Experimental report

31/03/2016

Proposal: **9-10-1438**

Council: 4/2015

Title: The effect of DC electric field onordering colloidal dispersions - comparison of interfaces and in the bulk.

Research area: Soft condensed matter

This proposal is a resubmission of 9-10-1416

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Samples: Polystyrene latex in D2O

Instrument	Requested days	Allocated days	From	To
D33	6	0		
D22	6	5	30/10/2015	04/11/2015

Abstract:

Understanding the self-organization of colloidal particles into larger structures has paved the way for the development of electronic devices, new medical techniques and solution to environmental challenges. Fine control over all the parameters governing the assembly process and the final structure is an important research topic. The aim of this experiment is to investigate the effect of an applied electric field on the structure and assembly process of colloidal particles (latex) at the solid/liquid interface and in the bulk. The experiment is designed to probe interfacial and bulk structure of sulfated polystyrene nanoparticles in D2O. In particular new developments in the analysis of GiSANS identify the separation of the packed particles from the interface as well as their lateral structure. A combination of GiSANS as well as SANS will be used because of the controllable penetration depth to investigate interfacial layers and to compare with the bulk structures. Extensive measurements in multiple orientations of the sample and field will be required to determine these structures.

Introduction

Neutron scattering and Q-CMD data have shown that polystyrene latex particles can form large domains of oriented and regular structure close to but not at solid/liquid interfaces [1]. These structures can be used directly as templates to modify large area, two-dimensional metallic structures such as photonic, memory, or single electron microelectronic devices and etc. Understanding the formation of these structures is a great challenge in tuning and controlling them into desired structures. The aim of this experiment was to model the near surface structure of latex particles and probe their spacing from the interface in the presence and absence of an applied DC field.

Experiment

The charge-stabilized polystyrene latex with 720 Å radius (polydispersity < 5%) and ~ -35mV surface potential dispersed in D_2O has been characterized using different methods including zeta potential, SEM, AFM, TEM, light microscopy, SAXS, SANS and GiSANS [1, 2, 3] was used for this experiment. The sample holder in the form of a cell, similar to the previous studies by our group [4] was used with some modifications in order to apply an electric potential. Thin aluminium sheets were placed close to backside of the crystals but were separated from the crystals with 0.5mm plastic spacers to avoid current passing through the sample. The cell was mounted with silicon and sapphire substrates. The measurements were made at the silicon surface due to the contrast of silicon/D_2O for neutrons but transparent sapphire enabled to check filling of the cell and condition of the sample. Silicon substrates immersed in water at pH ~ 7 acquire a negative surface charge density due to their low isoelectric point. Similar charges between the particles and the substrate results in an electrostatic repulsion and a spacing from an interface. Applying positive potential to the silicon substrate therefore attracts the particles, decrease the spacing and change the particles structure. The primarily calculations of the systems provided the values for the voltages that should be applied across the cell in order to have up to a few volts across the dispersion (below ionizing potential of water). 30, 60, 120, 150 and 210 V were chosen to be applied from the supplier to the electrodes, giving 0.3, 0.6, 1.2, 1.5 and 2.1 V across the dispersion.

Results and discussions

Penetration depth in GiSANS experiment has been described in different studies [5, 6, 7] as:

$$z_{1/e} = \frac{\sqrt{2}\lambda}{4\pi\sqrt{\sqrt{\left(\theta_i^2-\theta_c^2\right)^2+\left(\frac{\lambda}{2\pi}\mu\right)^2}-\left(\theta_c^2-\theta_i^2\right)}}$$

where λ is the beam wavelength, θ_i the incidence angle θ_c the critical angle for the given interface and wavelength and μ is the scattering coefficient. In the literatures, this equation has been described as a straightforward solution to depth sensitivity of the technique, whereas depending on the instrument resolution, the signal from the structure can show up way below the critical angle. In a system like latex particles where the spacing from the interface is the scientific question in modeling the particle/particle or particle/interface interactions probing the depth becomes crucial, the penetration depth must be modeled more accurately.

