Abstract:

Simulation of solvent and multichain effects on polymer folding and cold denaturation

Jenni Portman
Phillip Duxbury

Polymer chains display great potential for various biological applications, ranging from controlled drug delivery to biological tissue scaffolds, thanks to their interesting thermodynamic properties. The available experimental methods allow to measure properties of polymers both in dilute and semidilute regimes, while most theoretical works focus on the behaviour of single chains, as this case is theoretically fairly well understood and simulated. In the present work we study the coil to globule transition and how it is influenced by inter chain interactions. Using molecular dynamics simulations of bead-and-spring polymer chains immersed in an explicit solvent, we investigate the transition from a low polymer density regime, in which each chain folds independently, to a high density regime in which multiple chains interact with each other to form a two phase mixture. In both regimes, the simulation results show evidence of a lower critical solution temperature corresponding to cold denaturation. In the case of single chain folding, the coil to globule transition temperature for varying density and pressure, strongly depends on what numerical parameter is used in its determination (radius of gyration, end to end distance or structure factor), due to chain finite size effects. At high polymer densities, the coil to globule transition temperature shows a marked dependence both on the number of chains and on the length of each chain, indicating a collective ordering phenomenon. We also show that simple Flory theory, modified to take finite solvent compressibility into account, describes to first approximation the transition temperatures for the low density regime, both at fixed density and pressure, but fails in predicting the behaviour of the high density case.

MOLECULAR DYNAMICS SIMULATIONS OF COLLOIDAL PARTICLES APPROACHING LIQUID-LIQUID INTERFACES

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The tendency of colloidal particles to reside at a fluid interface at equilibrium position as predicted by Young's equation is the basic concept underlying the behavior of Pickering emulsions. Recently colloids of tunable wettability have been produced by partial modification of their surface, which yields so-called Janus particles with asymmetric surface properties. Despite the vast literature on colloidal particles at interfaces, little information is available with respect to the behavior of Janus particles and the dynamics of colloidal particles moving towards and onto an interface. We have investigated the movement of colloids toward the interface between two immiscible fluids via Molecular Dynamics (MD) Simulations. Although micron-sized particles are used for most practical applications, we focus on nanometer-sized particles in our simulations due to computational constraints. However, our initial results show that the behavior of larger particles is captured reasonably well by the MD calculations. We present simulation results for both ordinary symmetric particles and Janus particles, and compare the results to experimental observations.

Translocating Polymer as a Heat Pump Captured into a Nanopore by Electric Field

Payam Rowghanian and Alexander Y. Grosberg

Department of Physics, New York University, New York, NY

April 29, 2012

Abstract

We study the threading and capture of a long and flexible polymer molecule through a nanopore. For a polymer driven electrically inside the pore, we formulate the threading dynamics by modifying a previously developed trumpet model and accounting for the dramatic deformations of the polymer during its passage. Introducing the concept of "iso-flux trumpet", we show that the trailing part is properly characterized by a flux scale which determines the translocation rate and time. Although the speed of the process is determined by the friction which is dominated by the trailing part moving through the solvent, only a small portion of the energy provided by the electric field to the polymer is dissipated by the friction far from the pore, and it is mostly dissipated by the irreversible stretching and contracting of the polymer squeezed into the small pore. Due to the presence of the membrane, the polymer segment inside the pore is pulled by the strongly stretched pieces of the polymer on both sides of the pore. Although the two strong pulling forces almost balance each other, they cause a net heat transfer during translocation from the trans to the cis side of the membrane. Currently, the theory is being improved by accounting for the nonzero field outside the pore and considering the coupling between the electric and hydrodynamic fields. The interaction of the DNA molecule with the electro-hydrodynamic field outside the pore is such that if the entropic barrier for entering the pore is large, the capture rate increases with the DNA length. Moreover, the field outside the pore significantly deforms the initial state of the polymer from which the threading process starts.

a Poster Title: NONLINEAR ELASTICITY OF ENTANGLED POLYMER NETWORKS

Authors: Ozan S. Sarıyer*, Sergei Panyukov^, and Michael Rubinstein*

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Abstract: We develop a microscopic model for nonlinear elasticity of entangled polymer networks. Traditionally, entanglement effects are modeled by tube potentials or virtual chains. One of the latest efforts in the field is the slip-tube model, in which the entanglements are represented by slip-links that can glide along the network chains but elastically constrained in space. The model we study improves over the original slip-tube model by taking into account harmonic interactions along the chain between such slip-links. This improvement restores the gauge invariance which was lost in the original slip-tube model. We analytically and numerically solve the new gauge-invariant microscopic model and present our results in comparisons with experimental and simulation data for uniaxial deformation.

