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Project Proposal for the Investigation of Particle-Stabilised Emulsions and Foams by Microgravity Experiments

The utilisation of particle-surfactants nanostructures as stabilising agents represents today the technologic and scientific frontier in the stabilisation of liquid films in emulsion and foams. This topic will be addressed by the proposal STEFAN (Stabilisation of Emulsions and Foams by Nanoparticles), proposed by European groups in the framework of the ESA AO-2004 for Life and Physical Sciences and Applied Research proj-

ects Similarly to what can be observed for surfactant-stabilised emulsions and foams, microgravity provides ideal conditions for the investigation of the hierarchy of involved objects: interfacial layer, liquid film, dispersed systems foam or emulsion. Microgravity experiments are planned by refurbishing the Experimental Container FASES for the ISS Fluid Science Laboratory and the facility FASTER for the European Drawer Rack, already under development in existing research programmes. Here the scientific guidelines of the project are presented together with examples and preliminary results on the effect of nano-particle-surfactant structures adsorbed at liquid interfaces. First experimental results have been achieved for particle monolayers at the water/air interface and a thermodynamic model was derived to describe the obtained surface pressure-area isotherms.

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1. Introduction

Particle stabilised emulsions, so-called Pickering emulsions, do exist for quite a while [i, ii]. First basic research goes back to the sixties and seventies [iii, iv]. The state of the art on particles at liquid interfaces was summarised recently in reviews, such as by Aveyard *et al.* [v], Binks [vi], or Sukhorukov [vii]. Recent books also deal with this topic, such as the one by Kralchewski and Nagayama [viii], by Lu, Pugh and Forssberg [ix], or by Kruglyakov [x]. While Kralchewski and Nagayama discuss the basics of interfaces and particles attached to them, Lu *et al.* discuss essentially the problem of flotation of particles, a well-know classical separation process. In flotation exactly those processes happen which we are focussing on in our project, however, we want to insert particles into systems for their stabilisation or destabilisation. The control of the particles' attachment to rising bubbles in flotation is typically made by changes in pH, ionic strength, addition of polymers or surfactants.

Some new basic knowledge about the particles at interfaces is obtained via monolayer studies, for example as given in [xi].

The characterisation of particles' properties, the hydrophilic/lipophilic balance (HLB) as the main approach, was discussed for example by Kruglyakov in [xii]. This methodology will be another red line in our approach.

There are very few attempts given in literature with the aim of stabilizing and destabilizing foams [xiii, xiv, xv] and single foam or emulsion films [xvi, xvii]. Often, particles are used as antifoaming agents or for breaking emulsions [xiv].

What regards fundamental studies on the change of particles' properties by adding salts [xviii] or surfactants [iii], there is a wide spectrum of possibilities yet untouched and is the main field of activities in the presented project.

Recently nano-particles have been utilised to produce monodisperse emulsion with controlled droplet size, according to the concept of limited coalescence process [xix]. Further than containing a large application potential, this concept opens interesting possibilities in the development of predictive and interpretative tools for the general emulsion behaviour.

Metal foams [xx] are very challenging materials as their manufacture involves the simultaneous occurrence of solid, liquid and gaseous phases at varying temperatures and the morphology of the solidified foam is quite complex. In production routes of metal foams one can find similarities to their non-metallic counterparts. Several metals and metal alloys can be foamed, such as Al, Zn, Mg, Pb, Fe. Among these alumina is the most important for applications. Quite some manufacturing technologies for foamed metals are now known [xxi].

One extremely important field of particles at liquid interfaces is the petrol industry. Natural bitumen particles are present in crude oil and act as stabilizers. Also clays may substantially be present in the oils. These clays, in contrast to bitumen, are good candidates for breaking water in oil emulsions. Therefore, petroleum industry is very interested in systematic studies on emulsions containing nano-particles in order to set up separation processes to get pure oil and release clear process waters.

2. Main targets of the project

The main of the present project is to develop a new strategy for the stabilisation or destabilisation of foams and emulsions by using nano-particles, the properties of which are modified by

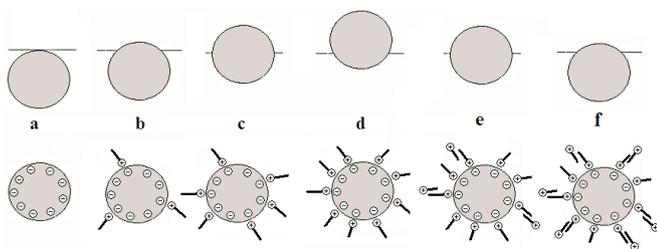


Fig. 1: Position of a spherical particle at the water/air interface with changing hydrophobicity (from a to f); top – position of modified particles in the interface, bottom – modification of particles via adsorption of ionic surfactants.

addition of surface active molecules, such as surfactants and polymers and their mixtures.

