Laboratory for Neutron Scattering and Imaging
Paul Scherrer Institute

Invitation for an LNS PhD Student Presentation

Date: Thursday, June 17, 2021, 10:30

Location: **Auditorium (WHGA/001)** /via **ZOOM: https://psich.zoom.us/j/66792776905**
Meeting ID: 667 9277 6905

Speaker: Boyang Zhou, LNS, Paul Scherrer Institut, Villigen PSI, Switzeland

Title: **Direct measurements of the pNipam Microgel Counter-ion Cloud via Small-Angle Neutron Scattering**

Microgels are formed by cross-linked polymer networks. Due to their stimuli-sensitive nature, their responsiveness towards changes in external conditions such as temperature, pH, pressure and concentration lets microgels reversibly change between a swollen and collapsed state. Their responsiveness also makes them interesting for applications and a good model system for soft colloids. Unlike hard colloids, soft colloids like microgels are not well understood, especially at high concentrations because of the complex interplay of internal and colloidal degrees of freedom, which is not present in hard colloids. In this study, we use temperature sensitive pNipam microgels that have an uncharged polymer network and a lower critical solution temperature close to room temperature. However, due to the initiator used during synthesis, pNipam microgels carry charged groups and counter-ions at the periphery, which we have found to play a crucial role for the observed spontaneous deswelling behavior at high concentrations; the counter-ion clouds percolate at high concentration and cause the suspension osmotic pressure to increase [1,2]. When the osmotic pressure exceeds the bulk modulus, deswelling occurs. This deswelling mechanism can also resolve point defects that would otherwise hinder the crystallization in the case of a hard-incompressible particle suspensions.[3,4] Importantly, our model for microgel deswelling relates the particle softness and surface charges with the phase behavior. We present the first direct measurements of the counter-ion cloud via small-angle neutron scattering (SANS). Note that the form factor can be decomposed as P(q) = Fp2(q) + 2Fp(q)Fc(q) + Fc2(q), where Fp2(q) and Fc2(q) are the form factors of the pNIPAM polymer and the counter-ion cloud, respectively. We prepare one suspension with Na+ ions and another with NH4+ ions via dialysis and use the scattering-length-density difference between Na+ and NH4+ to obtain a signal from the counterion cloud. The difference of their form factors at dilute conditions is given by the cross term 2Fp(q)[FNH4+(q)-FNa+(q)], which gives detailed information on the configuration of the counter-ions and charged groups. By using this method, we are able to detect the signal of the cloud, even though the concentration of the counter-ions is very low. Our results show the counter-ion clouds are indeed located at the particle periphery, which corroborates our theory. Lastly, I will discuss the deswelling of the microgels below random close packing density where particles are not in direct contact, which can further rationalize our results extracted from the counter-ion cloud measurement. These findings are crucial for developing a more systematic understanding of soft and deformable colloids at high concentrations and for formulating a model for the phase behavior of microgels that takes spontaneous deswelling at high concentrations into account.

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