

# **Self-Assembly of Block Copolymers: Theoretical Models and Mathematical Challenges**

## **May 23 – May 28, 2010**

### **MEALS**

\*Breakfast (Buffet): 7:00 – 9:30 am, Sally Borden Building, Monday – Friday

\*Lunch (Buffet): 11:30 am – 1:30 pm, Sally Borden Building, Monday – Friday

\*Dinner (Buffet): 5:30 – 7:30 pm, Sally Borden Building, Sunday – Thursday

Coffee Breaks: As per daily schedule, 2nd floor lounge, Corbett Hall

**\*Please remember to scan your meal card at the host/hostess station in the dining room for each meal.**

### **MEETING ROOMS**

**All lectures will be held in Max Bell 159 (Max Bell Building accessible by walkway on 2nd floor of Corbett Hall). LCD projector, overhead projectors and blackboards are available for presentations.** *Note that the meeting space designated for BIRS is the lower level of Max Bell, Rooms 155-159. Please respect that all other space has been contracted to other Banff Centre guests, including any Food and Beverages in those areas.*

### **SCHEDULE**

#### **Sunday**

16:00 Check-in begins (Front Desk – Professional Development Centre - open 24 hours)

Lecture rooms available after 16:00 (if desired)

17:30-19:30 Buffet Dinner

20:00 Informal gathering in 2nd floor lounge, Corbett Hall  
Beverages and small assortment of snacks are available on a cash honor system.

#### **Monday**

7:00-8:45 Breakfast

8:45-9:00 Introduction and Welcome by BIRS Station Manager, Max Bell 159

9:00 – 10:30 Friederike Schmid -- Introductory Minicourse

10:30 – 11:00 Coffee Break, 2nd floor lounge, Corbett Hall

11:00-11:45 Feng Qiu

11:45 - 14:00 Lunch

14:00 – 14:45 Mark Matsen

14:45 – 15:15 Coffee Break, 2nd floor lounge, Corbett Hall

15:15 – 16:00 Carlos Garcia-Cevera

16:00 - 16:45 Marcus Muller

16:45 – 17:00 short break

17:00 – 17:45 Michael Schick

17:45-19:30 Dinner

## **Tuesday**

7:00-9:00 Breakfast

9:00 – 9:45 Takao Ohta

9:45 – 10:30 Masao Doi

10:30 – 11:00 Coffee Break, 2nd floor lounge, Corbett Hall

11:00 – 11:45 JF Williams

11:45 - 13:00 Lunch

13:00-13:50 Guided Tour of The Banff Centre; meet in the 2nd floor lounge, Corbett Hall

13:50 - 14:00 Group Photo (stairs outside the front if Corbett Hall)

14:00 – 14:45 Karl Glasner

14:45 – 15:15 Coffee Break, 2nd floor lounge, Corbett Hall

15:15 – 16:00 Cyrill Muratov

16:00 - 16:45 Yoshihito Oshita

16:45 – 17:00 short break

17:00 – 17:45 Xiaofeng Ren

17:45-19:30 Dinner

## **Wednesday**

7:00-9:00 Breakfast

9:00 – 9:45 Baohui Li

9:45 – 10:30 Toshihiro Kawakatsu

10:30 – 10:50 Coffee Break, 2nd floor lounge, Corbett Hall

10:50 – 11:35 Andrei Zvelindovsky

11:35 – 12:20 Friederike Schmid

12:20 - 13:30 Lunch

AFTERNOON FREE

17:30-19:30 Dinner

## **Thursday**

7:00- 9:00 Breakfast

9:00 – 9:45 David Morse

9:45 – 10:30 Zhen-Gang Wang

10:30 – 11:00 Coffee Break, 2nd floor lounge, Corbett Hall

11:00 – 11:45 Zhaoyan Sun

11:45 - 14:00 Lunch

14:00 – 14:45 Chun Liu

14:45 – 15:15 Coffee Break, 2nd floor lounge, Corbett Hall

15:15 – 16:00 Tetsuo Deguchi

16:00 - 16:45 Vanessa Weith

16:45 – 17:45 Poster Session

17:45 - 19:30 Dinner

## **Friday**

7:00-9:00 Breakfast

9:00 – 9:45 Qiang Wang

9:45 – 10:30 Weihua Li

10:30 – 11:00 Coffee Break, 2nd floor lounge, Corbett Hall

11:00 – 11:45 Concluding Lecture and Discussion

11:45 - 13:30 Lunch

### **Checkout by 12 noon.**

\*\* 5-day workshop participants are welcome to use BIRS facilities (2nd Floor Lounge, Max Bell Meeting Rooms, Reading Room) until 3 pm on Friday, although participants are still required to checkout of the guest rooms by 12 noon. \*\*