In order to study the structure formed by the particles, GiSANS intensity was modelled accounting for the wavelength distribution and angular dispersion of the beam on D22 instrument. Figure 1 shows the simulated GISANS intensities for the 9 wt% PS3 latex (720 Å radius, fcc ordered structure lattice parameter equal to 404 nm) with solid/dashed lines, comparing different lattice parameters and spacing from the interface. When the sample was injected in the cell the structure was measured in fine angles

(0.02 degree steps) in order to compare the smearing of the intensity around the critical angle to that of the model and the structures spacing from the interface. Data points on the graph show the integral of the intensity of the first order Bragg peaks in each angle. The model can simulate the smearing due to the instrument resolution and describe the intensities measured below the critical angle well, which has not been fully described in previous studies.

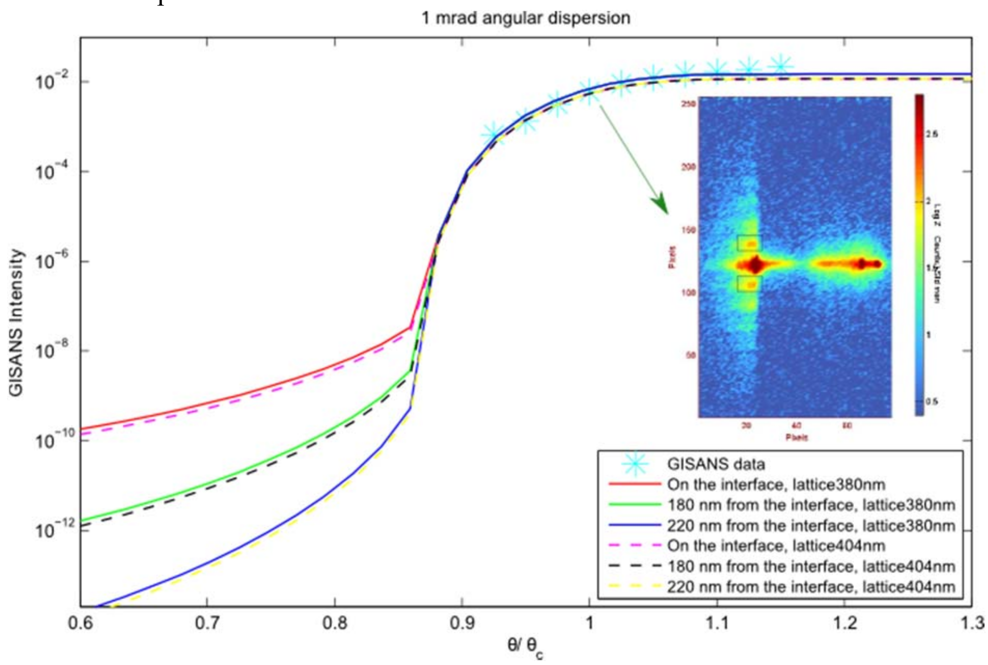
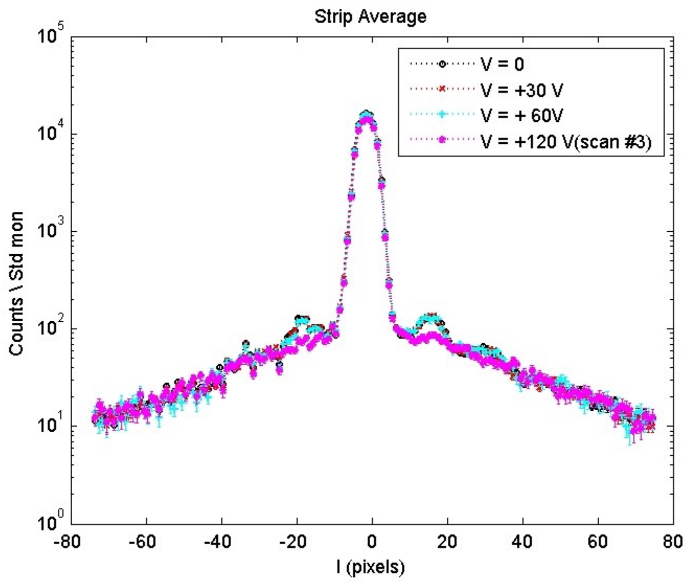
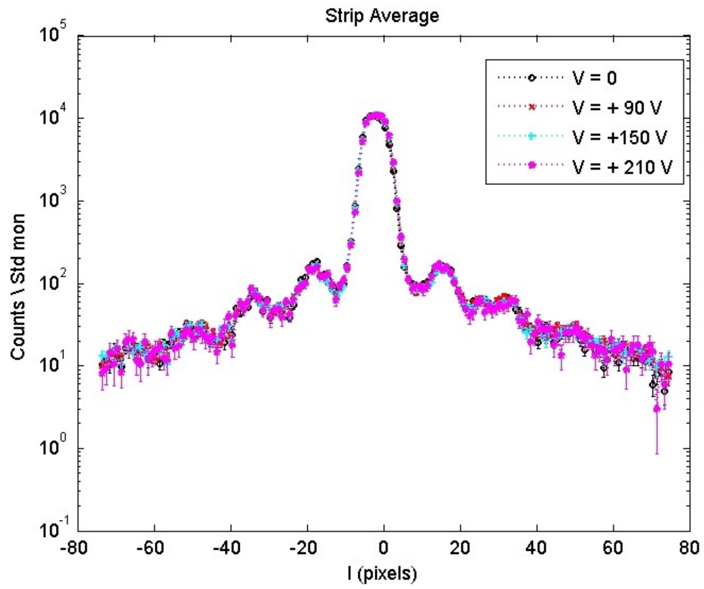


