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## Microscopic dynamics of nanoparticle monolayers at air-water interface

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#### 1. Introduction

Nanoparticles at air-water or fluid-fluid interface [1-6] is being extensively studied due to their importance in wide ranging systems from stabilizing pickering emulsion to photonic or plasmonic membranes [7-11]. Confining nanoparticles to the air-water interface in the form of a Langmuir monolayer using Langmuir-Blodgett [LB] technique is an ideal method to understand the structure and properties of such interfacial nanoparticle layers [9,12-17]. Significant amount of work has now emerged in the last decade for the detailed structure of a range of single or binary nanoparticle high density interfacial layers at the air-water interface, mostly using grazing incidence X-ray scattering technique [16,18–20]. Moreover, real space imaging techniques like scanning transmission electron microscopy (STEM) or atomic force microscopy (AFM) have also been used on such interfacial layers after being transfer to a solid substrate [3,15,21]. Relatively less amount of work has been performed to understand the mechanical or flow properties of such interface confined nanoparticle layers [16,22-29]. Studying such properties are very crucial in understanding the conditions under which such layers could be successfully transferred to solid substrates in an undisturbed manner for effective utilization of the designed properties [2,3,9-11,15,30,31]. From a fundamental perspective, interface nanoparticle layers, especially those encapsulated by surfactant or polymeric stabilizers, are of enormous interest as model two-dimensional (2D) soft colloidal systems with tunable interaction and surface densities [3,12,15,16,32]. Thus

#### ABSTRACT

We present results of surface mechanical and particle tracking measurements of nanoparticles trapped at the air–water interface as a function of their areal density. We monitor both the surface pressure ( $\Pi$ ) and isothermal compression modulus ( $\epsilon$ ) as well as the dynamics of nanoparticle clusters, using fluorescence confocal microscopy while they are compressed to very high density near the two dimensional close packing density  $\Phi \sim 0.82$ . We observe non-monotonic variation in both  $\epsilon$  and the dynamic heterogeneity, characterized by the dynamical susceptibility  $\chi_4$  with  $\Phi$ , in such high density monolayers. We provide insight into the underlying nature of such transitions in close packed high density nanoparticle monolayers in terms of the morphology and flexibility of these soft colloidal particles. We discuss the significance our results in the context of related studies on two dimensional granular or colloidal systems.

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various aspects of glass transition or jamming of soft colloids [33–37] especially in 2D, can be easily studied, in principle, using either surface density or temperature variation [38,39] using the LB technique. However, very few examples of such studies exist for nanoparticles [12,20,22,29], primarily, due to lack of experimental techniques to probe especially, the microscopic dynamics in high density close-packed interface layers of nanoparticles. We have shown earlier [38,39], how microscopic dynamics in interface polymer layers can be probed with the technique of interfacial microrheology (IMR). Here we report IMR studies on dense interface layers of surfactant stabilized gold nanoparticles at the airwater interface embedded with cadmium selenide (CdSe) quantum dots as both probe and constituent particles. We observe systematic variation of the isothermal compressional modulus ( $\epsilon$ ) as a function of increasing particle occupied area fraction ( $\Phi$ ) and observe non-monotonic variation of the both the characteristic relation time ( $t^*$ ) and the maxima of the dynamic susceptibility  $\chi_4^*$ which correlate with the observed variation of  $\epsilon$ , with  $\Phi$ . Interestingly, the  $\Phi$ , at which a maxima in  $\epsilon$  or a dynamical phase transition seems to occur, corresponds very closely to that for a jamming transition reported in 2D [33]. Our work thus provides unique insight into the mechanical properties of such interface nanoparticle layers of few nanometer thickness including the possibilities of existence of a quasi 2D jammed state and the underlying variations in microscopic particle dynamics accompanying such transitions.

#### 2. Experimental details

The results presented here are based on bi-disperse Langmuir monolayers of CdSe quantum dots and gold nanoparticles. The CdSe quantum dots were prepared using standard methods [40]

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while the Gold nanoparticles were prepared following the method described in [41]. The mean diameter of the CdSe quantum dots are 8 nm while that of the gold nanoparticles are 4 nm. Both the CdSe and the gold nanoparticles are capped with 1-Octadecanethiol (ODT). It has been demonstrated earlier that such ODT-capped nanoparticles form extremely well-packed solid-like monolayers at the air-water interface [9]. However, it would be impossible to visualize and track such small gold nanoparticles while for a purely quantum dot monolayer, even if it has the same extent of packing, would be difficult to track with any optical microscopy which is diffraction limited. The number density of CdSe and gold nanoparticles in solution was estimated from Transmission Electron Microscope (TEM) and Thermogravimetric analysis (TGA) of the respective nanoparticles. Both the particles were mixed in chloroform solution in the ratio of 1:4 (CdSe:Gold) and typically 800 ul of solution of concentration 0.2 mg/ml was spread at the air-water interface of a LB trough (KSV, mini, 240 cm<sup>2</sup>) at 25°C. The choice of this ratio is not unique in the sense that smaller fraction of CdSe could also be used (1:5 or 1:6). However, our observation was that there was considerable quenching of the CdSe emission by the gold nanoparticles, especially when they are in close contact. Thus, the chosen ratio of 1:4 allowed us to use the quantum dots effectively as fluorescence markers of the predominantly gold nanoparticle monolayer since their average separation was comparable to our resolution while at the same time their density was high enough to prevent complete fluorescence quenching by the gold nanoparticles. The trough was mounted on the inverted microscope stage of a Laser Scanning Confocal Microscope (Leica TCS SP5). The whole set up was enclosed in a temperature controlled chamber to minimize drift due to air circulation and thermal fluctuation. Several compression-decompression cycles were recorded on the monolayer, after allowing time (typically 10 min) for evaporation of chloroform to form a homogeneous monolayer. Using a fixed excitation line (488 nm) of an argon laser, time series emission images were collected at fixed trough area, typically at 400 kHz as described earlier [38,39]. The area fraction.  $\Phi$ , defined as the ratio of total area occupied by all the nanoparticles to a specific trough area, could be estimated from the known respective particle concentrations in solution (estimated from TEM and TGA measurements, as explained above) and from the volume of nanoparticle solution transferred on to the trough. Atomic force microscopy (NT-MDT, Russia) was performed on nanoparticle monolayers transferred on silicon substrates. Films were transferred by the vertical transfer method, with a typical dipping speed of 0.3 mm/min on silicon wafers cleaned using piranha solution as described earlier [42].

