

# Summary of Research Interests & Research plan

## Emergent Phenomena in Complex Systems

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### Research Interests, Philosophy and Vision

I am a theoretical physicist by training, broadly interested in understanding emergent phenomena in complex systems. In particular, I am interested in the statistical physics of soft matter (e.g., amorphous materials, liquid crystals, and self-assembled complex structures) and applications of statistical mechanics in solving material science problems.

I enjoy solving problems that offer nontrivial physical insights. In parallel, I also like to work on real-world problems that are interdisciplinary in nature and require applications of existing ideas. I believe both are important for the overall advancement of science. As a theoretical/computational physicist, I use both numerical and analytical tools of statistical mechanics to attack a problem. My way of solving a complex problem is to first construct a minimal model that captures the basic properties and then build complexities on top of that. I also take help of all-atom molecular simulations and first principle quantum mechanical calculations to gain insights into the real system when microscopic details are important.

Below, I describe three different research themes by posing the key question in each theme that I would like to address in my independent career:

- *Is there an ideal thermodynamic glass transition and how is it related to the “glassy slowdown”?*
- *How does shape anisotropy, interaction, and polydispersity of the building blocks affect the collective self-assembly in and out-of-equilibrium?*
- *How to optimize selective gas separation in materials with cooperative adsorption property under thermodynamic and driven conditions?*

I am going to tackle the first question using the skills I have acquired during my current postdoctoral work at Duke University within the *Simons Collaboration on Cracking the Glass Problem*. My current work, which involves pushing the limits of glassy simulations in various spatial dimensions by implementing algorithms with improved sampling, has provided me with the necessary experience in this regard. I propose to investigate the second question by primarily using the variants of the Monte Carlo algorithm (with nonlocal moves) that I developed during my Ph.D. and the experience I gained while studying entropy-driven phase transitions in systems of anisotropic particles. My research experience in nanoscale self-assembly at Berkeley will also be essential in shaping this project. Finally, for the last project, I will exploit my expertise in developing theoretical models to understand selective gas capture and separation by porous crystalline materials, namely Metal-organic frameworks (MOFs).

I believe that my research philosophy and goals would complement the current research themes of the Physics department at IIT, Hyderabad. Given an opportunity, I would be privileged to contribute to the growth of a vibrant soft-matter group and an excellent Physics department. My vision is to grow as a part of a world-class collaborative research group that can compete globally. I would like to be actively involved in organizing national and international conferences and inviting visiting scientists to the department to build a vibrant scientific culture. I am also keen to collaborate across different departments and with the industry to perform interdisciplinary and applied research. Below I describe my research plan in detail.

### I. Quest for the “Glassy Slowdown” and the Glass transition

Upon cooling or increasing packing fraction, glass-forming liquids exhibit a marked dynamical slowdown without any significant structural change before it falls out of equilibrium at a low temperature or high density. One of the most compelling theories that explain this glassy slowdown is the Random First Order Transition (ROFT) theory [Biroli *et al.* arXiv:0912.2542]: it predicts the existence of an ideal glass transition with a diverging static length scale at a finite temperature  $T_K$ , known as Kauzmann temperature where the residual entropy (log of the number of metastable glassy states) of the supercool liquid vanishes. There exists another school of thought that advocates purely kinetic origin of glassy slowdown derived from certain lattice gas models with kinetic constraints and disapproves the idea of a thermodynamic glass transition [Chandler *et al. Annu. Rev. Phys. Chem.* **61**, 191 (2010)]. Unfortunately, numerical or experimental verification of the Kauzmann transition scenario has not been possible as the system falls out of equilibrium much above  $T_K$ . Confirmation of this scenario would be very strong evidence for the ROFT picture. My research goal in this theme is to resolve this issue and tackle the question of the origin of glassy slowdown.

