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Bridging induced by multivalent counterions in polyelectrolyte brush NICOLAS LAUGEL, ROBERT FARINA, Lawrence Berkeley National Lab, PHILIP PINCUS, Materials Research Laboratory, University of California in Santa Barbara, MATTHEW TIRRELL, Dept of Bioengineering, University of California in Berkeley — When the counterions of a polyelectrolyte brush are multivalent, significant changes in its behavior are observed. One example is its shrinkage at values of ionic strengths where osmotic pressure would be expected to keep chains extended. This effect could be explained through the existence of a bridging phenomenon, with the multivalency of each counterion enabling attractive interactions with more than one polymeric charge at a time. Here we present a variational and phenomenological free energy model in a description of the charged brush as an homogeneous layer subject to classical energy contributions related to both chains and counterions. Two mean-field order parameters are introduced to describe counterion condensation and bridging. The model predicts an abrupt collapse of the brush height upon very fine changes in values of the parameters value which is reminiscent of the experimentally observed behavior.

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