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Mathematical Challenges  
May 23 – May 28, 2010**

**ABSTRACTS**

(in alphabetic order by speaker surname)

**Speaker:** Masao Doi

**Title:** *Computational Implementation of Ohta-Kawasaki Density Functional for Block Polymers having General Architecture*

**Abstract:** The Ohta-Kawasaki theory gives a simple expression for the free energy of the melt of block copolymers as a functional of the density distribution of each blocks. Here I will discuss how to generalize this theory for the block copolymers of general architecture, and how to implement it in computational code. This talk is based on the work: "Density functional theory for block copolymer melts and blends", Takashi Uneyama and Masao Doi, *Macromolecules*, **38**, 196-205 (2005).

**Speaker:** Tetsuo Deguchi, Department of Physics, Ochanomizu University

**Title:** *Random Knotting and applications to Polymer Physics*

**Abstract:** Recently, topological effects of ring polymers have attracted much attention in various fields of science such as physics, biology and chemistry. DNA knots, knots in proteins, and synthetic ring polymers have been extensively studied not only theoretically but also experimentally. Interestingly, their mesoscopic or macroscopic properties may depend on their topology. The topology of a ring polymer is given by its knot type, and it does not change under thermal fluctuations. Here the conformations of real ring polymers in solution are modeled by those of random polygons or self-avoiding polygons under some topological constraint.

In this talk, we discuss application of knot invariants to the statistical mechanics of

physical systems of ring polymers in solution. We first formulate simulation scheme making use of knot invariants, and then systematically evaluate physical quantities of the system of ring polymers in solution [1,2,3]. In order to analyze the simulation data, we introduce so called scaling arguments, and derive approximate formulas for describing the parameter-dependence of some physical quantity. As such a parameter, we often consider the number of segments,  $N$  (in the unit of the Kuhn length).

In particular, we discuss the probability of random knotting and the average size (mean square radius of gyration) of random polygons with a fixed knot type as functions of  $N$ . We show swelling of ring polymers due to topological constraints in the theta solution. We also introduce an effective formula for the distribution function of the distance between two given segments of a polygon.

Through some examples we show that simulation using knot invariants should be useful in application to real ring polymers. In fact, the results of the present talk can be checked in experiments of polymers near future. We thus connect the mathematics of knots with polymer physics.

[1] T. Deguchi and K. Tsurusaki, Random knots and links and applications to polymer physics, in ``Lectures at Knots '96'', edited by S. Suzuki, (World Scientific, Singapore, 1997) pp. 95-122.

[2] M. K. Shimamura and T. Deguchi, Finite-size and asymptotic behaviors of the gyration radius of knotted cylindrical self-avoiding polygons, *Phys. Rev. E* **65**, 051802 (2002). (9 pages)

[3] M. K. Shimamura and T. Deguchi, On the mean gyration radius and the radial distribution function of ring polymers with excluded-volume under a topological constraint, in ``Physical and Numerical Models in Knot Theory'', edited by J.A. Calvo, K.C. Millett and E.J. Rawdon, (World Scientific, Singapore, 2005) pp. 399 -- 419.

**Speaker:** Karl Glasner, Department of Mathematics, University of Arizona

**Title:** *The Subcritical Regime of Copolymer Mixtures*

**Abstract:** Most of the attention given to theoretical descriptions of BCPs is concerned with supercritical pattern formation, in particular periodic or nearly periodic equilibria. In contrast, nontrivial localized equilibria can also exist over a range of parameters below the point of phase separation. In the abstract theory of pattern formation (described e.g. by the Swift-Hohenberg equation) this phenomenon has been studied at length. For A-B copolymer mixtures, these describe localized micelles or bilayer structures. This talk will discuss recent advances in understanding the complex bifurcation diagram for localized equilibria, and their implications for density functional models of BCPs. Aspects of dynamics will also be considered, including instabilities and self-replication phenomenon.

