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

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1 Overview of the Field

Block copolymers are macromolecules composed of two or more chemically distinct polymer chains linked together by covalent bonds. The thermodynamical incompatiblility between the different sub-chains drives the system to phase separate. However the covalent bonds between the different sub-chains prevent phase separation at a macroscopic length scale. As a result of these two competing trends, block copolymers undergo phase separation at a nanometer length scale, leading to an amazingly rich array of nanostructures. These structures present tremendous potentials for technological application because they allow for the synthesis of materials with tailored mechanical, electrical and chemical properties (see [2, 8, 11]).

The main challenge of block copolymer self-assembly is to describe and predict the possible nanostructures for a given set of molecular parameters such as the polymer architecture and monomer-monomer interactions. Searching different nanostructures and constructing phase diagrams for block copolymers have been very active research areas in soft matter physics involving physicists, chemists and materials scientists. Due to the virtually endless possibilities of block copolymer architectures, the phase space of the possible nanostructures is formidably large. Therefore theory and simulation are indispensable in the study of block copolymer self-assembly. In particular, theoretical results provide crucial understanding of the formation mechanism of these nanostructures, as well as useful guidance to the synthesis of block copolymers for particular complex nanostructures.

Most of the theoretical studies of block copolymers are based on a framework termed the self-consistent field theory (SCFT) [8]. The SCFT of polymers is a field theoretical representation of the statistical mechanics of polymers. It transforms the formidable task of integrating contributions to the partition function from many-chain interactions to the computation of the contribution of one polymer in a self-consistent field. Efforts from the physics and materials science communities have shown that SCFT is a powerful framework which is capable of describing and predicting the nanostructures of block copolymers ([8, 14, 21]). Specifically, the mean-field equations of SCFT are a set of highly nonlinearly and nonlocally coupled equations, whose solutions can be periodic functions corresponding to ordered three-dimensional structures. The challenge is to finding these solutions without *a priori* knowledge about the phases, which is equivalent to finding solutions of a nonlinear and nonlocal optimization problem. Although great progresses on the SCFT of block copolymers have been made in the last decades, many challenges still remain ([8, 14, 10]). From the

perspective of applied mathematics, two of these challenges are the understanding of the mathematical structure of the SCFT equations and the development of efficient computation techniques for complex ordered nanostructures.

To date, most mathematical work has centered on a simple theoretical model of block copolymers, the Ohta-Kawasaki model. Using an expansion in terms of monomer densities, the SCFT of block copolymers can be approximated by a Landau-type free energy functional, as shown by Leibler [13] in 1980. A variation of this expansion was proposed by Ohta and Kawasaki [18], leading to a simple theoretical model for diblock copolymers. As first noted in [17], the Ohta-Kawasaki model gives rise to a nonlocal perturbation of the ubiquitous Cahn-Hilliard problem which has been the generator of an immense body of work in applied math and nonlinear partial differential equations ([7]). However simple, the Ohta-Kawasaki functional has a tremendously rich mathematical structure, and is in fact the natural higher-dimensional analogue of a functional written down by S. Müller [15] as a toy problem to capture multiple scales. It can also simply be viewed as a paradigm for pattern formation induced by short and long-range interactions. The study of its rich energy landscape is central to our understanding of nonconvex and nonlocal variational problems, and it has lead to new mathematics. Examples include a deep and intricate spectral analysis [19]; a novel application of modular functions [5]; a rare two-dimensional result characterizing certain aspects of the ground state [16]; fascinating geometric questions on the relationship to stable constant mean curvature surfaces [20]; the creation of nonlocal extensions to standard second variation inequalities involving the mean curvature [6]; the analysis of rich multiscale variational problems [9]. Furthermore, it has fostered a very general result on the inherent periodicity of minimizers in the presence of long-range interactions [1].

