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The Ordinary-Extraordinary Transition in Dynamics of Solutions of Charged Macromolecules

MURUGAPPAN MUTHUKUMAR, University of Massachusetts

Dynamic light scattering measurements on dilute salt-free polyelectrolyte solutions have shown over the past three decades that there are two distinctive diffusive modes: fast and slow. The diffusion coefficient deduced from the fast mode has been found to be essentially independent of molar mass and polymer concentration and it is merely a factor of four smaller than that of small electrolyte ion such as sodium or potassium ion. The diffusion coefficient deduced from the slow mode is much smaller suggestive of clumps of many chains although these chains are similarly charged. Upon addition of sufficient amount of small molecular salts, the fast and slow modes merge together and the deduced diffusion coefficient is within the expected value for uncharged polymers. We will present a theory for these observed behaviors based on the coupling between the polyelectrolyte chains and their counterions.