**Speaker:** Carlos Garcia Cevera, Department of Mathematics, UC Santa Barbara

**Title:** *Numerical advances in Self-Consistent Field Theory simulations, and applications to block copolymer lithography*

**Abstract:** I will discuss some recent developments in the numerical simulation of self-consistent field theory (SCFT) for block copolymers. I will focus on the following applications:

SCFT simulations of block copolymers laterally confined in a square well: Here we explore the conditions for which self-assembly in laterally confined thin block copolymer films results in tetragonal square arrays of standing up cylinders. More specifically, we study the equilibrium phase behavior of thin films composed of a blend of AB block copolymer and A homopolymer laterally confined in square wells. By using suitable homopolymer additives and appropriately sized wells, we observed square lattices of upright B cylinders that are not stable in pure AB block copolymer systems. Considering the potential application of such films in block copolymer lithography, we also conducted numerical SCFT simulations of the role of line edge roughness at the periphery of the square well on feature defect populations. Our results indicate that the tetragonal ordering observed under square confinement is robust to a wide range of boundary perturbations.

SCFT simulations of block copolymers on the surface of a sphere: In this model, we assume that the composition of the thin block copolymer film is independent of the radial direction. Using this approach we were able to study the phase separation process, and specifically the formation of defects in the lamellar and cylindrical phases, and its dependence on the radius of the sphere. If time permits, I will discuss recent work on polymer brushes.

Numerical Solution of the complex Langevin (CL) equations in polymer field theory: I will discuss some improved time integration schemes for solving the nonlinear, nonlocal stochastic CL equations. These methods can decrease the computation time required by orders of magnitude. Further, I will show how the spatial and temporal multiscale nature of the system can be addressed by the use of Fourier acceleration.

**Speaker:** Toshihiro Kawakatsu, Department of Physics, Tohoku University

**Title:** *Self-consistent field theory for polymers under confinement*

**Abstract:** In the problem of polymer confinement in a narrow container, reduction in the entropy of the chain conformation plays an important role. As a result of this conformation entropy effect, confined block copolymers show various complex mesophases such as hexagonally perforated lamellar phase (in a thin layer) or helical domain phase (in a thin cylinder), which are not be stable in 3-dimensional bulk phase. We simulate the dynamics of phase transitions of such confined systems by using dynamical self-consistent field theory with which one can take the conformation entropy into account. We also discuss effect of soft confinement by flexible container as another interesting topic on polymer confinement.

**Speaker:** Baohui Li, School of Physics, Nankai University

**Title:** *Block Copolymers Under Various Spatial Confinements*

**Abstract:** Block copolymers have attracted increasing interest both scientifically and in view of a growing number of technological applications because they are capable of forming different ordered phases at nanoscopic length scales. Nano-confinement of block copolymers can be used to produce novel morphologies with potentially novel applications. The influence of confinement on the microphase separation and morphology



of block copolymers is also of fundamental interest in polymer science. In a spatially confined environment, structural frustration, confinement-induced entropy loss and surface-polymer interactions can strongly influence the molecular organization. We have systemically investigated the self-assembly of diblock copolymers in various geometric confinements using a simulated annealing simulations. A rich variety of novel morphologies is obtained, depending on the copolymer component and the confinement geometry. The morphological transitions can be understood based on the degree of structural frustration parametrized by the ratio of the confining size to the characteristic length of the bulk phase. The studies demonstrate that confined self-assembly of block copolymers provides a robust method to produce nanoscopic structures which are not accessible in the unconfined state.

**Speaker:** Weihua Li, Department of Macromolecular Science, Fudan University

**Title:** *Applications of real-space SCFT on the study of self-assembly of block copolymers*

**Abstract:** The self-consistent field theory (SCFT) has been proven to be one of the most successful theories in the study of self-assembling behaviors of block copolymers. The application of the real-space approach of SCFT has been broadened by the development of the high-efficient pseudo-spectral method. It can be readily used to study the self-assembly of block copolymers under geometrical confinement and the self-assembly of complex block copolymers. Though it cannot have free energy accuracy as high as that of reciprocal method, it can calculate reliable phase diagrams. A few examples of its applications, including AB diblock copolymers in nanopores, linear multiblock copolymers, and ABC star triblock copolymers, are discussed here. A lot of interesting structures are observed in these block copolymer systems, and some of them have been seen by experiments.

