immersed in organic solvents, both PE gels and single chains collapse. The reason of this phenomenon is counterion binding with charges in polymer chains, which is more favourable in low polar media due to higher energy gain from ion association.

It is natural to start consideration of counterion association in PEs with the case of macroscopic gels owing to their electroneutrality. Association/dissociation equilibrium in low-molecules-weight electrolytes ( $AB \leftrightarrow A^+ + B^-$ ) is well understood, and the law of mass action defines concentrations of all species in the solution. However, this approach cannot be directly applied to PE gels because of following reasons:

- (i) Concentration of ionic groups within the gel is not fixed. Their dissociation favours network swelling and results in a decrease of their concentration. In turn, it promotes further dissociation as well as further gel swelling;
- (ii) Gel shrinking/swelling is accompanied by changes in a gel media polarity because a dielectric constant of a dry polymer is usually much lower than that of a pure solvent. Thus, energy gain from ion pairing depends on the state of the gel, swollen or collapsed;
- (iii) Each counterion electrostatically interacts not only with the respective charge in polymer chain but also with its spatial neighbors. Manning condensation of counterions in swollen networks and multiplet formation within the collapsed gels are manifestations of this fact.

In highly swollen PE gels it is useful to describe ion association as a two-step process with the first step being Manning condensation and the second being ion pairing. Retaining of a part of counterions within PE microgel or micelle with PE corona can be treated as a third step of ion association. Type of counterion strongly influences PEs swelling, though counterion specificity directly affects only one ion association step, namely ion pairing.

June 23, 13.30-14.30

## POLYELECTROLYTE GELS AND MICROGELS

Igor I. Potemkin

*Lomonosov Moscow State University, Russia*

Basic effects in polyelectrolyte micro- and macrogels, which arise due to the interplay between mobility of counterions, elasticity of the subchains, electrostatic and hydrophobic interactions, will be overviewed. They include superabsorbing properties of polyelectrolyte (macro)gels, peculiarity of their collapse and microphase segregation upon worsening of the solvent quality. Recent results on peculiarities of swelling and collapse of polyelectrolyte nano- and microgels will be reported.

Internal structure of polyelectrolyte nano- and microgels (mGs) resembles elements of macroscopic polymer network: linear charged chains (subchains) are covalently linked with each other into three-dimensional frame of the size in the range between tens of nanometers and few microns. Similarly to the macroscopic gels, they exhibit different properties at different length scales. Liquid-like behavior is characteristic at the length-scales smaller than the mesh-size, where each subchain does not feel connectivity into the network. Elastic, solid-like response is revealed at the length scales larger than the mesh-size. In contrast to macroscopic polyelectrolyte gels, electric neutrality of the mGs in dilute solutions is violated due to partial escape of monovalent counterions into the outer solvent caused by their thermal motion (entropy). As a result, the mGs are highly swollen in a good solvent due to both long-range repulsion of unscreened charged monomer units and exerting osmotic pressure of mobile counterions which are trapped inside the mG.

In this lecture, we report about new effect comprising equilibrium a center-to-periphery mass redistribution with formation of a quasi-hollow structure of strongly stretched subchains in the center of the mG and dense “skin” at the periphery. This effect is a consequence of a competition between long-range repulsion of unscreened charged monomer units tending to bring them to the periphery of the particle and elasticity of the subchains preventing long-distance migration of the charges.

### **Acknowledgements**

Financial support of the Russian Science Foundation, project # 15-13-00124 is gratefully acknowledged.



**June 23, 14.40-15.40**

## **NATURAL POLYELECTROLYTES**

Alexey Shaytan

*National Center for Biotechnology Information, National Institutes of Health, USA, Lomonosov Moscow State University, Russia*

Natural polyelectrolytes are essential building blocks of all living organisms. All major classes of biological macromolecules (nucleic acids, proteins, lipids and polysaccharides) incorporate charged and ionizable groups that are essential for their structure and function. This lecture will introduce these main classes of biological polyelectrolytes, discuss their structure and properties. I will describe several examples from my own research where physical interactions between charged biomacromolecules are essential for the biological function.