Title: Exact enumeration of self-avoiding walks

Raoul Schram

The self-avoiding walk model is a simplified model of a polymer in a good solvent. Exact enumeration of self-avoiding walks is very time consuming: the number of self-avoiding walks grows exponentially as a function of the number of steps of the walk N. We created a new method called the length-doubling algorithm to exactly enumerate all self-avoiding walks up to a length of N=36. This is an improvement from the previous best result N=30. Compared to this previously best algorithm, our algorithm is about a 1000 times faster. In this talk I will explain the general idea behind this length-doubling algorithm.

Vittore Scolari

“Bioinformatic and polymer physics approaches to the description of the E. coli nucleoid”

Tethered Polyelectrolytes: Driving and Dragging Flow

Tyler Shendruk

Abstract reads:

Despite it's simplicity, the **electro-hydrodynamic equivalence principle** accurately describes the mobility of polyelectrolytes in many situations including end-labeled free-solution electrophoresis, electrophoresis through arrays of nanoengineered posts and translocation through highly confining channels. The equivalence principle finds such widespread application because it replaces a full consideration of electrostatic and hydrodynamic interactions with a simple, effective local flow when any mechanical force is also present. Comparing the conformations of tethered polyelectrolytes in electric fields to tethered polymers in uniform flow fields long ago validated the electro-hydrodynamic equivalence principle from the point of view of the polymer.

However, the accuracy of the equivalence principle with respect to the fluid is seldom considered. We compare the flow generated by a tethered polyelectrolyte to the perturbation of a uniform flow field over a tethered polymer. In this way, we assess to what extent a polyelectrolyte subject to electric and mechanical forces actually generates a uniform velocity field equal to the speed that the polymer would be electrophoresising if subject to an electric field alone. Our study utilizes a mesoscale method to simulate the fluid based on multi-particle collision dynamics (MPCD). Our new algorithm applies the Debye-Hückel approximation to assign an effective charge to MPCD particles within a few Debye lengths of each charged monomer in order to efficiently model the effect of the counterion sheath without resorting to simulating the explicit long-time and long-range behavior of individual counterions. The resulting flow fields verify the high degree of accuracy offered by the electro-hydrodynamic equivalence principle but also demonstrate the principles short comings with respect to the electro-osmotic flow generated by polyelectrolytes.

Title: Facilitated diffusion in fractal environment.

Jan Smrek

Abstract:

Proteins locate their specific target on DNA by mechanism of facilitated diffusion. It consists of repetitive tours of non-specific adsorption of the protein to the DNA, subsequent diffusion along the genome, combined with three dimensional diffusional relocations and re-adsorption on a different DNA site. We address the influence of recently discovered fractal architecture of chromatin in cell nucleus on the facilitated diffusion mechanism. Using scaling arguments, different regimes for the binding rate of the protein are identified based on relations between important length scales, fractal and walk dimensions of the system and the strength of the adsorption of protein to the DNA. We also discuss limitations of the present model.

Title: Mechanisms of myosin force exertion and transmission through cross-linked actin networks

Samantha Stam

Abstract:
Biological polymers in a cell produce a structural framework and determine the cell's ability to respond to external stimuli. Networks of the biopolymer actin are important for resistance of external mechanical stress and generating internal stress to drive processes such as cell motion or division. Internal forces are produced by the motor protein myosin, which slides actin filaments past one another via its conversion of chemical energy to mechanical work. Regulation of the network structure and the internal stress may produce architectures that either resist deformation or dynamically contract. Here, we conduct computer simulations to characterize the internal forces being exerted by in situ myosin motors that have been benchmarked to reproduce available experimental data (Alberts & Munro, unpublished data). We then go on to conduct in vitro experiments to visualize the length scales of strain that these forces produce in networks of varying structure. This work is part of a larger scale modeling effort to understand how forces propagate through and may either stabilize or deform networks of biopolymers.

Joris Stegen

Phase behaviour of a model protein solution:

Highly concentrated protein systems are of increasing interest to the food industry. However, the behaviour of such systems, which tend to be quite unstable, is still poorly understood. At high concentrations a lack of hydration water can cause the (partial) unfolding of proteins, which affects the mesoscopic and macroscopic properties of the dispersion by the further expulsion of water. I will present a simple two-state protein model, in which for one state the solvent is poor. The model highlights the effect of unfolding of proteins on the phase behaviour in solution. It predicts a competition between a dilute phase of native proteins and a dense phase of denatured proteins. The resulting phase diagram shows rich and non-trivial phase behaviour, including a multi-critical point

Title: Distance Controlled Optical Properties of Binary Heterogeneous Assemblies

Ye Tian

Abstract:

Spontaneous emission of light at AuNP surfaces near or in contact with QDs is noticeably modified because of a complex interplay of enhancement and quenching processes.