**Speaker:** Chun Liu, Department of Mathematics, Penn State

**Title:** *Energetic Variational Approaches in the Modeling of Ionic Solutions and Ion Channels*

**Abstract:** Ion channels are key components in a wide variety of biological processes. The selectivity of ion channels is the key to many biological processes. Selectivities in both calcium and sodium channels can be described by the reduced models, taking into consideration of dielectric coefficient and ion particle sizes, as well as their very different primary structure and properties. These self-organized systems will be modeled and analyzed with energetic variational approaches (EnVarA) that were motivated by classical works of Rayleigh and Onsager. The resulting/derived multiphysics multiscale systems automatically satisfy the Second Laws of Thermodynamics and the basic physics that are involved in the system, such as the microscopic diffusion, the electrostatics and the macroscopic conservation of momentum, as well as the physical boundary conditions. In this talk, I will discuss the some of the related biological, physics, chemistry and mathematical issues arising in this area.

**Speaker:** Mark Matsen, Department of Mathematics, University of Reading

**Title:** *The strong-segregation limit of SCFT*

**Abstract:** Helfand's SCFT for block copolymer melts has two analytical limits: the weak-segregation regime described by Leibler's RPA theory and the strong-segregation regime treated by Semenov's SST calculation. The validity of the weak-segregation theory is easily established, but all previous attempts have failed to demonstrate the convergence of the SCFT to the analytical strong-segregation theory. This raises a question of whether or not something is missing from the current formulation of SST. We re-address the convergence by pushing the numerical SCFT calculations to ultra-high degrees of segregation and by examining finite-segregation corrections to SST.

**Speaker:** David Morse, Chemical Engineering and Materials Science, University of Minnesota

**Abstract:** *Block Copolymer Theory Beyond the Self-Consistent Field Approximation*

**Title:** Correlations in homoogenous block copolymer liquids and polymer mixtures, as measured by small-angle x-ray and neutron scattering experiments, are often analyzed by

comparing to the random-phase approximation (RPA) theory. The RPA theory for the structure factor  $S(q)$  is an integral part of the SCFT theory of inhomogeneous liquids, and can be obtained by using SCFT to calculate the freeenergy cost of small composition fluctuations.

I will discuss progress in the development and testing of a systematic theory of corrections

to the RPA theory for  $S(q)$  in homogeneous liquids. A dimensionless measure of the degree of chain overlap (" $N_{\text{bar}}$ ") appears as a natural small parameter, and SCFT is recovered in the limit of infinitely strong overlap (i.e., infinitely long chains). We have carried out explicit calculations of the lowest order "one-loop" corrections to the RPA.

One important qualitative prediction, which appears to extend beyond the one-loop level, is the existence of a universal form for the free energy functional for polymer liquids that depends only upon the dimensionless parameters of SCFT (composition,  $\chi N$ , etc.), plus  $N_{\text{bar}}$  as one additional parameter. The most important technical challenge that has been addressed by relatively recent work by several groups is the extreme sensitivity of the theory for

incompressible liquids upon model-dependent details of very short wavelength correlations, and the need to interpret the theory in a way that takes this into account.

A substantial part of the talk will be devoted to presenting results of molecular simulations that have been carried out to test the one-loop theory, and to test the predicted degree of universality among different simulation models.

**Speaker:** Marcus Muller, Institut für Theoretische Physik Georg-August-Universität

**Title:** *Structure formation in block copolymers and polymer blends*

**Abstract:** Using soft, coarse-grained models we study the kinetics of structure formation in dense, multi-component polymer liquids. In the first part, I will discuss the consequences of soft potentials that naturally arise from a coarse-graining procedure and allow for an overlap of the coarse-grained interaction centers (segments). This feature allows to increase the segment density and to model experimental values of the invariant degree of polymerization resulting in a realistic strength of fluctuations. The softness, however, does not prevent the bonds to cross each other during the course of their motion. The role of non-crossability on the kinetics of self-assembly is briefly illustrated and a slip-link model à la Likhtman is employed to mimic entanglement effects in an effective way.

