

## RESEARCH SYNOPSIS

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My research interests center on soft condensed matter and statistical physics. Soft condensed matter physics deals with soft materials like colloids, liquid crystals, polymers, and complex fluids that are “soft” to touch as their elastic modulus is much lower compared to “hard” materials, and for which thermal fluctuations dominate over quantum fluctuations. It is a discipline with a wide range of phenomena and materials that are both intellectually challenging and of importance in fields ranging from oil recovery to biology, medicine, and currently nanotechnology. Soft materials provide an ideal testing ground for many fundamental ideas of physics such as the relation between elasticity, long-wavelength dynamics, topological defects and broken symmetry, critical phase behaviors, and self-assembly of complex materials. Statistical physics provides us with a language and tools to describe everything from fluctuations in ferromagnets to charge distribution and size variations in polyelectrolytes (charged polymers), and it is critically important for the study of soft materials.

My postdoctoral research (Adviser: Prof. Murugappan Muthukumar) focuses on the physics of polymers in various physical environments. Polymeric materials are unique in nature as they can assume structures and conformations of astonishing variety, both in biological and synthetic systems. Due to their connectedness and flexibility, polymers possess very rich statistical features, and are treated as candidate structures to apply the basic concepts of statistical and soft matter physics. Polymers ideally represent soft materials that showcase a competition between energy minimized states and states in which entropic contribution to free energy dominates. Enormous experimental efforts in recent years have explored a multitude of new equilibrium and dynamic properties of both uncharged and charged polymers, and this has led to the discovery and synthesis of various novel materials that include nanocomposites and bio-templates. These materials have notable impact on modern manufacturing and medicine, especially in the fields of biotechnology (such as gene therapy or drug delivery), and materials science (such as molecular electronics, semiconductor circuit industry, or designing of materials of higher strength), and virtually in every emerging advanced technology. A synergistic integration of the observations from these experiments with theoretical and computational approaches can provide much insight into the pertinent complex processes, and the gleaned physical insight can facilitate further applied research. To that end, I have used the techniques of statistical mechanics and concepts of soft-matter physics to theoretically study the properties of polyelectrolytes, polymers with charged groups having electrostatic interactions between them.<sup>1</sup> These long-range Coulomb interactions in polyelectrolytes lead to significant conformational modification of the polymer chains to the uncharged systems. I study both the equilibrium and kinetic properties of these systems, ranging from a single molecule to gels in solutions, both in the presence and absence of small electrolytes (salts). In a generic polyelectrolyte solution the overall electroneutrality is preserved by the dispersed counterions (Fig. 1a,b) - either from salt or the polymer itself - of equal or different valency to that of the charged monomer, and depending on the physical parameters (temperature, the dielectric heterogeneity of the surrounding solvent in the vicinity of the polymers such as proteins, the amount of salt etc.), there can be substantial variation in the ion distribution around the polymer as well as within the solution. Further depending on the prevailing electrostatic (Coulomb) strength, regulated by the relative intensity of electrostatic interactions to thermal fluctuations, a sizable number of counterions might adsorb on to the charged groups of the monomer (also known as counterion condensation), where higher temperatures favor entropic freedom of ions leading to less adsorption. Formation of these charge complexes, further, modifies the effective charge of the polymer and consequently affects its size (Fig. 1c,d) and density in the solution. Minimization procedures self-consistent in terms of charge and size of the chains are thus necessitated to find equilibrium properties of polyelectrolytes.

