Ferroionic States: Coupling Between Surface Electrochemical and Bulk Ferroelectric Functionalities on the Nanoscale

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Ferroelectricity on the nanoscale has remained a subject of much fascination in condensed matter physics for the last several decades. It is well recognized that stability of the ferroelectric state necessitates effective polarization screening, and hence screening mechanism and screening charge dynamics become strongly coupled to ferroelectric phase stability and domain behavior. Previously, the role of the screening charge in macroscopic ferroelectrics was observed in phenomena such as potential retention above Curie temperature, back switching of ferroelectric domains, and chaos and intermittency during domain switching. In the last several years, multiple reports claiming ferroelectricity in ultrathin ferroelectrics based on formation of remanent polarization states, local hysteresis loops, and pressure induced switching were made. However, similar phenomena were reported for traditionally non-ferroelectric materials, creating significant level of uncertainty in the field. We pose that in the nanoscale systems, the ferroelectric state is fundamentally inseparable from electrochemical state of the surface, leading to emergence of coupled electrochemical-ferroelectric states. I will present the results of experimental and theoretical work exploring the basic mechanisms of emergence of these coupled states including the basic theory and phase-field formulation for domain evolution. I further discuss the thermodynamics and thickness evolution of this state, and demonstrate the experimental pathway to establish its presence based on spectroscopic version of piezoresponse force microscopy. Finally, the role of chemical screening on domain dynamics is explored using phase-field modelling. This analysis reconciles multiple prior studies, and set forward the predictive pathways for new generations of ferroelectric devices and applications.

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