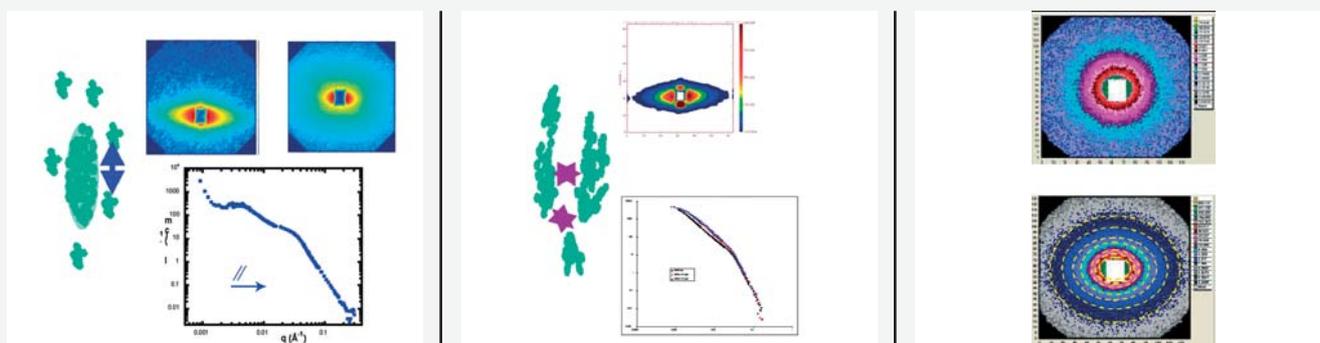


**[C6. J. Jestin] Dispersions of polymer grafted nanoparticles in a same polymer matrix : the effect of deformation**

Recently nanoparticles with grafted chains were synthesized owing to grafting from controlled radical polymerization in polar organic solvent. After purification, we obtain a stable sol, with silica cores of the same size as in the original sol, and characterize the polymer layer around the silica core using contrast matching [1]. We then disperse these particles in a polymer matrix of the same polymer as the grafted one. We observe that they **re-aggregate**, in different ways depending on the synthesis. Observation under deformation permits to refine the differences between two cases: left, coexistence of large deformable compact aggregates (responsible for a elongated scattering pattern) with small aggregates responsible for a correlation peak in  $I(q)$  along the parallel ( $//$ ) direction; middle: large deformable fractal-like aggregates (elongated scattering pattern,  $I(q)$  curves shifted along  $q$ ). We can also observe the polymer corona among matrix chains of different labelling. We conclude from the patterns anisotropy (silica core, right above, corona, below) that the corona is interpenetrated with the matrix chains, and deformed with a similar ratio.

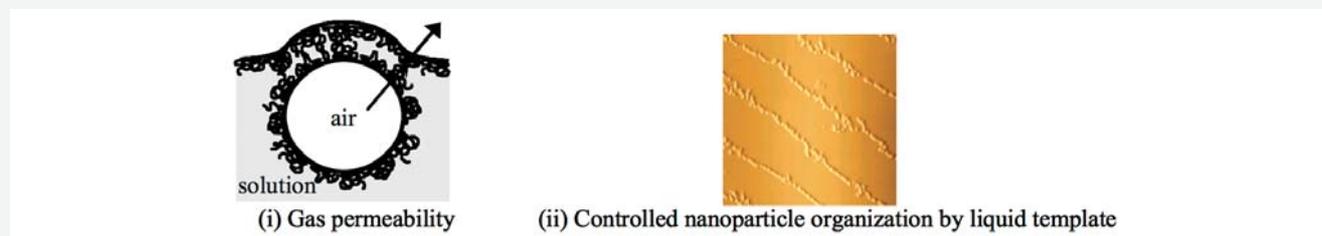
[Collaboration : A. El Harrak, S. Lorrain, G. Carrot, J. Oberdisse, J. Jestin, F. Boué, LLB]



[1] G. Carrot, A. El Harrak, J. Oberdisse, J. Jestin, F. Boué, *Soft Matter*, in press

**[C7 & C8 L.T. Lee] Interfacial and thin-film properties of complex systems**

This project aims to correlate interfacial structures of complex systems (polymer-surfactant-nanoparticle) with their thin film properties that are of relevance in potential applications. Neutron reflectivity used in conjunction with isotopic substitution provides a unique route to obtain structural and compositional information of surface layers in multicomponent systems. Here, we show two examples where structural and compositional information of adsorbed mixed layers are correlated with: (i) soap film stability and gas permeability, and (ii) thin-film dewetting as liquid template for nanoparticle organization on solid substrates.