We have argued in our recent work<sup>2</sup> that the entropy of free ions and the adsorption energy of bound ions are the key factors in regulating the effective charge of a polyelectrolyte chain in the expanded state. The closed form, analytical expression for the charge we obtain as a function of polymer density, temperature, and salt concentration is valid for a surprisingly wide range of physical conditions. We found that the dielectric constant of the polymer material is as crucial as the temperature. Electrostatic repulsion between charged monomers (Fig. 2b) resists the collapse (volume shrinkage of a polymer chain to way below its Gaussian dimensions) of a polyelectrolyte to a certain degree of solvent

poorness (hydrophobicity of monomers) (Fig. 2a), beyond which the short-range hydrophobic attraction between monomers overwhelms the repulsion, effecting a coil-to-globule collapse (Fig. 1a,b). By observing that almost all counterions condense when the chain collapses, we determined the collapse transition point and the phase diagrams in a simple schematic way, substantially reducing the rigors of traditional self-consistent minimization. Our finding that the size of a chain is uniquely determined by its charge with identical critical points (Fig. 1c,d) marks a significant shift in the understanding of charged polymers. The Edwards' variational theory we used agreed remarkably<sup>3</sup> well with the rigorous self-consistent field theoretic calculations. Thus, with its transparent formulation, the variational approach serves a better candidate to calculate the effective charge of a chain. We have, using the same model, interpreted recent data of an experiment designed<sup>4</sup> to study the polyion collapse in response to degrading solvent quality keeping the temperature (hence the relative Coulomb strength) fixed. We found that the collapse of a polyelectrolyte in a poor solvent occurs purely due to solvent-polymer chemical mismatch. Our theory helped quantify the solvent quality for non-electrostatic (hydrophobic or excluded volume) interactions, and verified a substantial degree of counterion adsorption (Fig. 1e,f) observed in the experiment but otherwise forbidden by classical arguments.

In a previous work,<sup>5</sup> we demonstrated the occurrence of charge inversion (in which the original polymer charge is reversed) resulting from the adsorption of multivalent counterions, and a different type of chain collapse due to electrostatic bridging mediated by divalent counterions (Fig. 2c) between non-bonded monomers for a single, flexible polyelectrolyte chain. We found that divalent salt cations replace monovalent counterions on the backbone of the chain through a competitive adsorption process. A modest presence of divalent salt first compensates and then reverses the original polymer charge, and consequently the chain shrinks and re-swells (Fig. 2d). The charge reversal, observed in experiments and simulations, is predicted to sensitively depend on the local chemistry of the polymer, and requires a minimum Coulomb strength supported by a low enough temperature or strong enough dielectric heterogeneity of the medium. Additionally, the divalent cations may induce an effective attraction of electrostatic nature between monomers, and hence create a poor solvent condition in an otherwise good solvent. We have shown<sup>5</sup> that a modest presence of divalent salt at nominal physical conditions leads to a first order coil-to-globule collapse (Fig. 2e). We plan to further apply the theory to analyze the volume collapse transition in synthetic or bio-polymer gels, polyelectrolyte brushes, semi-flexible polymers (DNA compaction), and to phenomena involving complex formation (“complexation”).

