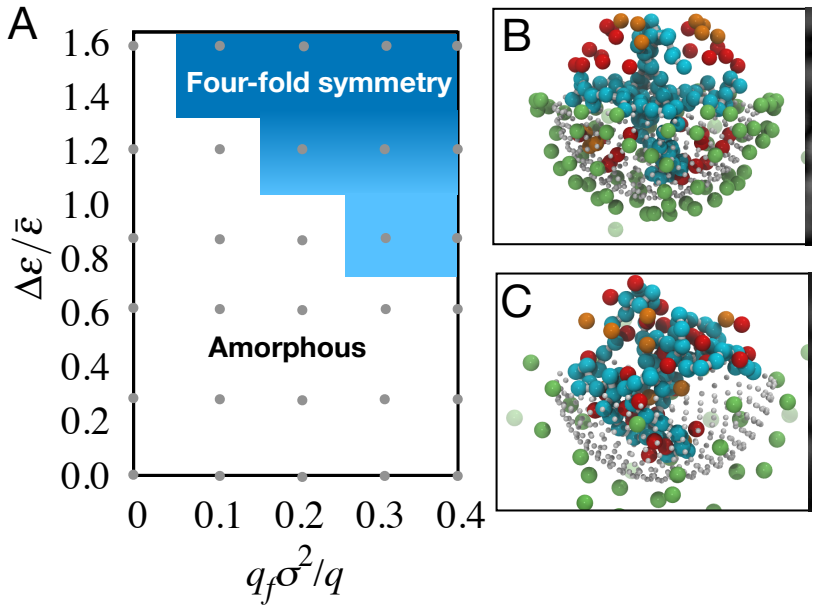
Manipulation of confined polyelectrolyte conformations through dielectric mismatch

Trung Dac Nguyen and Monica Olvera de la Cruz

The collective effects of spatial confinement and dielectric mismatch on the conformational behavior of a polyelectrolyte are investigated. We demonstrate that a highly charged polyelectrolyte confined in a spherical cavity undergoes reversible transformations between amorphous conformations and a four-fold symmetry morphology as a function of dielectric mismatch between the media inside and outside the cavity. Surface polarization due to dielectric mismatch exhibits an extra “confinement” effect, which is most pronounced within a certain range of the cavity radius and the electrostatic strength between the monomers and counterions and multivalent counterions. For cavities with a charged surface, surface polarization leads to an increased amount of counterions adsorbed in the outer side, further compressing the confined polyelectrolyte into a four-fold symmetry morphology. Our findings offer insights into the effects of dielectric mismatch in packaging and delivery of polyelectrolytes across media with different relative permittivities. Moreover, the reversible transformation of the polyelectrolyte conformations in response to environmental permittivity allows for potential applications in biosensing and medical monitoring.



A) Phase diagram of equilibrium morphologies of the confined polyelectrolyte as function of the surface charge density vs dielectric mismatch.
B-C) Representative snapshots of the four-fold symmetry conformations and amorphous conformations, respectively.

Northwestern

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