ABSTRACT

Title of Dissertation:MOLECULAR-SCALE EXPLORATION OF
INTERACTIONS BETWEEN DROPS AND
PARTICLES WITH A POLYMERIC LAYER

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Surface-grafted polymer molecules have been extensively employed for surface modifications as they ensure changes to the inherent physical/chemical properties of surface. Bottom-up surface processing with well-defined polymeric structures becomes increasingly important in many current technologies. Polymer brushes, which are polymer molecules grafted to a substrate by its one end at close enough proximity (thereby ensuring that they stretch out like the "bristles" of a toothbrush), provide an exemplary system of materials capable of achieving such a goal. In particular, producing functional polymer brushes with welldefined chemical configurations, densities, architectures, and thicknesses on a material surface has become increasingly important in many fields.

In my dissertation, I employ Molecular Dynamics (MD) simulations to study the interplay of interactions between nanoparticles (NPs), solvent drops and polymer grafted surfaces under various system conditions. This study will help us to understand (1) the wetting dynamics of brush grafted surfaces and the associated brush conformational changes, (2) polymer-insoluble solvophilic NP assembly in brush grafted surfaces and the steric interactions driven establishment of direct contacts between a NP and a polymer layer (highly phobic to the NP), and (3) microphase separation and distillation-like behavior of grafted polymer bilayers interacting with a binary liquid mixture, and the resulting nanofluidic valving behavior of swollen polymer bilayers in a weak interpenetration regime.

In Chapter 1, I provide the background and motivation of the research presented in this thesis.

In Chapter 2, I study the spreading and imbibition of a liquid drop on a porous, soft, solvophilic, and responsive surface represented by a layer of polymer molecules grafted on a solvophilic solid. These polymer molecules are in a crumpled and collapsed globule-like state before the interaction with the drop, but transition to a "brush"-like state as they get wetted by the liquid drop. We hypothesize that for a wide range of densities of polymer grafting (σ_g), the drop spreading is dictated by the balance of the driving inertial pressure and balancing viscoelastic dissipation, associated with the spreading of the liquid drop on the polymer layer that undergoes globule-to-brush transition and serves as the viscoelastic solid. Finally, I argue that these simulations raise the possibility of designing soft and "responsive" and widely deployable liquid-infused surfaces where the polymer grafted solid, with the polymer undergoing a globule-to-brush transition, serving as the responsive "surface".

In Chapter 3, I employ coarse-grained molecular dynamics (MD) simulations and establish that under appropriate conditions, it is possible to develop numerous stable direct contacts between a polymer-insoluble NP and a solvated polymer layer (the polymer layer is phobic to the NP, while the solvent/liquid is philic to both the NP and the polymer). The NP is driven inside a layer of collapsed and phobic (to the NP) polymer molecules by a drop of this liquid (which is philic to both the NP and the polymer layer). The liquid molecules imbibe and diffuse inside the polymer layer, but the NP remains localized within the polymer layer, due to large Steric effects, ensuring the establishment of highly stable numerous direct contacts between the NP and the highly phobic polymer molecules. Finally, I argue that our finding will open up avenues for leveraging NPpolymer interactions for a myriad of applications even for cases where the polymer molecules are phobic to the NPs.

In Chapter 4, I study the interaction of a binary mixture drop, containing two-miscibleliquids, with a polymer functionalized nanochannel that is philic to one of the liquids and phobic to the other. Liquid-liquid phase separation is achieved due to the asymmetry of interaction of the liquid species and we observe distillation like behavior wherein the drop becomes progressively concentrated with the phobic liquid with each "'pass" with the polymer bilayer absorbing an increasing fraction of the philic liquid molecules and transitioning into the polymer brush regime. Depending on the nanochannel height, the number of allowed passes varies, as the polymer chains stretch out until the oppositely grafted layers overlap and create a dense region of liquid infused polymer layers that act as a valve. Any further passage of drops through this nano-confined interpenetrating brush bilayer requires a much greater magnitude of applied force on the drop. I finally propose a design of nanovalves based on this mechanism of creating partially porous interpenetrating polymer brush layers.