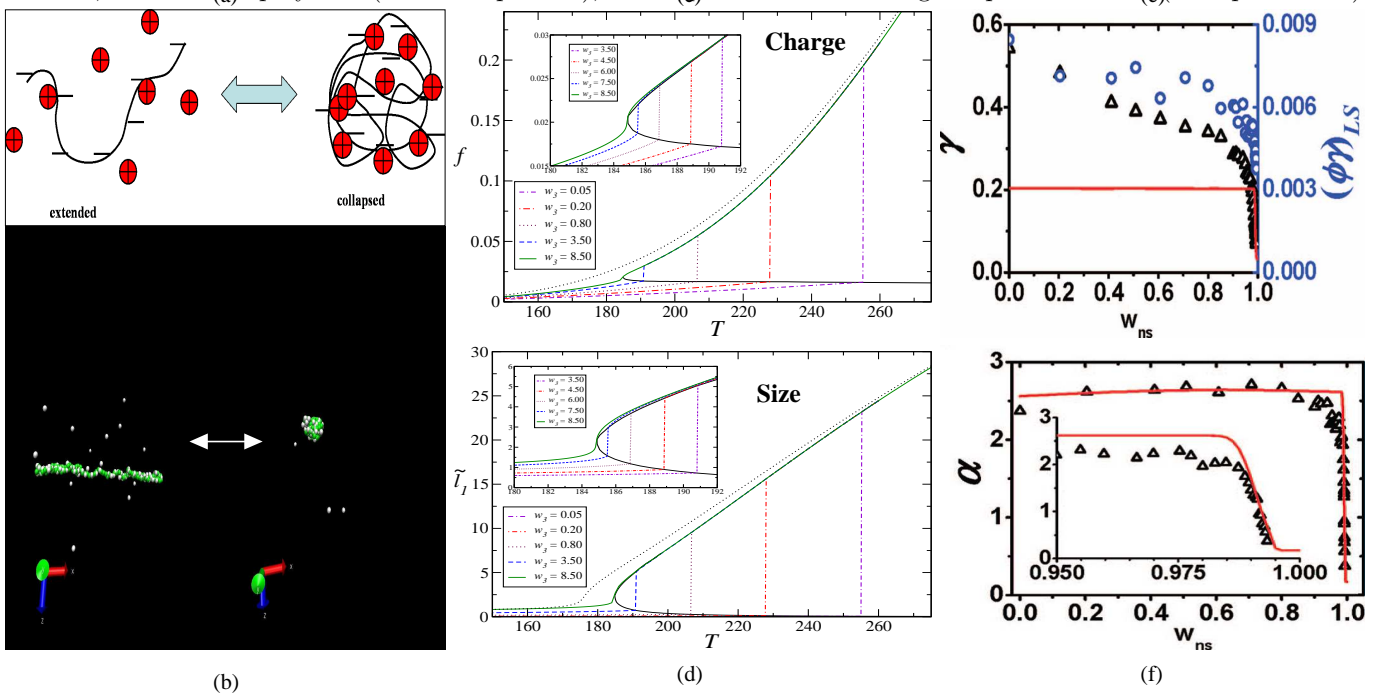


FIG. 1: Collapse of a polyelectrolyte: (a) counterions adsorb in collapsed state, (b) simulation of collapse (Courtesy: A. Panwar, M.Kelly, B. Chakrabarti, and M. Muthukumar, unpublished work), (c-d) phase boundaries and critical point<sup>2</sup> for charge and size of the chain, (e-f) comparison with experiment of solvent induced collapse.<sup>4</sup>

The kinetics in polymeric systems in the presence of charges can be fascinating. Currently, I am studying the dynamic properties of swelling and solvent diffusion in polyelectrolyte gels (Fig. 2e), and focus especially on two important possibilities - one in which physical stress relaxation is the dominant mechanism (e.g., in polar solvents), where the distribution of inhomogeneous stress determines the time-scale for polymer conformational changes, and the other in which chemical reaction is the key process (e.g., for new-generation photoresists in aqueous-base developers) that controls the rate of polymer swelling and dissolution. Polyelectrolyte gels are observed to undergo sudden volume changes of immense order when the solvent quality is changed either chemically or thermally (and by various other means). I have been studying the role of the counterions in modifying the solvent quality, the effective osmotic pressure and chemical potentials. This has been a very challenging theoretical problem of late in the polymer community with promise to provide mechanistic explanation and design rules to synthesize new materials and processes in various fields of advanced medicine and manufacturing which include drug delivery, gene therapy, or photolithography.

In the early phase of my postdoctoral research, I studied the role of the conformational entropy of chains in polymer crystallization. We developed a continuum theory<sup>6</sup> applicable to polyethylene type systems starting from the basic premises of the theory of small molecular crystallization. We proposed a kinetic model involving entropic barriers (Fig. 3a) that recovers the limits of both nucleation and diffusion control for polymer crystal growth in both melts and solutions. We numerically calculated the growth details of a single crystal in dilute solutions, and recovered conventional experimental trends of concentration and molecular weight dependencies. The concept of an entropic barrier has critical relevance to biological processes such as ordering in protein crystals or amyloid fibril formation. For these kinetic problems - first, the crystallization in uncharged polymers and then, the swelling of polyelectrolytes - I used numerical techniques to solve diffusion equations in the presence of moving boundaries. In addition, using a very similar methodology, I have developed numerical programs involving moving boundary conditions in non-trivial, multi-dimensional geometries to calculate the temperature diffusion and related volume changes in polymeric materials.