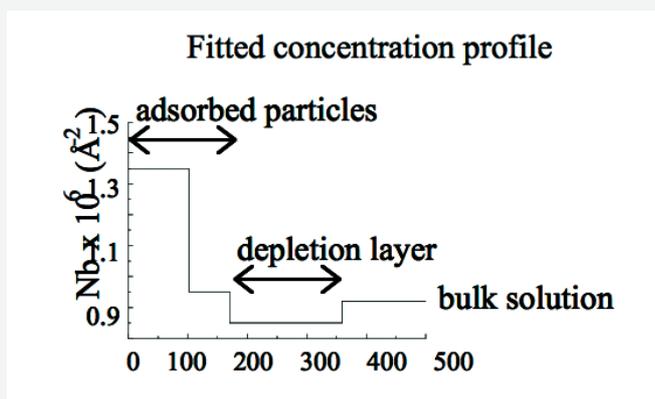
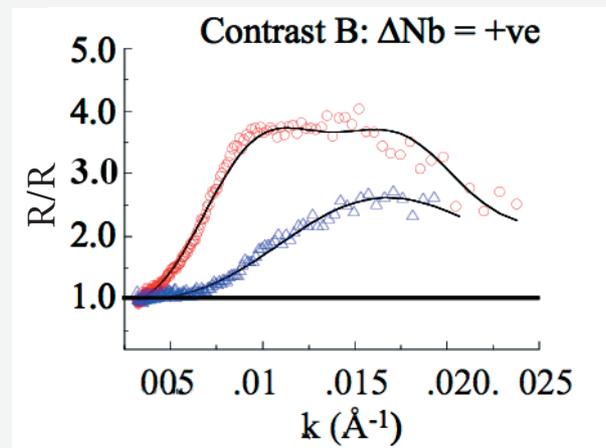
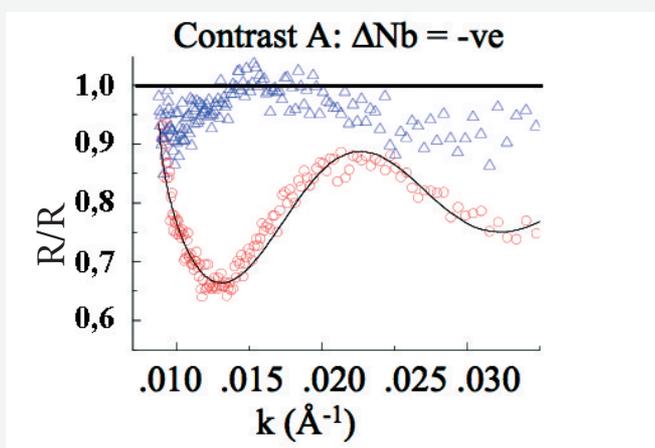


(i) Gas permeability of polymer-surfactant layers The structural properties of adsorbed poly(N-isopropylacrylamide) (PNIPAM) and mixed PNIPAM-SDS layers are correlated to gas permeation behavior of thin foam films. The gas permeability coefficient ( $K$ ) of the liquid film is evaluated from the rate of diminishing size of microbubbles ( $d \sim 250$  nm) formed on the surface of the solution. Irrespective of film thickness and physical appearance, the gas permeability of a film stabilized by PNIPAM alone is low ( $K \approx 0.045$  cm/s) compared to that stabilized by SDS alone ( $K \approx 0.10$  cm/s). This is explained by the characteristic concentration profile of the adsorbed polymer layer: a monomer-rich proximal zone ( $\phi_p \sim 1$ ) and a solvent-rich central zone. The closed-packed structure of monomers in the proximal zone thus acts as an efficient barrier to gas permeation - an explanation supported by the non-dependence of the proximal zone and of  $K$  on polymer chain length. For polymer-surfactant mixtures,  $K$  increases with surfactant/polymer ratio in the adsorbed layer up to  $K \approx 0.14$  cm/s. Mixed layers therefore show reduced efficiency as gas barrier, a result attributed to mutual decrease in the structural order of the adsorbed species.