2 Objectives of the Workshop

Given this rich mathematical progress, it is timely to draw the attention of applied mathematicians to the full self-consistent field theory and other recent developments in the statistical physics of inhomogeneous polymers.

The main objective of this workshop is to bring together for the first time two groups of researchers:

1) applied mathematicians with training in the calculus of variations and nonlinear PDE, scientific computing, applied probability, and with core interests in problems stemming from the material sciences, particularly polymeric materials;

2) physicists and engineers at the forefront of equilibrium models for inhomogeneous polymers, particularly self-assembly of block copolymers, whose work has a substantial mathematical component.

Given the tremendous activities and interests in block copolymer structures, it is important and timely to bring together these two communities, who have, as yet, had only limited interactions. So far, most mathematical work on block copolymer phases has centred on the simplified Ohta-Kawasaki model. These activities have lead to some rich mathematics and will no doubt continue to drive mathematical work in the future. It is therefore natural to extend the activities of applied mathematicians to other underlying equilibrium theories of inhomogeneous polymers. From a scientific point of view, the field theoretical models such as the SCFT have had a massive impact in many areas of physics and engineering. However these models have largely been untouched by applied mathematicians. Given the complex nonlinear and nonlocal structure of the SCFT equations, it is very likely that the SCFT model could lead to some interesting new mathematics. Furthermore, the substantial computational components in the theoretical studies of block copolymers makes the area ripe for a more mathematical perspective – be it in terms of rigor or in terms of computational sophistication. For the latter, recent collaborations [3, 4] of applied mathematicians with the Fredrickson group at UC Santa Barbara have revealed that such interactions can be fruitful. On the other hand, the materials sciences have proven to be an important source of problems in the modern calculus of variations and PDE, often provide a guiding force behind the exploration of certain classes of nonlinear PDEs and infinite dimensional, non-convex variational problems [12]. In this respect, exposing mathematicians to widely-used variational theories in contemporary polymer physics could only prove beneficial.

3 Presentation Highlights

The speakers at this workshop represent a wide array of progresses in the study of self-assembly of block copolymers. Topics include numerical implementation of SCFT and Ohta-Kawasaki density functional theory, methodology to obtain solutions of ordered phases for complex block copolymers, self-assembly of block copolymers under confinement, dynamics of structural formation, as well as the effect of electrostatics. Among these diverse problems addressed by the speakers, a few important topics emerged from them.

The first challenge to the applied mathematics and physics community is the development of efficient methods for the discovery of new ordered phases. Within the content of SCFT, this task corresponds to finding solutions for a nonlinear and nonlocal optimization problem. The theme of exploring complex ordered phases of block copolymers are contained in a number of talks, noticeably the presentations by Feng Qiu, Friederike Schmid, Marcus Muller, Weihua Li, Maso Doi, Zhao-Yan Sun and Carlos Garcia Cevera. A recent progress in this area is the development of a generic reciprocal-space method, as given by Feng Qiu. In this method, the SCFT theory is formulated in the Fourier space, leading to a set of nonlinear algebraic equations. Feng Qiu demonstrated that this method can be used to obtain a large number of preciously unknown ordered structures for ABC linear and start triblock copolymers. Another interesting progress in this area is the development of more realistic and fast simulation methods for block copolymers (Marcus Muller, Qiang Wang). Despite all these progresses, obtaining novel ordered phases from SCFT is still a challenging task. The general theme emerged from the discussions at the workshop is that a combination of real-space and reciprocal space methods presents a possible route for the search of ordered phases within the content of SCFT.

The second challenge to the applied mathematics and physics community is the understanding of block copolymers under confinement. In the talks by Baohui Li, Toshihoro Kawakatsu, and to some extent Xiaogfeng Ren, it has been clearly shown that confinement can lead to an amazingly rich array of ordered structures, which are not available in the bulk systems. In fact, block copolymers under confined have become an intensively researched area in the past few years in polymer physics community. From a theoretical point of view, confinement leads to extra controlling parameters for the self-assembly of block copolymers, corresponding to a nonlinear, nonlocal optimization problem within a finite domain of complex boundary conditions. So far, most of the novel structures were discovered from simulations. It is desirable to develop mathematical techniques for the systematic search of ordered phases for the confined system.