The primary focus of my doctoral and predoctoral studies was on equilibrium and non-equilibrium physics of soft condensed matter systems. In my doctoral thesis<sup>7</sup> (Adviser: Prof. Tom Lubensky), I calculated using a generalized Abrikosov vortex lattice theory the detailed nature of smectic and director ordering in twist-grain-boundary-C (TGB<sub>C</sub>)

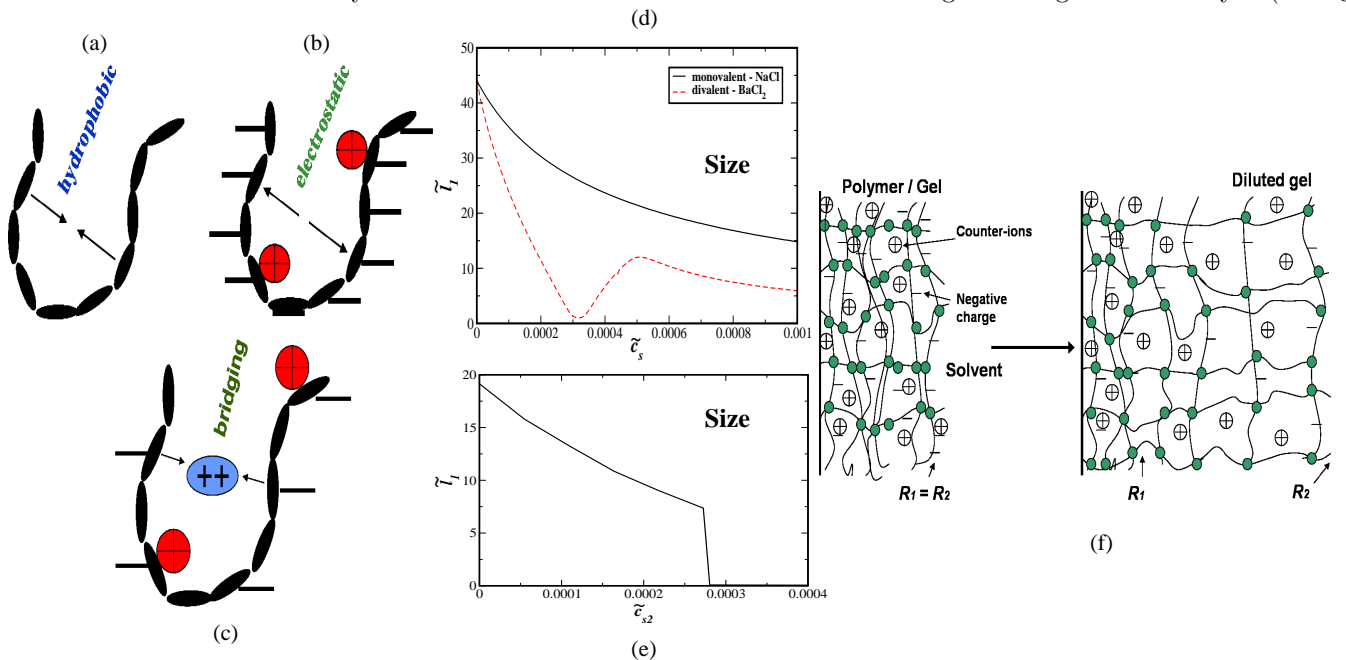


FIG. 2: Monomer-monomer interactions in a polyelectrolyte chain : (a) hydrophobic, (b) electrostatic, (c) ion-bridging (electrostatic); Size of the polymer as function of divalent salt concentration<sup>5</sup> for (d) overcharged chain, (e) ion-bridged chain (note the change in scale); (f) Polyelectrolyte gel swelling.

phases in liquid crystals, and the nature of transitions to them from the cholesteric phase. We numerically calculated the eigenfunctions of the stability kernel and used them to construct a variational order parameter from which we determined the spatially varying smectic order in the  $TGB_C$  phases. In particular, we had shown<sup>8</sup> that there can be two different  $TGB_C$  phases (Fig. 3b,d) with kernels of a remarkable duality in displacement and momentum, and their stability depends on the ratio of elastic stiffnesses (Fig. 3c). We found robust smectic order even in the grain boundaries and no evidence of “melted” structures, with vanishing smectic order, along them.