In the second part, I will discuss how to couple a particle model of a dense, binary polymer melt to a Ginzburg-Landau description. Coupling the order-parameter field,  $\phi$ , of the Ginzburg-Landau description to the particle model by restraining the

composition fluctuations of the particle model, we can calculate the chemical potential field,  $\mu$ , that corresponds to the order-parameter field,  $m$ . This information allows to reconstruct the underlying free-energy functional of the Ginzburg-Landau description. We use a simple trial form of the free-energy functional containing a small number of parameters -- i.e., the Flory-Huggins parameter and the coefficient in front of the square gradient term -- and determine these free parameters from a short simulation of the coupled system. Then, we use the so-parameterized Ginzburg-Landau description to propagate the order-parameter field in time and couple the particle-based model to the new order-parameter field configuration. The strong coupling makes the particle-based model quickly adapt to the new  $m$ , and the simulation cycle commences again. The advantages of this computational technique are two-fold: (i) it provides an approximation for the free-energy functional for the Ginzburg-Landau description of the particle model and (ii) the coupling speeds up the simulation of the particle-based system. The latter effect is related to the scale separation between the strong bonded forces, that dictate the time step in the particle model, and the weak non-bonded forces, that drive the structure formation.

**Speaker:** Cyrill Muratov, Department of Mathematical Sciences, NJIT

**Title:** *Droplet phases in compositionally asymmetric diblock copolymer melts in two dimensions*

**Abstract:** In this talk, I will discuss the energetics of diblock copolymer melts under strong segregation and high compositional asymmetry, which favor periodic lattices of compact droplets of the minority phase as energy minimizers. I will begin by identifying the contribution of the lattice geometry to the energy which is responsible for the lattice selection and show that in two dimensions a hexagonal lattice is optimal among simple lattices. I will then present an analysis of the same problem in the two-dimensional Ohta-Kawasaki model near the onset of multi-droplet patterns. As a first step, I will show that under suitable scaling the energy of minimizers becomes asymptotically equal to that of a sharp interface energy with screened Coulomb interaction. I will then show that the minimizers of the corresponding sharp interface energy consist of nearly identical

circular droplets of small size separated by large distances. I will finally show that in a suitable limit these droplets become uniformly distributed throughout the domain.

**Speaker:** Takao Ohta, Department of Physics, Kyoto University

**Title:** *Dynamics of gyroid structure in microphase separation*

**Abstract:** We study dynamics of microphase separation in diblock copolymer melts focusing on the double gyroid structure based on the Cahn-Hilliard type equation for local concentration. The theoretical results by means of the mode expansion method are given for formation of gyroid, structural transitions between gyroid and other states [1], and the viscoelastic response [2]. The real space numerical results for a coexistence state of gyroid and lamellar structures are also shown [3]. Some of the related results obtained by the self-consistent mean field theory [4] are discussed. Furthermore, we describe formation of interconnected structures in Turing pattern in three dimensions, which is mathematically related to the microphase separation problem [5]. Extension of the theory introducing the variables other than concentration is also briefly mentioned.

[1] K. Yamada, M. Nonomura and T. Ohta, "Kinetics of morphological transitions in microphase-separated diblock copolymers," *Macromolecules* **37**, 5762 (2004).

[2] R. Tamate, K. Yamada, J. Vinals, and T. Ohta, "Structural rheology of microphase separated diblock copolymers", *J. Phys. Soc. Jpn.*, **77** 034802 (2008).

[3] K. Yamada and T. Ohta, "Interface between lamellar and gyroid structures in diblock copolymer melts", *J. Phys. Soc. Jpn.*, **76**, 084801 (2007).

[4] C. A. Tyler and D. C. Morse, "Linear elasticity of cubic phases in block copolymer melts by self-consistent field theory", *Macromolecules*, **36**, 3764 (2003).

[5] H. Shoji, K. Yamada, D. Ueyama and T. Ohta, "Turing patterns in three dimensions" *Phys. Rev. E* **75**, 046212 (2007).