Generally, hydrophilic or hydrophobic particles reside in a bulk phase like water or oil, respectively. Only if the particles are partly hydrophilic/hydrophobic, which is given by the HLB, contact angle etc., they attach to interfaces.

Increase of the wetting angle (from a to d) results in changing the particle's position at the interface. When surfactants are added, the HLB of the particles will be changed, as it is schematically shown in Fig. 1. By screening the surface charge, a particle becomes more hydrophobic. In addition, the hydrophobic chain of a surfactant (here a cationic surfactant is adsorbed at a negatively charged particle surface) provides additional hydrophobicity to the particle. Further addition of surfactant could lead subsequently to a hydrophobization of the particles (e and f). In contact with an oil phase, particles first soluble in water, could move to the oil phase due to their hydrophobization by surfactants and back. The proper HLB, i.e. the appropriate ratio of hydrophilicity/hydrophobicity, will allow assembling the particles at an interface.

Also modelling in addition to experimental work, will be performed in the present project, dedicated to the three levels of the studied subject:

- particles at single liquid interfaces;
- particles in thick and thin liquid films;
- physico-chemical properties of mixed particle-surfactant interfacial layers.

Note, all systems, during the formation as well as in the existing state, are governed by dynamic processes, which include liquid flow as well as transport of material to and from the interfaces.

To support the project, key experiments in microgravity conditions are planned, by refurbishing facilities already under development in the existing ESA MAP research programme FASES (Fundamental and Applied Studies in Emulsion Stability) [xxii].

The Experimental Container FASES for the ISS Fluid Science Laboratory will be utilised to investigate the basic processes involved in stabilisation and destabilisation of emulsions and foams. Droplet aggregation and coalescence (destabilisation of the film between droplets/bubbles), will be studied in the absence of segregation for model emulsions/foams containing nano-particle and surfactants/polymers. In fact, during emulsion and foam destabilisation, droplets larger than ten microns are rapidly segregating, making impossible on earth the investigation of the above processes in controlled conditions. Microgravity experiments will then provide information about the features and characteristic times of these processes to be utilised to check and develop the models.

A second set of microgravity investigations will utilise the

facility FASTER, designed for the ISS European Drawer Rack. This is a fully refurbished version of the facility FAST, flown on recent Space Shuttle missions [xxiv]. The planned experiments will be devoted to the characterisation of rheological properties of droplet/bubble interfaces and of liquid films in the presence of nano-particles and surfactants/polymers (see schematic situation in Figs. 1, bottom).

Microgravity experiments will be aided by extended experimentation under ground conditions, aimed at setting-up and at developing the needed experimental tools and to create a large base of characterising data and observations about the basic processes involved. These investigations are necessary to clarify

the links between particle-surfactant nano-structural properties, surface/interfacial properties, film stability and emulsion/foam stability. The concentration and composition dependent synergy effects between nano-particles and surfactants or polymers when both are adsorbed at a fluid interface need to be identified.

The detailed definition of these experiments and of the scientific requirements for the utilisation of microgravity facilities represents then an important target of the project as well.

3. First Results

Preliminary experiments have been performed with silica particles Levasil ®200/30 from H.C. Starck GmbH, Germany (amorphous silica SiO₂ produced via particle growth from a molecularly dissolved silica solution without any additives) modified by addition of increasing amounts of the cationic surfactant CTAB. The Zeta potential and size distribution at different CTAB concentrations are shown in Fig. 2. At CTAB concentrations between 10⁻³ M and 3·10⁻³ M a charge inversion takes place. At the same time, the silica particles become unstable and aggregate, seen by the large peak in the particle size curve of Fig. 2.

