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Osmotic Pressure and Swelling of Permeable Ionic Microgels

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Ionic microgels are soft, permeable, colloidal particles, made of crosslinked polymer networks, that ionize and swell in a good solvent. Their sensitive response to changes in environmental conditions, e.g., temperature and pH, and their capacity to encapsulate drug or dye molecules, have spawned applications of microgels to drug delivery, biosensing, and filtration. Swelling of these soft colloids involves a balance of electrostatic and gel contributions to the single-particle osmotic pressure. The electrostatic contribution depends on distributions of mobile microions and fixed charge. Working within the cell model and Poisson-Boltzmann theory, we derive the electrostatic contribution to the osmotic pressure from the free energy functional and the gel contribution from the pressure tensor. By varying the free energy with respect to microgel size, we also derive exact statistical mechanical relations for the electrostatic osmotic pressure for models of planar, cylindrical, and spherical microgels with fixed charge uniformly spread over their surface or volume. To validate these relations, we solve the Poisson-Boltzmann equation and compute microion densities and osmotic pressures [1, 2]. We show that microgel swelling depends on the nonuniform electrostatic pressure profile inside the particles and on the distribution of fixed charge. Finally, we discuss implications for interpreting experiments.

[1] A. R. Denton and M. O. Alziyadi, *J. Chem. Phys.* **151**, 074903 (2019).
[2] M. O. Alziyadi and A. R. Denton, *J. Chem. Phys.* **155**, 214904 (2021).

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