**Speaker:** Yoshihito Oshita, Department of Mathematics, Okayama University

**Title:** *A rigorous derivation of mean-field models for diblock copolymer melts*

**Abstract:** We study the free boundary problem describing the micro phase separation of

diblock copolymer melts in the regime that one component has small volume fraction such that micro phase separation results in an ensemble of small balls of one component. Mean-field models for the evolution of a large ensemble of such spheres have been formally derived in Glasner and Choksi (Physica D, 238:1241–1255, 2009), Helmers et al. (Netw Heterog Media, 3(3):615–632, 2008). It turns out that on a time scale of the order of the average volume of the spheres, the evolution is dominated by coarsening and subsequent stabilization of the radii of the spheres, whereas migration becomes only relevant on a larger time scale. Starting from the free boundary problem restricted to balls we rigorously derive the mean-field equations in the early time regime. Our analysis is based on passing to the homogenization limit in the variational framework of a gradient flow.

**Speaker:** Feng Qiu, Department of Macromolecular Science, Fudan University

**Title:** *Discovering Ordered Phases of Multi-block Copolymers: A Generic Fourier-Space Approach*

**Abstract:** We propose a generic approach to solve the self-consistent field theory (SCFT) equations for the discovery of complex ordered structures of block copolymers. In our method, all spatially varying functions are expanded in terms of Fourier series which are essentially determined by computational box parameters. Then SCFT equations can be cast in terms of expansion coefficients. The solutions of the SCFT equations can then be obtained using any of the available numerical techniques. The essence of this approach is to use the full-power of the spectral method, in which the symmetry of the ordered phases is not presumed. Furthermore, our Fourier-space method has the advantage of identifying new complex structures, especially continuous structures, more easily and definitively.

With this method, we successfully reproduce phases observed in diblock copolymers. We have confirmed that the generic Fourier-space method leads to equilibrated lamella, cylinder, gyroid,  $O^{70}$ , and sphere phases at the compositions and  $\chi$  values consistent with the Matsen-Schick phase diagrams. Our emphasis has been focused on phase behaviors

of ABC linear and star-shaped triblock copolymers, in which both centro- and noncentro-symmetric phases can be formed. The phase diagram of a model “frustrated” ABC triblock copolymer is constructed. A number of new phases are predicted for the linear triblock copolymers. Then the method is further applied to a more realistic model of SEBM triblock copolymer, in which the fascinating KP phase is predicted to occur at the parameters that mostly match the experiment conditions.

For ABC star triblock copolymers, the most important architectural feature is that their three blocks are joined at one junction point. In an ordered phase the junction points are constrained in one-dimensional lines, resulting novel microphase-separated morphologies such as tiling patterns. A variety of tiling patterns in ABC star triblocks have been predicted using the Fourier-space method and relevant phase diagrams have been constructed. The predicted phase transition sequences from the SCFT calculations are in qualitative agreement with experimental and Monte Carlo simulation results.

We believe that the generic Fourier-space approach is a powerful method to predict novel ordered phases for complex block copolymers. These ordered structures can be used as input for the more accurate and efficient real-space or reciprocal-space methods.

**Speaker:** Xiaofeng Ren, Department of Mathematics, George Washington University

**Title:** *Ansätze of the curvature-potential equation from morphology and morphogenesis problems*

**Abstract:** Pattern formation problems arise in many physical and biological systems as orderly outcomes of self-organization principles. Examples include animal coats, skin pigmentation, and morphological phases in block copolymers. Recent advances in singular perturbation theory and asymptotic analysis have made it possible to study these problems rigorously. In this talk I will discuss a central theme in the construction of various patterns as solutions to some well known PDE and geometric problems: how a single piece of structure built on the entire space can be used as an ansatz to produce a near periodic pattern on a bounded domain. We start with the simple disc and show how

the spot pattern in morphogenesis and the cylindrical phase in diblock copolymers can be mathematically explained. More complex are the ring structure and the oval structure which can also be used to construct solutions on bounded domains. Finally we discuss the newly discovered smoke-ring structure and the toroidal tube structure in space. The results presented in this lecture come from joint works with Kang, Kolokolnikov, and Wei.