Lecture plan:

- 1) Main types of biological macromolecules. Specific nature of biological macromolecules. Interplay of various types of interactions, evolutionary selection of sequences, self-assembly. Correspondence between sequence, 3D shape and properties. Role of charged groups in biomacromolecules
- 2) Proteins: structure, properties and functions. Influence of local environment on ionization.
- 3) DNA and RNA: structure, properties and functions. Screening of charge interactions. Example: packing of DNA in the cell nucleus from nucleosomes to higher order chromatin structure.
- 4) Lipids: structure and properties. Self-assembly of lipid bilayers. Example: interaction of charged protein fibrils with charged membranes enhances viral transfection.
- 5) Polysaccharides: structure, properties and function. Examples: heparin – biological molecule with highest negative charge density, an anticoagulant drug.

June 23, 16.50-17.20

## **STRONG COLLAPSE OF SINGLE POLYELECTROLYTE CHAIN**

Nikolai Brilliantov

*Lomonosov Moscow State University, Russia  
University of Leicester, England*

I will open the lecture with the discussion, how a dimension of a polyelectrolyte chain depends on the electrostatic interactions strength. Namely, I will consider the dependence of the gyration radius of a chain on the reduced Bjerrum length. In particular, I will focus on strongly charged polyelectrolytes in dilute salt-free solutions. I will mention that as the Bjerrum length increases, a polyelectrolyte chain undergoes a series of conformation changes, arriving at a final state of a compact globule. I will discuss the available experimental and numerical studies where the electrostatic collapse of a polyelectrolyte has been addressed; different mechanisms of this phenomenon, proposed in literature, will be also discussed.

In the second part of the lecture I will report the results of our recent simulation ( )TJ-0.0004 T  
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June 23, 17.30-18.00

## MULTISCALE SIMULATIONS IN ORGANIC ELECTRONICS

Viktor Ivanov

*Lomonosov Moscow State University, Russia*

In this case study I will mainly focus on a particular example of multiscale simulations in organic electronics. We have performed <sup>1</sup> computer simulation study of the temperature dependence of the dynamic disorder in the crystalline lamellar arrangement of the highly crystalline conjugated polymer, poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene), PBTTT-C14, and established a link between the microscopic ordering and the charge-transport parameters. The structure disorder has been characterized by three order parameters: dynamic order parameter, nematic order parameter and paracrystallinity. An abrupt decrease of the side-chain dynamic order, observed around 400 K, correlates well with a sharp increase of the backbone paracrystallinity, while all nematic and dynamic order parameters of the backbone as well as the unit-cell expansion along the  $\pi$ -stacking direction show a monotonic linear temperature dependence. The morphological disorder leads to broadening of distributions of the electronic coupling elements and site energies. The variation in electronic couplings was found to occur on a much faster time scale (hundreds of femtoseconds) than a typical time required for a single electron-transfer event. Hence, the electronic coupling elements were preaveraged before calculating electron-transfer rates. Site energies, by contrast, were found to change on a significantly slower scale and thus could be treated as static on the time scale of charge transport. Finally, the hole mobility, reproduces well the value measured in a short-channel thin-film transistor. Preaveraging the electronic couplings (due to their fast dynamics) leads to a factor of 5 increase in the average mobility. We came to the conclusion that, in order to secure polymeric organic semiconductors with large charge-carrier mobilities, it is not enough to have large electronic coupling averages. In addition, the fast time-scale dynamics of the polymers and, even more importantly, the small energetic disorder (which evolves on a much slower than the chargecarrier dynamics time scale) are desirable. From the point of view of chemical design, it should be noted that the alkyl side chains that are added for solubility purposes can affect the backbone paracrystallinity and hence increase the energetic disorder if they do not remain in a highly crystalline state. It is therefore important that both backbones and side chains maintain good crystalline order. In this study we have used a combination of several methods for different time and length scales, so that this case can be considered as an example of multiscale computer simulations: (1)

reparametrisation of bonded degrees of freedom in atomistic force field (OPLS-AA) using DFT (B3LYP) for matching potential energy surfaces; (2) atomistic molecular dynamics (NPT, Gromacs) to calculate structure and dynamics; (3) Thole model to compute electrostatic + polarization contributions to site energies for molecules as found in the morphology (distributions of site energies); (4) semi-empirical ZINDO method to calculate distributions of electronic couplings; (5) correlations between these distributions and dynamic, nematic and paracrystallinity order parameters; (6) comparison of decay times of respective autocorrelation functions with typical charge transfer times (to average or not); (7) DFT (B3LYP) to calculate reorganization energies; (8) semi-classical Marcus charge transfer theory.

### **References**

[1] Poelking C., Cho E., Malafeev A., Ivanov V., Kremer K., Risko C., Brédas J.-L., Andrienko D., *J. Phys. Chem. C* **117**, 1633–1640 (2013).