In my master’s thesis (Adviser: Prof. Chandan Dasgupta), I studied using computer simulations the presence of multi-exponent scaling (“multi-scaling”)<sup>9</sup> and extended self-similarity (ESS)<sup>10</sup> in the height fluctuations in atomistic surface growth models, and their similarity to the phenomena of fluid turbulence. Scale-independent power-law behavior was observed for a significantly longer time-range when two correlation functions of different order were compared. Multiscaling was found to be a slow transient in the atomistic growth models, and that was a result of the higher-order non-linearities used to control the instabilities in the conserved growth equations.

**Future research:** My research in immediate future will focus on expanding our understanding of charged polymers. As mentioned before, polymers have unique, specific properties at the molecular level and process advantages unattainable in other kinds of materials. As examples one finds that integration of functional polymers in energy generating devices serves as basis for advanced batteries; polymer membranes are used in low-temperature fuel cells, polymer photovoltaic diodes (solar cells), and in water purification/desalination processes; they are critical components in food production, storage of delicate, time-sensitive materials like medicines, and in myriads of biological processes. Polymers are light, robust, low-cost, and extremely effective materials possessing smart properties of different phases of matter. Charged polymers, in addition to their neutral counterparts, bring a variety of newer concepts and phenomena to the table. Due to their delicately matched spatial correlations of electrostatics and chain conformations, charged macromolecules present serious complexities to polymer scientists. The same attributes, however, enable to create hierarchical structures of significantly large cohesive strength by manipulation of charge interactions. Polyelectrolytes are thus central to future polymer research in both biosciences and nanotechnology, and will continue to be ideal systems elucidating basic concepts of soft-matter physics. From the theoretical perspective, numerical

