

Abstract Submitted  
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**Spontaneous deswelling of pNIPAM microgels at high concentrations** URS GASSER, Paul Scherrer Institut, ANDREA SCOTTI, RWTH Aachen, EMILY S. HERMAN, MIGUEL PELAEZ-FERNANDEZ, Georgia Institute of Technology, JUN HAN, ANDREAS MENZEL, Paul Scherrer Institut, L. ANDREW LYON, Chapman University, ALBERTO FERNANDEZ-NIEVES, Georgia Institute of Technology — Polydisperse suspensions of pNIPAM microgel particles show a unique, spontaneous particle deswelling behavior. Beyond a critical concentration, the largest microgels deswell and thereby reduce the polydispersity of the suspension [1]. We have recently unraveled the mechanism of this spontaneous, selective deswelling. pNIPAM microgels carry charged sulfate groups originating from the ammonium persulfate starter used in particle synthesis. Most of the ammonium counterions are trapped close to the microgel surface, but a fraction of them escapes the electrostatic attraction and contributes to the osmotic pressure of the suspension. The counterion clouds of neighboring particles progressively overlap with increasing volume fraction, leading to an increase of free counterions and the osmotic pressure outside but not inside the microgel particles. We find particles to deswell when the resulting osmotic pressure difference between the inside and the outside becomes larger than their bulk modulus [2]. For pNIPAM microgels synthesized with the same protocol, the largest particles are the softest and deswell first. (1) A. St. Iyer and L.A. Lyon, *Angew. Chem. Int. Ed.* 48, 4562-4566 (2009). (2) A. Scotti et al., *PNAS* 113, 5576 (2016).

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