**June 24, 9.30-10.30**

## **SCALING IN POLYELECTROLYTE SOLUTIONS**

Michael Rubinstein

*University of North Carolina at Chapel Hill, USA*

Dilute Theta solvent case. The lecture will start from description of the scaling theory of a single polyelectrolyte chain in a theta solvent for polymer backbone. The idea of electrostatic blob will be introduced and the conformation of an isolated polyelectrolyte chain in dilute solution with no added salt will be described. If time permits – the idea of counterion condensation and its effect on chain size and conformations will also be introduced. The electrostatic persistence length controversy will be briefly mentioned and the resulting effect of added salt on the size of a polyelectrolyte chain in dilute solution will be summarized.

Dilute poor solvent case. Scaling description of the cascade of necklace transitions of polyelectrolytes in dilute solution of poor solvent for polymer backbone will be presented.

Semidilute polyelectrolyte solutions. Scaling estimate of the overlap concentration will be given and the idea of the correlation length in semidilute solutions will be explained. Concentration dependence of correlation length for polyelectrolytes with hydrophilic and with hydrophobic backbones will be outlined. The number of important length scales will be emphasized.

June 24, 10.40-11.40

## **POLYELECTROLYTES AT INTERFACES AND IN THE BULK**

Frans A. M. Leermakers  
*Wageningen University, The Netherlands*

To understand how polyelectrolytes behave at interfaces, we first have to get insight in the generic and molecular specific feature of the neutral analogues. Hence we first need to know how polymers behave at interfaces. In turn, for a good understanding of polymers at interfaces, we need to have insight in the solution properties. Hence in my lecture I will briefly review these aspects in reversed order. We will start in the solution and work towards the adsorption problems. The working horse for this is the Edwards diffusion equation.

Key aspects that will be discussed are: (i) the relevant polymer length scale in dilute and semi-dilute solutions. (ii) the appearance of a critical adsorption energy in polymer adsorption and the nature of the adsorption transition; depletion vs adsorption (iii) The de Gennes self-similar adsorption profile for strong adsorption from dilute solutions. (iv) numerical SCF calculations a la Scheutjens and Fler (v) analytical approximations based on the ground state approximation. (vi) Generic versus molecular specific effects for polymer at interfaces (the role of molecular architecture). Polyelectrolyte adsorption is a rich topic. On top of the interactions discussed for neutral polymer adsorption we have the electrostatics. We will discuss the Poisson-Boltzmann (PB) equation for the description of ions near electrified interfaces. In this equation the ions are point charges and this is far from the polyelectrolyte case. However we will discuss how to extend the PB approach towards ions with excluded volume and then towards chains that carry charges. In short we will need to solve Edwards diffusion equation in combination with the Poisson equation, which is possible using the Scheutjens-Fler SCF approach.

We will argue that in PE systems the nature of the charge on the backbone and the diffuse cloud of ions around it, causes extreme departures from the generic effects discussed above for homopolymer adsorption. Often for PE adsorption the chains are in 'flat' train-like conformations. Just next to this thin layer there is a Coulomb hole from which the PEs are strongly depleted. As a consequence, we need to have extremely long PEs before the generic self-similar profile can be expected and molecular specific features dominate.

We will only briefly touch upon the many possible regimes that can be distinguished for polyelectrolyte adsorption. We have the case that electrostatics dominates (adsorption onto oppositely charged interfaces and low ionic strength). We may also

have the case that adsorption is dominated by non-electrostatic interactions (as in homopolymer adsorption). In PE adsorption problems the ionic strength is a natural control parameter. One can easily find literature wherein the adsorbed amount of PE increases or decreases with ionic strength. There are also cases wherein the adsorption is non-monotonic. We will see that the interpretation for such results may not necessarily be unique.

June 24, 13.30-14.30

## **SOLUTION PROPERTIES OF BRANCHED POLYELECTROLYTES**

Oleg V. Borisov

*Université de Pau et des Pays de l'Adour, France*

*Institut of Macromolecular Compounds, St*

*Petersburg, Russia*

The interplay of long-ranged Coulomb interactions with branched topology leads to a number of distinctive features in conformations of branched polyelectrolytes in aqueous solutions, as compared to those of linear polyelectrolytes. We discuss conformations of branched ionic macromolecules with diverse topologies (star- or comb-like, regular dendritically or randomly branched) in aqueous solutions, with the main emphasis on conformational transitions triggered in such macromolecules by variation in environmental conditions (temperature, pH, ionic strength of the solution). Interactions and complexation of branched macroions with oppositely charged polyelectrolytes and nanocolloids are addressed as well. The predictions of the analytical Poisson-Boltzmann theory are compared to the result of numerical self-consistent field modelling, molecular dynamics and Monte Carlo simulations.