## Statistical physics of constrained glasses

A novel idea to bypass this problem has been introduced in [Cammarota *et al.* *PNAS* **109**, 8850 (2012)]: by freezing or pinning a fraction of randomly chosen particles one can increase both the dynamical transition temperature ( $T_d$ ) (where the system becomes nonergodic in the mean-field limit) and the Kauzmann transition temperature ( $T_K$ ), and access the ideal glass transition for moderate supercooling. The phase diagram in the temperature–pinning density ( $T - c$ ) plane of a spin-glass model derived using Mean-field (MF) approximation, and Renormalization group calculation is shown in Fig. 1. The phase transition lines  $T_d(c)$  and  $T_K(c)$  approach each other with increasing  $c$  and finally meet at a higher-order critical point (shown by red circles). Even if  $T_K$  increases with increasing pinning fraction  $c$ , the line  $T_K(c)$  ends pretty early and thus, one still needs to equilibrate the system at least up to that critical temperature if not below to access the ideal glass transition. So, it reduces to the same old problem of “glassy simulations”. Due to this bottleneck, the phase behavior of this system has not been clearly determined, although a few attempts have been made [Kob *et al.* *PRL* **110**, 245702 (2013), Ozawa *et al.* *PNAS* **112**, 6914 (2015)].

*Phase behavior of randomly pinned liquids-* The recent implementation of the swap Monte Carlo algorithm (SWAP) and parallel-tempering sidesteps the difficulty of computational sluggishness and allows one to supercool the system up to an unprecedented low temperature or high packing fraction in bulk and within a cavity [Berthier *et al.* *PNAS* **114**, 11356 (2017)]. I propose to revisit the problem of pinned liquids and determine the phase diagram neatly using algorithms with improved sampling. The main challenge, in this case, is to equilibrate the system up to  $T_K$ . In my current postdoc, I have optimized polydisperse systems of hard spheres in high dimensions to maximize the efficiency of SWAP [Berthier *et al.* arXiv:1810.06950]. I plan to follow similar strategies to achieve equilibration of the pinned liquid systems using different *smart* algorithms, e.g., SWAP, parallel-tempering, rejection-free geometric cluster algorithm, and optimizing the system accordingly. Achieving equilibration up to a sufficiently low temperature would enable us to determine the lines  $T_K(c)$  and  $T_d(c)$  very accurately. We will perform finite-size scaling analysis to determine the nature of the transition-line  $T_K(c)$  in detail which is essential to validate this entire picture. I plan to test the mean-field theory prediction that the line  $T_K(c)$  ends at a critical point belonging to the Random field Ising model (RFIM) universality class using finite-size scaling analysis. It would also be interesting to check what happens in two dimensions given that for the unpinned system  $T_K(c = 0) = 0$  [Berthier *et al.* arXiv:1805.09035]. I further propose to measure the structural and dynamical correlation length scales around  $T_K(c)$  and verify if they diverge at  $T_K$ .

*Anomalous dynamics near higher order criticality-* I also plan to explore the dynamics near the critical point where the lines  $T_d(c)$  and  $T_K(c)$  meet—usually, the dynamics near a higher order critical point exhibit unconventional subdiffusive/logarithmic behavior which is quite different from the usual glassy dynamics [Gnan *et al.* *PRL* **113**, 258302 (2014)].

*The fragility transition, and the Widom line-* I propose to test the existence of the ideal glass transition scenario by verifying the presence of a Widom line that emanates from a critical point. Crossing the Widom line may correspond to a dynamic crossover or a fragility transition (fragile–strong). This study will involve calculations of the diffusion constant as a function of the pinning density. If there exists a fragility transition, the behavior of the diffusion constant will change from super-Arrhenius to Arrhenius. Another important part of this study would be to measure some response function (derivatives of a state function with respect to  $c$  or  $T$ ) and verify if the maximum of the response function coincides with fragility transition point as observed in the case of the liquid-liquid transition in water [Xu *et al.* *PNAS* **102**, 16558 (2005)]. This study will shed light on the connection between entropy fluctuations and dynamic properties which is essentially the key idea of the ROFT theory.

