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Responsive Grafted Polymer Layers: the role of pH, temperature and surface geometry

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The competition between chemical equilibrium, e.g. protonation, and physical interactions determines the molecular organization and functionality in biological and synthetic systems. Charge regulation by displacement of acid-base equilibrium induced by changes in the local environment provides for a feedback mechanism that controls the balance between electrostatic, van der Waals, steric interactions and molecular organization. What are the mechanisms that determine the interplay between all these different factors? In this talk I will describe a molecular theory to address this question. In particular, the theory will be used to study the structural and thermodynamic properties of end-grafted polyacids with hydrophobic backbones. The molecular theory explicitly includes the size, shape, conformations, charge and charge distribution of all the molecular species in the system and incorporates excluded volume, van der Waals and electrostatic interactions coupled with acid-base equilibrium. On planar surfaces, the theory predicts the formation of surface micelles with morphologies that depend upon the bulk pH, solution ionic strength, temperature and surface coverage. The self assembled aggregates, present domains of varying local pH that is very different from that of the bulk solution. We show that a qualitatively new form of local organization arises that is only found when there is explicit coupling between charge regulation and physical interactions. The different morphologies can be manipulated by changing the bulk solution conditions and they provide for local domains with controlled charge and pH with large gradients with a characteristic size of a few nanometers. Following this we will discuss how ion conductivity in nanopores functionalized with polybases changes as a function of solution pH. The predictions of the theory are in quantitative agreement with experiments and they provide a physical explanation of the interplay between molecular organization and charge in the nanopore. The last part of the talk will be devoted to a new system in which we show how to use the theory under non-equilibrium conditions to study the flux of ions in finite nanopores with grafted polybases (or polyacids) in the presence of external potentials.