**June 24, 14.40-15.40**

## **COLLECTIVE DYNAMICS OF POLYELECTROLYTE SOLUTIONS**

Murugappan Muthukumar

*University of Massachusetts, Amherst, USA*

The diffusion of a charged macromolecule in an electrolyte solution is not a single-molecule behavior, but it is self-consistently coupled to the omnipresent counterion cloud surrounding the molecules. Basic concepts for treating this collective dynamical behavior of polyelectrolyte solutions will be presented. Specific examples will include diffusion coefficients and electrophoretic mobility of flexible polyelectrolytes, and viscosity of polyelectrolyte solutions.

**June 24, 16.50-17.20**

## **SCFT EQUATIONS**

Frans A. M. Leermakers

*Wageningen University, The Netherlands*

I will dispatch the technical details of how to implement electrostatic interactions in the SCF machinery to a dedicated talk of 0.5 hours. The plan is to discuss a relatively easy to understand standalone c-program which solves for a standard PE adsorption problem. Such small program can be of help to understand better how SCF theory works in practice and may be a stepping stone for further research in this field.

June 24, 17.30-18.30

## COUNTERION ASSOCIATION REGIMES

Artem M. Rumyantsev

*Lomonosov Moscow State University, Russia*

*DWI – Leibnitz Institute for Interactive Materials, Aachen, Germany*

High swelling of polyelectrolytes (PEs) in comparison with neutral counterparts in aqueous media is usually ascribed to the presence of ionic groups capable of dissociation. In macroscopic polymer gels counterions are trapped within the network interior and create exerting osmotic pressure providing high gel swelling. Single chains in dilute solutions obtain non-zero charge owing to release of counterions, and their extended conformations are the consequence of Coulomb repulsion of ionic groups. Immersed in organic solvents, both PE gels and single chains collapse.<sup>1,2</sup> The reason of this phenomenon is counterion binding with charges in polymer chains, which is more favourable in low polar media due to higher energy gain from ion association.<sup>3-4</sup>

It is natural to start consideration of counterion association in PEs with the case of macroscopic gels owing to their electroneutrality. Association/dissociation equilibrium in low-molecules-weight electrolytes ( $AB \leftrightarrow A^+ + B^-$ ) is well understood, and the law of mass action defines concentrations of all species in the solution. However, this approach cannot be directly applied to PE gels because of following reasons:

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## References

- [1] Klooster, N. T. M., van der Touw, F., Mandel, M. *Macromolecules* **1984**, *17*, 2070.
- [2] Philippova, O. E., Sitnikova, N. L., Demidovich, G. B., Khokhlov, A. R. *Macromolecules* **1996**, *29*, 4642.
- [3] Kramarenko, E. Yu. Khokhlov A. R. *Macromol. Theory Simul.* **1994**, *3*, 45.
- [4] Muthukumar, M. *J. Chem. Phys.* **2004**, *120*, 9343.
- [5] Philippova, O. E., Rumyantsev, A. M., Kramarenko, E. Yu, Khokhlov, A.R. *Macromolecules* **2013**, *46*, 9359.

**June 25, 9.30-10.30**

## **MOLECULAR DYNAMICS OF POLYELECTROLYTES**

**Kurt Kremer**

*Max Planck Institute for Polymer Research, Germany*

The lecture will give an introduction to computer simulation methods for polyelectrolyte systems. Electrostatic interactions can either be taken into account through screened Coulomb interactions or by explicitly considering all counter and salt ions. The first has been extensively used to study the persistence length of semiflexible polyelectrolytes, while the latter is needed for all cases, where charge fluctuations play a role. The focus of the present lecture will be on exemplary systems, where counter and salt ions are explicitly considered. Besides introducing some basic concepts characteristic examples like swelling-deswelling of gels, pearl necklace structures, condensation of ions onto semiflexible objects as well as wrapping of charged colloids will be given.