**Speaker:** Michael Schick, Department of Physics, University of Washington

**Title:** *Ionic Effects on the Electric Field needed to Orient Dielectric Lamellae*

**Abstract:** We consider the effect of mobile ions on the applied potential needed to reorient a lamellar system of two different materials placed between two planar electrodes. The reorientation occurs from a configuration parallel to the electrodes favored by surface interactions to an orientation perpendicular to the electrodes favored by the electric field. The system consists of alternating A and B layers with different dielectric constants. The mobile ions are assumed to be insoluble in the B layers and hence confined to the A layers. We find that the ions reduce the needed voltage most strongly when they are constrained such that each A lamella is electrically neutral. In this case, a macroscopic separation of charge and its concomitant lowering of free energy, is attained only in the perpendicular orientation. When the ions are free to move between different A layers, such that charge neutrality is only required globally, their effect is smaller and depends upon the preferred surface interaction of the two materials. Under some conditions, the addition of ions can actually stabilize the parallel configuration. Our predictions are relevant to recent experiments conducted on lamellar phases of diblock copolymer films with ionic selective impurities.

**Speaker:** Friederike Schmid, Institut fuer Physik. Universitaet *Mainz*

**Introductory Minicourse:** *Self-Consistent Field Theories of Inhomogeneous (Co)polymer blends*

**Abstract:** The course gives an introduction into basic concepts of the theory of polymer/copolymer blends, with a particular emphasis on the so-called 'self-consistent



field theory' (SCF theory). It is aimed at an audience who is not familiar with this theory. Everybody else should sleep in or have coffee instead. The topics to be covered include

General introduction in polymer models

Flory Huggins theory and chi-parameter

Detailed introduction into the SCF theory

Limiting behavior at 'strong' and 'weak' segregation, in particular, connection to

Ginzburg-Landau theories like the Ohta-Kawasaki functional

Fluctuation effects

Time-dependent density-functional theory and time-dependent Ginzburg-Landau theory

Applications

**Speaker:** Friederike Schmid, Institut fuer Physik, Universitaet *Mainz*

**Title:** *Copolymer self-assembly at nonequilibrium and in networks*

**Abstract:** The talk will have two parts. The first part deals with the kinetics of nanostructure formation in amphiphilic copolymer solutions. Copolymers in solution spontaneously aggregate into a variety of nanostructures, e.g., micelles or vesicles, which can be tuned by tuning system parameters such as the chain lengths, the block lengths, the composition etc, This can be used to prepare nanoscaled materials with well-defined properties. Using a dynamic density functional approach, we studied the dynamical processes leading to spontaneous vesicle formation in copolymer solutions. Depending on the system parameters, vesicle formation is found to proceed via different pathways. The final structure depends on the pathway. Under certain conditions, toroidal and even cage-like micelles (i.e., perforated vesicles) can be obtained.

In the second part, a method to construct a self-consistent field theory for crosslinked systems is proposed. The original SCF theory is devised for polymer fluids; however, many polymeric materials have a network structure, which means that they respond

elastically to stress and that deformations are restored. A generalized SCF theory for networks shall be devised and first application examples shall be presented.

**Speaker:** Zhao-Yan Sun, Changchun Institute of Applied Chemistry

**Title:**

*Effects of Architecture and Composition on the Microphase Separation of Block Copolymers*

**Abstract:** It is well-known that block copolymer systems have fascinating ability to self-assemble into a variety of smart soft materials and well-controlled micro-phase structures on nanometer scale. With the development of synthetic methods, multi-component block copolymer systems with complex chain architectures such as pi-shaped and H-shaped block copolymer can be synthesized easily in experiments. These block copolymers may have some important applications in the fields such as macromolecular self-assembly, controlled drug delivery, and the preparation of advanced materials. Therefore, it is very important to explore the self-assembly of block copolymers with complex chain architecture. In this work, the combinatorial screening method based on the self-consistent field theory (SCFT) proposed by Drolet and Fredrickson is employed to investigate the self-assembly of pi-shaped and H-shaped block copolymers. Our results may provide some theoretical guidance for exploring the self-assembly of multi-component block copolymer systems with complex chain architectures.