*Effect of pinning approach-* The above scenario is valid for random pinning from an equilibrated liquid configuration. In this case, one can access the ideal glass phase without encountering a phase transition. Mean-field calculation shows that a different pinning approach where the particles are pinned from a completely random configuration would exhibit a different phase behavior. In this case, one can *not* transform the liquid phase into the glass phase without encountering any singularity [Cammarota *et al.* *JCP* **138**, 12A547 (2013)]—a line of either continuous or discontinuous transition (depending on  $c$ ) separates the glass phase from the liquid phase. The critical point where these two lines meet is predicted to be in the Ising universality class in this case. I will verify these predictions using extensive numerical simulations and further address the following question: what is the qualitative difference between the two ideal glass phases generated from different pinning approaches?

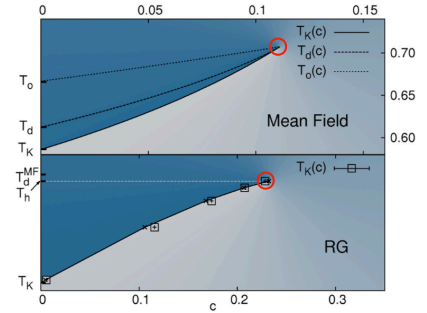


Figure 1: Phase diagram of a spin glass model using Mean-Field approximation, and Renormalization group analysis (including nonperturbative fluctuations) [*PNAS* **109**, 8850 (2012)].

The above projects will establish the thermodynamics of glass transition. But its connection with dynamics remains elusive. Is the dynamics near glass transition (in physical dimensions) governed by the existence of locally preferred structures? Or is there a growing amorphous order that controls the dynamics? Isolating these two contributions in physical dimensions is nontrivial. Despite recent advances in calculating a static point-to-set length scale measuring the amorphous order, the question of what actually controls the dynamics remains open. My research efforts will attempt to answer these questions.

## II. Self-assembly of Rod-like Particles in and out-of-equilibrium

Systems of rod-like particles exhibit a very rich phase behavior with a variety of self-assembled liquid crystalline phases and multiple phase transitions due to the interplay of orientational and translational degrees of freedom. Examples of such systems include colloids of polymethyl methacrylate, goethite, tobacco mosaic virus, *fd* virus, Silica particles, CdS, CdSe, and metal nanorods. These ordered superstructures are very useful for device applications. Understanding their self-assembly mechanism is essential to building target materials with specific functionalities. Models of rod-like particles serve as minimal models to study the self-assembly of such superstructures. However, standard simulation protocols suffer from huge relaxation times due to the shape anisotropy. I propose to study such systems using efficient numerical simulation schemes and analytical calculations. The broad focus of this research theme is to investigate the role of shape anisotropy, interaction and size polydispersity of the microscopic building blocks in designing self-assembled macroscopic soft materials with novel properties in and out-of-equilibrium.

*Equilibrium phase behavior of polydisperse hard rectangles*– As most of the natural systems are polydisperse, it is important to understand its effect on the phase behavior. Polydispersity usually acts to destabilize a crystal due to the emergent frustration in accommodating a range of particle sizes into a unique lattice structure. Thus it is nontrivial to identify the stable phases at high densities and to answer the question of the existence of any crystallization beyond a certain degree of polydispersity. Fairly recent Monte Carlo (MC) simulations of polydisperse hard spheres have shown that the system actually demixes into multiple coexisting crystalline phases at high densities [Sollich *et al.* *PRL* **104**, 118302 (2010)]. Interestingly, some of the demixing transitions were found to be nearly continuous where fluctuation are correlated over many lattice spacing. However, under what conditions a demixing transition becomes nearly continuous (otherwise usually discontinuous) is still an open problem. The entire scenario for rod-like particles with finite aspect ratio remains an open problem due to the lack of efficient algorithms. I propose to study the phase behavior of lattice gas models of hard rods with size (aspect ratio) polydispersity. The difficulty of simulating systems of rod-like particles on a lattice can be bypassed by using the efficient MC algorithm with nonlocal moves, developed by us, coupled with particle size swap moves and collective rotation moves [Kundu *et al.* *Phys. Rev. E* **87**, 032103 (2013)]. We will determine the complete phase diagrams of such systems using numerical simulations and entropic arguments, study the nature of the demixing transitions using finite-size scaling and investigate the criteria of a demixing transition being discontinuous or nearly continuous.