Enhancement of photoluminescence (PL) can be promoted by surface plasmon resonance (SPR) excited in gold nanoparticles and by a modified density of photon states in the nanostructured surface. Quenching process takes effect by nonradiative energy transfer from the QDs to AuNPs. Distance between AuNPs and QDs is a significant factor modulating the overall effect.

Linking the peptide molecular structure of amyloid fibers to their mechanical properties

Corianne C. vandenAkker,[1] Maarten F. M. Engel,[1] Krassimir P. Velikov,[2] Mischa Bonn,[1,3] Gijsje H. Koenderink[1]

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Nearly all proteins and peptides have the ability to self-assemble into amyloid fibrils when they are denatured. These fibrils are remarkably ordered and stable and they exhibit unique mechanical properties. The flipside of this stability is that fibrils which form in the context of conformational diseases are difficult to remove. Our aim is to unravel the link between molecular conformation and intermolecular forces with the mechanical properties of amyloid fibrils using a biophysics approach. In the long run, we hope that this knowledge will guide the rational design of compounds which influence amyloid self-assembly or break down the formed fibrils. As model systems, we used the natively disordered Alzheimer Aβ(1-42) peptide and two denatured model proteins (hen egg white lysozyme (HEWL) and β-lactoglobulin (β-lg)). We studied the secondary structure of the amyloid fibrils by vibrational sum frequency generation (VSFG) spectroscopy and tip-enhanced Raman spectroscopy (TERS), and measured the bending rigidity of the fibrils by fluorescence microscopy. Moreover, we measured the stiffness of networks of fibrils by rheology. Our results show that the bending rigidity of the amyloid fibrils and the stiffness of amyloid fibril networks are strongly dependent on the beta-sheet of the amyloid fibrils. Moreover, we show that the beta-sheet content can be influenced by addition of the polyphenol drug EGCG.

Title: The Internal Structure of Nanoparticle Dimers Linked by DNA

Fernando Vargas-Lara

Abstract:

The self-assembly of inorganic units controlled by the interactions of biological molecules, like DNA, has received attention for the possibility to specify higher-order structure, with potential biological, optical and electronic applications. In biology, self-assembly of complex materials (eg. bone, spider silk) frequently occurs in a stepwise, hierarchical fashion. Here, we consider a first step towards a hierarchical approach for synthetic nanostructures of nanoparticles (NPs) linked by DNA. The most basic unit in this multiscale approach is a dimer of NPs linked by DNA. We use a coarse-grained molecular model to explain experimental measurements of the separation of two DNA-coated NPs connected by linking single-stranded DNA (ssDNA). We show that the dimer separation is primarily controlled by the number of DNA links between NPs. If these links are not constrained to lie along the axis between NPs, the separation is limited by off-axis connections that force the NPs to be closer. We also show how the number of connections and their size alters the dimer separation. We summarize our findings in a simple theoretical model for the interparticle separation within the dimer that captures the interplay of the number of connections, their size, the particle's curvature and the exclude volume effects.

Interactions of elastin-like polypeptides with lipid membranes

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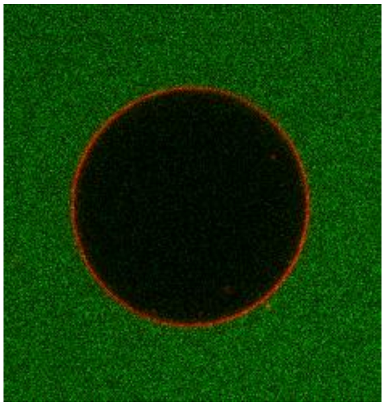
Abstract

Our research interests involve studies on bilayers self-assembled from new lipids and polymers. We study the formation of giant unilamellar vesicles from mixtures of phospholipids and diblock copolymers and the interaction of the resulting membrane structures with elastin-like polypeptides and other surface-active molecules. Control of self-assembly and of interactions requires developing new methods for vesicle formation, micro-manipulation and monitoring. In particular we have recently investigated how the interplay between lipid structure and mechanical stress influences membrane permeability.