Figure1. GiSANS intensity calculated by the model for the different spacing and different lattice parameters (Lines). Data points measured in the experiment when no field applied is applied (☼). GiSANS image of the structure at the critical angle. The regions of interest where the intensities are summed up are marked with rectangles.

The effect of applied potential was determined on two samples of the same batch, in two similar cells. Vertical strips summing up the intensities in q_y direction, close to the critical angle, when applying positive potential to the silicon substrates are shown for both samples in figure 2 and 3. The measurements for various voltages, in each angle were repeated up to three times to check the changes of the structure over the time, in the case of no changes all the scans were added for better statistics. In these systems where the particles order themselves by combination of flow and packing constraints, the structure formed against various substrates is similar but not identical. In this experiment, second sample showed more pronounced structure where four orders of Bragg peak were seen whereas in the first sample up to three orders were measured. Different response to the external field was observed for two samples. Neither of the cells showed any changes in the structure below +120V (1.2V across the dispersion). In +120V, particles in the first cell started moving towards the substrate. Continuous changes were observed scanning the sample over a long period of time (8-10 hours) and finally after about 10 hours the structure was disappeared as it is seen in figure 2. The change was not reversible with switching off or reversing the potential, referring to a possibility of particles sticking to the surface. For the second cell, in which particles had a better ordering, structure remained stable even after applying nearly two times stronger voltage across the dispersion. Hence when the particles are well ordered, the structure is more stable and stronger field is required to move them. AFM measurements after the experiment suggested that the particles which met the interface due to the attractive force between positive silicon and negative particles, stuck to the interface and were not removed switching off or reversing the voltage or rinsing with water.



Cell1. Less ordered structure: 2 to 3 orders Bragg peak can be seen



Cell2. More ordered structure: at least four order Bragg peak can be seen

Conclusions

- Penetration depth and intensity profile smear close to the critical angle, depending on the instrument resolution. This smearing is modeled for wavelength and angular resolution.
- Spacing of the structure from the interface can not be probed with GiSANS experiment, since one needs hundreds of more intensity which may not even be possible with 100 times longer beam time due to the restriction by the background.
- The response of the particles to an external field depends on the structure they form: the better particles order, the more stable structure is and the stronger field is required to change the structure.
- The response to the field can be very slow (several hours)
- When particles start moving and the regularity of the structure is lost, the system becomes unstable and the scattering pattern changes continuously over the time.
- Some particles are left on the substrate after the experiment.

Reflectivity measurement is required to provide complimentary information about sticking probability and surface coverage of the particles.

References

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