*Equilibrium self-assembly of interacting rods*– Next, we will introduce additional interaction between adjacent rods and develop a variant of our MC algorithm to study the phase behavior of such systems (starting with monodisperse systems). One of the motivations of this project comes from our ongoing collaboration with Pacific Northwest National Lab regarding an experimental observation of the self-assembly of helical repeat proteins on a mica surface into various liquid crystalline phases. The tools we will develop in this project would help to solve phase diagrams of various experimental systems of interacting complex molecules on structured substrates that act as templates to induce large-scale supramolecular structures [Theobald *et al.* *Nature* **424**, 1029 (2003)]. The outcome of this extensive study will shed light on the role interaction on equilibrium self-assembly of rod-like particles.

*Self-assembly far from equilibrium*– Self-assembly mediated by drying or solvent evaporation is a potent technique to prepare ordered nanostructures that are excellent candidates for a range of applications like electrochromic device, catalysts, sensors [Li *et al.* *Adv. Mater.* **15**, 408 (2003)]. This process is also a classic example of self-assembly far from equilibrium that needs further theoretical understanding. Coarse-grained lattice gas models have been instrumental in understanding different morphologies of the final structures seen in experiments [Rabani *et al.* *Nature* **426**, 271 (2003)]. Assemblies with liquid-crystalline ordering, however, requires the inclusion of shape anisotropy. I propose to construct a lattice model of hard rods and point particles (like a binary mixture) to represent a system of nanorods with a solvent on a structured substrate. The system will be simulated using kinetic Monte Carlo. The solvent concentration (which may control the interaction between adjacent rods) will be tuned grand canonically by a chemical potential, and the number of rods will be kept fixed. We will explore how different interaction potentials, the rate of evaporation of the solvent and the size of the rods lead to different target structures under kinetic conditions.

*Exploring novel glassy phases*– Another part of this research theme is to explore novel glassy phases of anisotropic particles. Although the glass physics of isotropic (spherical) particles is well-studied, very little is known about their anisotropic counterparts due to the computational difficulties to simulate such systems.

Experiments and computer simulations of two-dimensional colloidal ellipsoids indicate that interplay of translational or rotational degrees of freedom (dof) lead to novel phenomena, e.g., the formation of orientational glass, decoupling of rotational and translational dof, anticorrelation of rotational and translational cooperative motion [Zheng *et al.* *PRL* **107**, 065702 (2011)]. I propose to leverage the variants of above discussed *smart* MC algorithms and use suitably optimized (to avoid crystallization) polydisperse systems to achieve supercooling deep along the liquid branch. The equilibrium phase diagram (which will be determined in the first project) will guide us to access multiple glass transitions at various densities and new glassy regimes that have never been explored in simulations before. Finally, I hope that with these algorithms we can follow the equilibrium liquid-line up to a density very close to full packing– this would provide an excellent scope to verify if the configurational entropy goes to zero at an ideal glass transition without any extrapolation.

### III. Predicting Next Generation Porous Crystalline Materials for Optimized Gas Uptake Using Tools of Statistical Physics