Current studies in our group focus on the cell penetration potential of a new class of elastin-like polypeptides designed to penetrate the membrane of living cells. An important group of these cell penetration peptides are arginine rich polypeptides. Cell penetration can be controlled by the number of arginine units on the elastin-like polypeptide and by the density of arginine units in temperature-triggered self-assembled micelles.



Here we show how the peptide structure and the temperature influence the interactions with model membranes and discuss the importance of our findings in respect with peptide penetration potential.

Title:

'Effects of defects on the shear stress relaxation in self-assembled protein networks'

Ana West and James T. Kindt

Abstract:

The long-time reorganization of peptide networks formed by mixing “junction” and “linker” components, where the junctions contain multiple high-affinity, high-specificity binding sites for divalent “linkers”, is investigated using a mesoscale simulation model. An interesting feature of this type of system is that the concentration of defects can be controlled experimentally by varying the ratio of junction and linker concentrations in the system. In this study we use a simple simulation model to evaluate how the migration of defects controls the rate of relaxation of shear stress, and how this rate is related to junction multiplicity, defect concentration, and linker stiffness. The mean stress relaxation per defect migration event obtained through simulation was two to three times greater than assumed by standard simple theories. The results are used to develop a phenomenological theory to predict the dependence of shear viscosity on the equilibrium constant and rate constants associated with linker-junction binding, stoichiometric mismatch, and network topology. The shear stress relaxation time and viscosity are predicted to fall away sharply when junction and linker concentrations are mismatched by even 1%. Furthermore, the time-dependence of viscosity during gel “aging” is modeled as an approach to equilibrium through diffusion-limited recombination of complementary defects.

Title: Fluctuating Mobility Generation and Transport in Glasses

Apiwat Wisitsorasak

abstract:

On human length and time scales glasses seem static, yet glasses are in constant motion at molecular scales. Molecules in glasses change their location through activated events whose rates vary throughout the glass. Structural changes in one location cause or relieve constraints and stresses and thereby change the rate of activated transitions in neighboring regions. From these general considerations it follows that the apparent mobility of regions fluctuates both in space and time. In addition, the coupling between nearby regions implies that mobility will appear to be locally transported through the glass. In this work, we will explore using numerical methods the process of fluctuating mobility generation and transport in glasses as the glasses age after cooling and as they rejuvenate after heating. The framework we use is based on the random first order transition (RFOT) theory of glasses.

THERMODYNAMICS VS NETWORK STRUCTURE OF GLASS

LE YAN, GUSTAVO DÜRING, MATTHIEU WYART

Under cooling, the thermodynamics and the dynamics of super-cooled liquids are strongly correlated. The thermal evolutions of these quantities, characterizing the liquid fragility, depend greatly on the specific liquid considered. To date, there is no understanding of what controls these properties at a microscopic level. In chalcogenide glasses, the coordination of the covalent network can be changed continuously by varying their composition. Experiments show that as the coordination is increased, the jump of specific heat varies non-monotonously and is minimal at coordinations near the Maxwell threshold where the covalent network becomes rigid. At such a composition the liquid is strong. We introduce a simplified model for the thermal evolution of networks that captures this observation.

Hydrodynamics of Non-conserved Vicsek Model with Density-Dependent Motility

Xingbo Yang

Numerical and analytical studies of the Vicsek model first introduced in 1995 by Vicsek et al[1] have led to significant progress in our understanding the collective dynamical behavior of collections of self-propelled units, ranging from fish shoals to bacteria colonies. Here we describe the continuum hydrodynamics obtained from a model of self-propelled particles that generalizes the original Vicsek models in two ways. First, following recent work by Farrell et al [2], we introduce a density-dependent mobility to account for the crowding effect that may arise from the steric repulsion or biochemical signaling. In addition, we allow for cell division and death by introducing a logistic term that breaks number conservation in the density equation [3]. The effect of each of these two modifications on pattern formation in the system will be discussed.

[1] T. Vicsek et al. Phys. Rev. Lett. 75, 1226 (1995).
[2] Pattern formation in self-propelled particles with density-dependent motility (submitted)
[3] Cates et al. PNAS, vol. 107, 11715-11720 (2010)

Title: Concentration fluctuations of semidilute polymer solutions at an interface

Catherine Yeh

Abstract:

We consider Gaussian fluctuations about the mean field concentration profile of semidilute polymer solutions near repulsive surfaces in good and theta solvent conditions.   Using the Cahn-Hilliard square-gradient approach extended to polymer interfaces, we predict that semidilute solutions can exhibit localized concentration fluctuations associated with strongly repulsive surfaces in addition to fluctuations of the bulk polymer solution.