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Highly-correlated charges in polyelectrolyte gels CHARLES SING, JOHANNES ZWANIKKEN, MONICA OLVERA DE LA CRUZ, Northwestern University — Polyelectrolyte gels are ubiquitous in polymer physics due to their attractive combination of structural and chemical features that permit the realization of "environmentally responsive" systems. The conventional conceptual picture of the volume response of these systems is based on a competition between osmotic and elastic effects. We elaborate on this fundamental understanding by including ion correlations through the use of liquid-state integral equation theory. This allows for a statistical mechanical representation of the state of the system that not only surpasses traditional Poisson-Boltzmann theories but also renders structural features in a highly accurate fashion. In particular, the local ion structure is elucidated, allowing for detailed articulation of charge inversion and condensation effects in the context of gel swelling. The inclusion of correlations has a number of ramifications that become apparent, with enhanced gel collapse and excluded volume competitions that give rise to novel and ion-dependent reentrant swelling effects. We expect this rigorous theory to prove instructive in understanding any number of gelated structures, such as chromosomes or designed synthetic materials for drug delivery.

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