**Speaker:** Zhen-Gang Wang, Division of Chemistry and Chemical Engineering, California Institute of Technology

**Title:** *Self Energy of Small Ions*

**Abstract:** We address the issue of the self energy of the mobile ions in electrolyte solutions within a general Gaussian renormalized fluctuation theory using a field-theoretic approach. We introduce the Born radii of the ions in the form of a charge distribution allowing for different Born radii between the cations and anions. The model thus automatically yields a theory free of divergences and accounts for the solvation of the ions at the level of continuous dielectric media. In an inhomogeneous dielectric

medium, the self energy is in general position dependent and differences in the self energy between cations and anions can give rise to local charge separation in a macroscopically neutral system. Treating the Born radius  $a$  as a smallness parameter, we show that the self energy can be split into an  $O(a^{-1})$  nonuniversal contribution and an  $O(a^0)$  universal contribution that depends only on the ion concentration, valency, and the spatially varying dielectric constant. For a weakly inhomogeneous dielectric medium, the nonuniversal part of the self energy is shown to have the form of the Born energy with the local dielectric constant. This self energy can be incorporated into the Poisson-Boltzmann equation, in conjunction with other mean-field approaches, such as self-consistent field theory for polymers, as a simple means of including this local fluctuation effect at a mean-field level. We illustrate the application of this born-energy augmented Poisson-Boltzmann approach to the problem of interface tension between two salt containing solutions, highlighting the effects of the interfacial widths and salt concentration.

**Speaker:** Qiang (David) Wang, Department of Chemical and Biological Engineering, Colorado State University

**Title:** *Some Applications of SCFT and Its Quantitative Test by Fast Lattice Monte Carlo Simulation*

**Abstract:** I will first present some of our recent work using real-space self-consistent field (SCF) calculations with high accuracy to study (1) diblock copolymers (DBC) under nano-confinement, (2) stimuli-responsive surfaces from DBC brushes, and (3) polyelectrolyte adsorption and layer-by-layer assembly. I will then talk about comparisons between lattice SCF theory and fast lattice Monte Carlo (FLMC) simulations that are based on exactly the same Hamiltonian, thus with no parameter-fitting between the two. Such comparisons provide the most stringent test of the SCF theory, and unambiguously and quantitatively reveal the system fluctuations/correlations neglected in the theory.

**Speaker:** JF Williams, Department of Mathematics, Simon Fraser University

**Title:** *Asymptotic analysis and computation for minimizers of a modified Cahn-Hilliard energy in 3D*

**Abstract:** In this talk I will present an asymptotic analysis of the energy-driven pattern formation induced by competing short and long range effects in a model for self-assembly of diblock copolymers. This work shows that structures predicted by the self-consistent mean field theory may be constructed via asymptotic analysis of the associated PDE. Additionally, local minimizers, such as the perforated lamella, may also be understood. All asymptotic constructions are verified by simulation of an evolutionary PDE via modified gradient descent starting from random initial conditions.

**Speaker:** Vanessa Weith, Theoretische Physik I, Universitaet Bayreuth

**Title:** *Dynamics of Janus particles in a phase-separating binary mixture*

**Abstract:** Adding particles to a binary mixture induces an interesting dynamic coupling between the wetting of the particles and the phase separation of the mixture. Recently a new class of colloidal particles, so-called Janus particles, have been synthesized in large quantities [1]. Janus particles, named after the Roman god Janus, represent colloids with a different chemical composition of the surface of the two halves of a particle. Accordingly each half of a particle may be wetted preferentially by one component of the mixture. We present the results of numerical simulations of the dynamics of Janus particles immersed in a phase-separating binary mixture based on a meanfield approach. When the two constituents of a binary mixture wet the two sides of a Janus particle differently, the particle induces a spatial variation of the concentration in their neighborhood. Accordingly, Janus particles in phase separating mixtures are trapped to interfaces, which leads to a complex dynamics. Due to the strong localization of an interface, the diffusion of Janus particles is much more pronounced compared with isotropic particles. As a result of this fast diffusion the Janus particles placed initially at large distances may effectively approach each other and they can remain coupled in the case of an appropriate orientation.

[1] A. Walther and A. H. E. Mueller, *Soft Matter* **4**, 663-668 (2008).

**Speaker:** Andrei V. Zvelindovsky, University of Central Lancashire

**Title:** *Kinetics of block copolymer phase transitions under electric field*

**Abstract:** Mesophases of block copolymers with blocks of different dielectric constants might undergo transformations under an applied electric field. These include orientational phase transitions of a particular phase or order-order transitions between phases of different symmetries. We modified dynamic SCFT in order to account for a non-isotropic diffusion due to the dielectric mismatch of blocks. We review our works, in which we study lamellar, cylindrical, spherical and gyroid phases under electric field. The results are compared with available experimental data and findings based on Ginzburg-Landau type theories.