[Collaboration: L.T. Lee, LLB; G. Andreatta, J.-J. Benattar, SPEC-CEA, Saclay]

(ii) Thin-film liquid template for controlled nanoparticle organization Thin films of charged polymer solutions dewet a solid substrate to form complex patterns that depend on solution and drying conditions. The dewet morphologies offer a potential method for templating nanoparticles into 2-dimensional complex patterns. Here, we focus on forming nanoparticle chains. The method involves dragging the nanoparticles by the dewetting liquid followed by capillary attractions between particles; minimal nanoparticle-substrate attraction is thus required. For aqueous dispersions of charged polymers and nanoparticles deposited on hydrophilic substrate, 2-dimensional arrays of nanoparticle chains extending over several hundred microns can be formed (image above – cyclodextrin-grafted Au on mica,  $d \sim 5$  nm). On hydrophobic substrate, this liquid-template system fails. Neutron reflectivity results show that while nanoparticle (silica and gold colloids) adsorption to hydrophilic substrate (water-silica) is undetectable, adsorption at a hydrophobic surface (water-air) is significant and is mediated by the adsorbed polymer (PNIPAM). Addition of SDS reduces adsorption of the nanoparticles; interestingly, the concentration profile shows a depletion layer, indicating a progressive transformation from a hydrophobic to hydrophilic surface. This effect should enhance dewetting and nanoparticle organization.

[Collaborations: L.T. Lee, LLB; C. Rezende, F. Galembeck, University of Campinas, Brazil; F. Cousin, LLB]



Normalized reflectivity for silica nanoparticle ( $d \sim 15$  nm) adsorption at water-air interface in two contrast schemes.

In this representation, all deviations from  $R/R_F = 1$  are due only to the adsorbed layer.  $\Delta N_b$  = difference in scattering length density between nanoparticle and solvent. Polymer solution (circle), polymer+surfactant solution (triangle).

**Perspectives:** Current studies concentrate on modulating the concentration profiles of nanoparticles at interfaces with special interests in stabilization of soft interfaces, and in optical properties. Emphasis is placed on the thermosensitive nature of PNIPAM-based polymers to produce reversible stimulus-responsive systems.

[C9. C. Sanchez] **Conformation of arabinogalactane-peptide from Acacia gum: a new model based on SANS and *ab initio* calculations.**

Biopolymers of the arabinogalactane-protein (AGP) type are everywhere in vegetal world, with many biological functions. Those extracted from Acacia gum are largely used in industry (stabilisation, emulsion, dispersion or adhesion). Conformation of the major molecular fraction, F1, an arabinogalactane-peptide ( $M_w : 2.86 \cdot 10^5$  g.mol<sup>-1</sup>), is highly hypothetical. SANS (Fig.1) is used here, together with *ab initio* calculations and microscopy (MET, cryo-MET, AFM), to propose a first model: a flat oblate ellipsoid of diameter  $\sim 20$  nm, thickness  $\sim 1.5$ - $1.9$  nm et and radius of gyration  $\sim 6.5$  nm. The central part resembles a fractal-like network of branches and aggregates,  $d_{\text{fractal}} = 2.6$ , a seen directly on the scattering.

[Collaboration : C. Sanchez ENSAIA-INPL, Nancy, A. Lapp, LLB, C. Schmitt & E. Kolodziejczyk, Nestlé, Lausanne, C Gaillard & D Renard, INRA-Nantes].