The emission of CO<sub>2</sub> due to the burning of fossil fuels is a major contributing factor to climate change with associated damaging economic consequences; thus it is important to develop efficient technologies for CO<sub>2</sub> capture, and storage. Metal-organic frameworks– porous crystalline materials with a large surface area, and tunable molecular properties whose internal binding sites can host gas molecules are very promising candidates in this regard for clean energy applications [Furukawa *et al.* *Science* **341**, 1230444 (2013)]. Usually, most frameworks exhibit typical Langmuir-type isotherm where the amount of adsorbed gas varies gradually with pressure or temperature. But it is technologically much more convenient to have cooperative or step-like isotherm where gas uptake varies in an abrupt way with pressure or temperature due to their large working capacity. However, a handful of gas-framework combinations exhibit cooperativity e.g., CO<sub>2</sub> adsorption in diamine appended MOFs mmen-M<sub>2</sub>(dobpdc) [McDonald *et al.* *Nature* **519**, 303 (2015)], CO adsorption in Fe<sub>2</sub>Cl<sub>2</sub>(bbta) [Reed *et al.* *Nature* **550**, 96 (2017)]. Here I ask, how to exploit and control cooperative adsorption mechanism to design new strategies or materials for improved gas separation and capture capacity?

*Tuning cooperativity using mixed metal MOFs*– Our recent transfer-matrix based calculation has shown how cooperativity or step-like behaviour emerges in the absence of an underlying phase transition in the class of diamine appended MOFs (mmen-M<sub>2</sub>(dobpdc)) [Kundu *et al.* *PRL* **121**, 015701 (2018)]. This particular class of MOFs has drawn attention due to their rare capability of capturing CO<sub>2</sub> under humid condition [Mason *et al.* *JACS* **137**, 4787 (2015)]. It is desirable for industrial applications to have control over the step-position. I propose to extend the transfer matrix based calculation and perform numerical simulations to study the system of multi-metal and test how one can vary the adsorption step-position in a continuous fashion by varying the composition of metals in a MOF. This would be an extremely powerful tool to design new materials with different compositions to induce the *step* at a desired pressure. Usually, these MOFs contain a nonzero fraction of defect sites, e.g., a metal site without a diamine attached to it. These defects can be treated as quenched disorders within the transfer matrix method. Hence, I further propose to develop a more realistic model of mmen-M<sub>2</sub>(dobpdc) MOFs and study the effect of defects on cooperative adsorption.

*Comparing different types of cooperativity*– As described earlier, the class of diamine appended MOFs exhibit cooperativity in the absence of a phase transition. But, certain MOFs do undergo structural phase transition leading to cooperativity, e.g CO adsorption in Fe<sub>2</sub>Cl<sub>2</sub>(bbta) [Reed *et al.* *Nature* **550**, 96 (2017)]. Here, CO induces a spin-transition of the framework when the pressure crosses a threshold, resulting in a step-shaped isotherm. My idea is to construct a lattice model in three dimensions where each site will have a spin and an occupancy variable along with a coupling between them. We will solve the phase diagram of the model using mean-field calculations and multi-scale numerical simulations. The phase diagram will dictate the best operating regime for gas uptake. We will also perform a thorough comparison between cooperativity with and without a phase transition and identify the key features to distinguish them in an experimental setup.

*Gas uptake under driven conditions*– In case of equilibrium gas separation, a framework will harbor a desired gas selectively from a gas mixture if the framework binds most strongly to that gas-type compared to others. This clearly limits the space of protocols and materials for which selective gas capture can be effected. One useful strategy is to explore nonequilibrium gas-uptake protocols. The recent incorporation of phase-change MOFs into Mixed Matrix Membranes (MMMs) shows promises of performing gas uptake under nonequilibrium conditions [Maserati *et al.* *Nano Lett.* **17**, 6828 (2017)]. However, current theoretical understanding of gas separation under kinetic conditions is minimal. I propose to construct lattice-based diffusion-binding models with multi-component gas mixtures and investigate the kinetics of gas separation in MOFs with cooperative behavior out-of-equilibrium using extensive numerical simulations. We will also explore possibilities of inducing nonequilibrium phase transitions in frameworks where cooperativity is not associated with a phase transition by implanting kinetic constraints and study its role in gas separation.

In summary, my research proposal includes fundamental and applied problems in areas of statistical physics, soft-matter, and material science. In order to accomplish these projects, I would mainly require a good computing facility (cluster for High Performance computing).