The third challenge to the applied mathematics and physics community is the study of phase transition dynamics. A couple of talks have been devoted to this topic (Takao Ohta and Andrei Zvelindovsky). Phase ordering dynamics is an extremely important topic but our understanding of the dynamics is still quite limited. The two talks presented in the workshop present an effort to study the phase transition dynamics using an extension of the SCFT. This approach does give us some important information about the kinetic pathways of the order to order phase transitions. The phase transition pathways can also be examined by studying the landscape of the SCFT free energy functional (An-Chang Shi et al). Despite all these progresses, dynamics of order-to-order phase transitions in soft matter is still a major challenge to the scientific community.

A forth challenge lies in an understanding of the SCFT in the strong segregation limit. To this end, there were two talks (Matsen and Muratov) with similar goals but completely different approaches and perspectives.

Besides the above highlights, another important topic in soft matter is the effect of charges on the equilibrium and dynamic properties of the materials, as represented by Zhen-Gang Wang, Michael Schick and Chun Liu. The challenge in the charged system is that the Coulombic interaction between charged species is long-range. New ideas and methods are needed for the study of these systems. Charged soft matter is a rapidly developing research area. It is hoped that this topics can be discussed in future BIRS workshop.

Finally we would like to emphasize there is an importance existence of the applied mathematicians to the research in this area, as demonstrated by the large number of talks from this group of researchers (e.g. Garcia-Cevera, Glasner, Muratov, Oshita, Ren, Williams). One interesting observation is that theory of Ohta-Kawasaki is remarkably successful given its simplicity. We expect that the Ohta-Kawasaki framework will continue to provide a platform for the mathematicians to study the self-assembly of ordered phases. Furthermore, we hope that the SCFT framework, given its nonlinear and nonlocal nature, will provide a ground for the development of some interesting new mathematics.

4 Conclusions of the Workshop and Future Directions

The workshop was successful on many grounds. Firstly, it built new contacts between applied mathematicians with physicists and engineers which hopefully will result in future collaborations. It also exposed certain fundamental questions and problems for future study:

- Many issues surrounding the Self-Consistent Mean Field Theory (SCFT) remain unclear:
  (i) a rigorous framework and or some justifications/validations for the approximations used
  (ii) computational challenges in the strong segregation regime,
  (iii) the exact nature and predictions of the theory in the strong segregation limit,
  (iv) extensions to dynamics.
  To this end, it is hopefully that mathematicians can have an impact.
- Confinement issues are of great contemporary interest (both from the point of view of theory and synthesis). Restricting the size of the sample to length scales on the level of the chain length gives rise to an enormous number of complex structures. There is definitely a need for a geometric classification, and at the very least, the formation of a catalogue for experimentally and computationally observed structures.
- The (perhaps overly) simplified Ohta-Kawasaki theory is remarkable successful from a qualitative point of view. A full analysis of its predictions in 3D near the order-disorder transition could prove useful.
- Block copolymer thin films are also of significant interest, and computational tools for solving PDEs on surfaces will prove useful.

In view of these open problems and the recently developed connections, a second BIRS workshop could prove very fruitful.

5 Talks and Abstracts

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:
(i) 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.
(ii) 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.
(iii) Numerical Solution of the complex Langevin (CL) equations in polymer field theory: I will discussed 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: Marcus Muller, Institut fr Theoretische Physik Georg-August-UniversitŁt
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 a 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, m, 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-consistemt 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, 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, 238:12411255, 2009), Helmers et al. (Netw Heterog Media, 3(3):615632, 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 Qui, 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, O70, and sphere phases at the compositions and 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: Ansatze 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 cagelike 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.

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