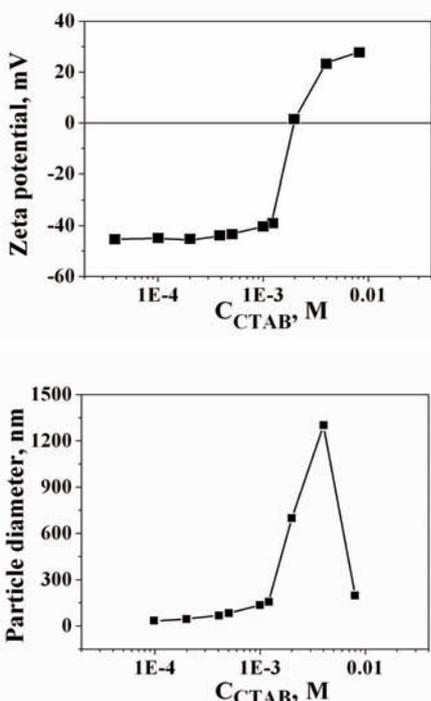


Fig. 2: Zeta Potential (top) and particle size (bottom) of a 1 wt% Levasil 200/30 in 10⁻³ M NaCl at increasing amounts of anionic surfactant CTAB; data from [xxiv].

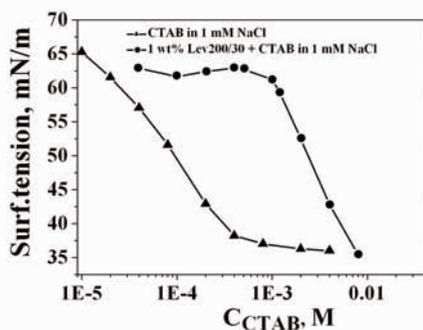


Fig. 3: Surface tension of aqueous CTAB solutions as a function of concentration in 10⁻³ M NaCl in absence (▲) and presence of 1 wt% Levasil 200/30 (●), data from [xxiv]

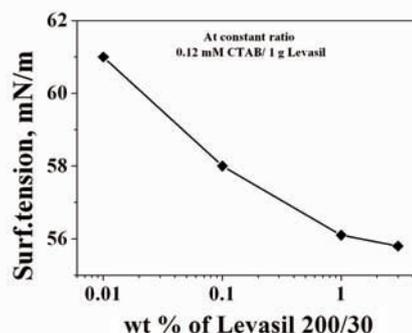


Fig. 4: Surface tension of Levasil dispersions as a function of particle concentration at a constant ratio 1.2·10⁻⁴ M CTAB/1 g Levasil, data from [xxiv]

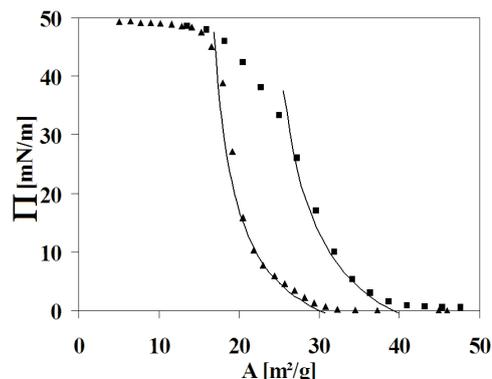


Fig. 5: Dependence of surface pressure Π on the monolayer coverage for polymeric particles 113 nm in diameter without dispersant (▲) and with dispersant (■), solid lines calculated from our new theoretical model, experimental data from [xxv]

The change in surface tension of CTAB solutions is shown in Fig. 3. The presence of 1 wt% Levasil leads to a quite broad range of almost constant surface tension. Again at a CTAB concentration of 10^{-3} M a dramatic change sets in, i.e. the surface becomes mainly governed by the free CTAB molecules. Note, the given CTAB concentrations are estimations taking into account the depletion due to surfactant adsorption at the Levasil particle surfaces. From a certain concentration on (about 10^{-4} M CTAB) we observe an almost constant surface tension, which can be explained only by the presence of modified particles, which are replaced by surfactants at CTAB concentrations above 10^{-3} M (for details see [xxii]).

Increasing amounts of Levasil lead to a decrease in surface tension, as demonstrated in Fig. 4. This effect is obviously due to adsorption of surfactant modified particles.

In a recently submitted paper an attempt was made to describe the surface tension isotherm of particle monolayers, the details of which are given in [xxvi]. The Fig. 5 shows an example how the newly derived thermodynamic theory allows to quantitatively describe the behaviour of particle monolayers. These are of course first studies only and a systematic analysis in particular also of the dynamic aspects of the formation of such complex interfacial layer is required.

4. Conclusions

The presented work summarises the experimental and theoretical work planned to be performed in a microgravity project. The project is yet pending, however, first experiments on particle modified interfacial layers in space are under way. The first experiments shown above demonstrate the suitability of available techniques and the feasibility of the proposed ideas. The thermodynamic model discussed in [xxvi] is a first step in describing the complex situation when modified particles adsorb in competition with free surfactant molecules.

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5. References

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