June 25, 10.40-11.40

## **BLOCK COPOLYMER POLYELECTROLYTES IN DILUTE SOLUTION**

Ekaterina B. Zhulina

*Institute of macromolecular compounds & ITMO University, Saint Petersburg,  
Russia*

1. We start with review of generic features of self-assembly of neutral diblock copolymers in solution: introduce critical micelle concentration, discuss different free energy contributions leading to scaling dependences of micelle characteristics, and consider transitions between different micelle morphologies.
2. In the main part of lecture we consider block copolymers with one polyelectrolyte and one neutral block, and discuss how micelles change due to introduction of the electrostatic interactions in the corona. We demonstrate that micelles with weak corona-forming polyelectrolyte block whose charge depends on pH, ionic strength and concentration of ionizable groups, demonstrate a more diverse behavior than micelles with strong polyelectrolyte corona.
3. We then briefly discuss conformations of diblock copolymer with oppositely charged blocks with focus on the effect of disproportionation, leading to many-chain micelles with almost neutral core and corona composed of only few charged tails.
4. In the final part of lecture we consider protein aggregates and discuss the differences between elastin-like protein micelles, casein micelles and cylindrical neurofilaments and synthetic polymer micelles.

June 25, 13.30-14.30

# **FUNDAMENTALS OF DIELECTRIC EFFECTS AND DIELECTRIC SPECTROSCOPY OF ELECTROLYTE AND POLYELECTROLYTE SOLUTIONS**

Roland Netz

*Freie Universität Berlin, Germany*

Dielectric spectroscopy is an important tool to study structural and dynamical properties of polyelectrolyte solutions since spectral features at different frequencies address competing processes in a vast range of time scales. We discuss several dielectric modes that arise from the dielectric response of PE chains themselves, counterions as well as water molecules. The dynamic and structural properties of water in the immediate vicinity of ions and charged groups are important for a number of technological and biological processes. Solvation water in electrolyte solution constitutes without doubt the simplest scenario, yet a number of open and puzzling questions exist. Infra-red spectroscopic studies demonstrate that solvation water next to ions is generally slowed down in its orientational motion. In contrast, experiments in the GHz and the THz regimes probe the collective water motion and demonstrate a speed-up (blue-shift) of the water relaxation with rising electrolyte concentration. This blue shift is due to collective dynamic effects, i.e., the coupling of the dynamics of one water molecule to its neighbors. The dielectric decrement and the blue shift of electrolyte dielectric spectra are connected and the consequence of the dielectric structure breaking influence of ions on the first solvation shell of water, in line with the Madden–Kivelson theory. In polyelectrolyte solutions additional low-frequency relaxation modes are observed that can be used to extract polymeric length scales and counterion dynamics. The slowest dielectric relaxation in salt-free PE solutions is suggested to follow from thermally activated barrier-hopping processes of counterions between neighboring PE chains. Similar barrier-hopping events of single protons in water clusters are shown to lead to broad spectral signatures in the infra-red regime.

**June 25, 14.40-15.40**

## **ASSEMBLY OF ANISOTROPIC FUNCTIONALIZED PARTICLES**

Monica Olvera de la Cruz  
*Northwestern University, USA*

The selectivity of DNA recognition inspires an elegant protocol for designing versatile nanoparticle (NP) assemblies. In recent years, a coarse-grained, scale accurate model for molecular dynamics was able to capture relevant kinetics of the DNA hybridization events and predict the crystallization behavior of various binary compounds of spherical DNA-functionalized nanoparticles. We have extended this model to describe the assembly of anisotropic shapes of functionalized nanoparticles. I will describe the assembly of functionalized gold nanoparticles with geometric shapes such as cubes and octahedra, as well as of DNA functionalized proteins. Addition of anisotropy can provide an analog to the atomic orbitals exhibited by conventional atomic crystals. We present results for various combinations of anisotropic shapes.



**June 25, 15.50-16.20**

## **DPD SIMULATION OF CHARGED SYSTEMS**

Alexei A. Gavrilov

*Lomonosov Moscow State University, Russia*

For polyelectrolyte systems, explicit treatment of the electrostatic interactions plays a key role in understanding phenomena that do not occur in noncharged systems. Dissipative particle dynamics (DPD) has proven to be a powerful tool to simulate the behavior of various polymer systems; however, the inclusion of the Coulombic interactions in DPD is somewhat complicated because of the soft-core nature of the volume interactions in DPD. The ways of introduction of the long-range Coulombic forces in coarse-grained DPD simulations will be discussed alongside with some usage examples.