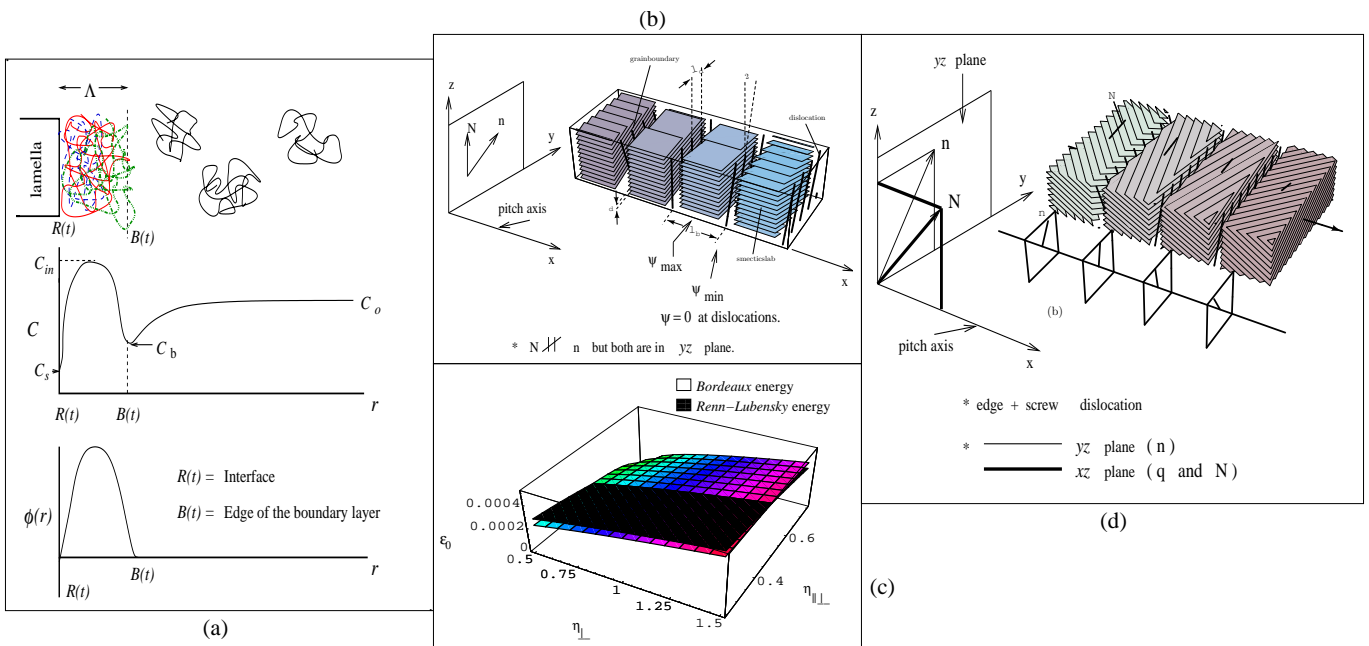


FIG. 3: (a) Schematic of the entropic barrier in polymer crystallization;<sup>6</sup> (b-d) Twist-grain boundary phases:<sup>8</sup> (b) the Renn-Lubensky phase, (d) the Bordeaux phase, and (c) their energy<sup>7</sup> (Courtesy: T.C. Lubensky and P.M. Chaikin). Periodically spaced smectic slabs, separated by the grain boundaries, produce the desired rotation of the planes. The grain boundaries are separated by  $l_b$  and the dislocations within a grain boundary are separated by  $l_d$ .  $l_b$  and  $l_d$  are the two parameters of  $TGB$  lattice structure.

solutions of macroscale empirical equations and ab initio computation based on statistical mechanics methodologies in the contexts of assembly phase behavior, transport, kinetics, and electronics may lead scientists to cover various classical phenomena in charged polymer systems over multiple length- and time-scales. New theories and simulations in synergistic collaboration with experimenters in polymer synthesis, characterization, and processing thus remain a necessity to bolster our basic understanding as well as expedite identification and discovery of new materials and structures. There is an excellent chance of meeting this grand challenge in the next few years.

In my previous research, I have shown that a great deal of complexity in charged systems arises due to its inherent dielectric inhomogeneity which prohibits to truly capture the local electrostatic potential gradients, especially within coexisting hydrophobic and hydrophilic domains in polar solvents. In an effort to better understand the processes, the self-consistent variational formalism and the corresponding free energy in terms of charge and size of a single polymer chain may be extended to a collection of chains, either separated (solution) or cross-linked (gel). There is excellent scope of applying both traditional and novel formalisms to study issues that include *the role of charge inversion in cellular processes such as DNA uptake by cell membranes, multivalent ion (polyamines) mediated condensation of DNAs to nanoparticles, the structure of an isolated polyelectrolyte chain in poor solvents, the thermodynamic viability of the elusive “pearl-necklace” structures observed trapped on mica surfaces in AFM measurements, the role of polymer stiffness (semiflexibility) in forming toroids under collapse (dsDNA for delivery in gene therapies), equilibrium phase diagrams and critical phase behaviors of polyelectrolyte gels with applications in technology ranging from medical-to food-engineering, the complexities of a multicomponent system and the ensuing multi-dimensional minimization in presence of salts, the bridging effect due to multivalent ions in gels and its application to muscle contraction or effective trapping and release of nanoparticles, the role of entropic frustration in the complexation of flexible polyelectrolytes and protein molecules (which have zones of opposite charges), kinetic protocols of volume changes both in single molecules and gels for novel delivery matrices, the swelling and deprotection extent in photoresists for desired circuit patterns in semiconductor industry, dynamics of volume change in single molecules relevant for protein folding and target localization in life processes (such as specific association of EcoRV restriction enzymes onto collapsing DNA)* and myriads of other problems with significant impact on synthetic and biological processes.

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