#### 3. Results and discussion

Fig. 1 shows a plot of the variation of surface pressure  $(\Pi)$  as well as the isothermal compression modulus  $\epsilon = \Gamma(\frac{\partial \Pi}{\partial \Gamma})$ , where  $\Gamma$ is the surface concentration) as a function of  $\Phi$ . The surface pressure of the monolayer increases in a monotonic manner up to  $\Phi \approx 0.69$  before it starts increasing rapidly. The compression modulus, on the other hand, increases in a similar manner, but unlike  $\Pi$ reaches a maximum at  $\Phi$  = 0.79 and starts decreasing with further increase in  $\Phi$ . This indicates a change in the mechanical properties of the monolayer which could be triggered by some morphological phase transition like buckling or collapse, as observed earlier [43,44] or simply due to multilayer formation. To rule out such effects we have both imaged and measured the thickness of the monolayer under continuous compression using imaging ellipsometry (EP3-SW, Accurion). The measurements clearly reveal formation of a compact monolayers of nanoparticles with increasing  $\Phi$ , but no visible change in thickness or morphological transition



**Fig. 1.** Variation of surface pressure ( $\Pi$ ) and isothermal compression modulus ( $\epsilon$ ) as a function of  $\Phi$  at 25 °C for Cdse–gold hybrid nanoparticle monolayer, as described in the text.

around  $\Phi = 0.79$ , where  $\epsilon$  reaches a maximum or at  $\Phi = 0.69$  where  $\Pi$  starts increasing significantly. The AFM images in Fig. 2 clearly confirm the ion clusters drawn from the images i.e increasing compactness of the monolayer with increasing  $\Phi$  and no visible morphological transition within the range of  $\Phi$  at which  $\Pi$  or  $\epsilon$  have been measured (Fig. 1). The average thickness of the monolayer is  $\approx 6$  nm corresponding to the size of gold nanoparticle. We have also transferred the monolayer onto silicon substrate or carbon coated copper (Cu) TEM grids for high resolution imaging of the monolayer (Fig. 3) shows the fairly homogeneous dispersion of the gold nanoparticles and CdSe quantum dots. The quantum dots seems to mostly exists in the form of small isolated domains of size  $\sim 50$  nm.

What is the origin of this phase transitions indicated by the changes in  $\epsilon$  as a function of  $\Phi$ . The maxima in  $\epsilon$  which is observed at  $\Phi \approx 0.27$  corresponds to formation of small domains or rafts of particles as observed earlier [12,41,42]. The monolayer at this stage, has lots of voids as as can be seen from the AFM images at  $\Phi \approx 0.4$  (Fig. 2a). The compression modulus starts decreasing with increasing  $\Phi$  due to the voids being filled up gradually till  $\Phi \approx 0.62$ , at which point the majority of particle rafts are in contact to form an almost continuous monolayer. The second maxima in  $\epsilon$ at  $\Phi \approx 0.8$  corresponds to the region where the ODT chains start inter-penetrating. Further compression does not lead to increase in  $\epsilon$ till a point is reached where the monolayer collapses (such a region is not shown here). We are interested in studying the nanoparticle monolayer dynamics at even higher area fraction, probably extending up to the  $\Phi \approx 0.82$ , the packing fraction for jamming of particle in 2D. Moreover, we would also like to understand whether there is a microscopic dynamical transition associated with the change in compression modulus, that the monolayer undergoes at  $\Phi \approx 0.8$ , as alluded to above. For this purpose, let us now turn our attention to the confocal images especially the time series data to obtain a possible understanding of the dynamical behavior of the nanoparticle monolayer. Typical fluorescence confocal images reveal the CdSe quantum dot clusters seen in TEM images. Using Particle tracking methods and Image-J software we have extracted the Mean-square displacement (MSD) of such quantum dot domains.

Some such typical MSDs are shown in Fig. 4. Although the MSDs are that of the CdSe quantum dots or their rafts it is fair to suggest that their behavior is also representative of the gold nanoparticles co-existing in the background monolayer. Several observations lead us to this plausible conclusion. We have observed that it is difficult to track these particles at low  $\Phi$  since the time scales of diffusion is too fast as compared to the time scale of our scanner. It is possible that at such low  $\Phi$  values either the rafts have not formed or even if they are formed they can, in principle move independent

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