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Smart and green interfaces: From single bubbles/drops to industrial environmental and biomedical applications

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SMART AND GREEN INTERFACES: FROM SINGLE BUBBLES/DROPS TO INDUSTRIAL ENVIRONMENTAL AND BIOMEDICAL APPLICATIONS

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Abstract

Interfaces can be called Smart and Green (S&G) when tailored such that the required technologies can be implemented with high efficiency, adaptability and selectivity. At the same time they have also to be eco-friendly, i.e. products must be biodegradable, reusable or simply more durable. Bubble and drop interfaces are in many of these smart technologies the fundamental entities and help develop smart products of the everyday life.

Significant improvements of these processes and products can be achieved by implementing and manipulating specific properties of these interfaces in a simple and smart way, in order to accomplish specific tasks. The severe environmental issues require in addition attributing eco-friendly features to these interfaces, by incorporating innovative, or, sometime, recycle materials and conceiving new production processes which minimize the use of natural resources and energy. Such concept can be extended to include important societal challenges related to support a sustainable development and a healthy population.

The achievement of such ambitious targets requires the technology research to be supported by a robust development of theoretical and experimental tools, needed to understand in more details the behavior of complex interfaces. A wide but not exhaustive review of recent work concerned with green and smart interfaces is presented, addressing different scientific and technological fields. The presented approaches reveal a huge potential in relation to various technological fields, such as nanotechnologies, biotechnologies, medical diagnostics, new or improved materials.

Keywords:

liquid-liquid interfaces; gas-liquid interfaces; gas-liquid-solid interfaces; wetting; spreading; nanomaterials; diagnostics

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1. Introduction

Bubble and drop (B&D) interfaces are fundamental to numerous industrial, environmental and biomedical applications. The scientific and industrial literature is flooded with information which deals either with phenomena at the scale of single B&D entities or with large scale applications. In this respect, progress has been made in the development of (a) novel instrumentation (e.g. X-ray tomography), (b) direct numerical simulations (e.g. volume-of-fluid or level-set methods) and (c) theoretical and computational tools (e.g. prediction of local fractions and size distributions) for the description of actual complex systems. The above advancements refer primarily to B&D interfaces, which are either clean or covered by conventional surfactants, and this constitutes the current state of knowledge in this field. Nanoscience and nanotechnology in composing new materials for applications, energy producing/saving technologies, environmental protection/restoration and health care have been identified as priority research areas around the globe. All these areas have direct relevance to B&D interfaces as the latter represent efficient means for controlled mass and heat transport across immiscible phases. Unfortunately the above efforts most often lack hierarchical research through multiple length scales and across diverse disciplines.

The increasing demand to tailor interfaces for new applications and for improving the performance of old ones necessitates a new generation of B&D interfaces. This calls for Smart and Green interfaces. Smart and Green (S&G) interfaces are tailored interfaces that can accomplish a technological task with high efficiency, adaptability and selectivity, while being also eco-friendly (biodegradable, reusable or simply more durable). The means to tailor S&G interfaces and accurately control their performance span from synthesis of novel materials to manufacturing processes and advanced diagnostics. A non-exhaustive selection of immediate industrial applications with high social relevance is: detergents that wet fibres uniformly, food foams and emulsions with long lasting stability, cosmetics and paints that are evenly spread, boilers/condensers with heat exchange surface renewal, distillation and flotation columns with homogeneous phase distributions, crude oil transportation, drug encapsulation and controlled drug delivery, “self-cleaning” solid surfaces which eliminate the need for regular washing/polishing.

Interfaces in the generalized notion constitute an interdisciplinary and multiscale subject spanning from fundamental to applied sciences and from molecular to macroscopic size scales. Parallel to the theoretical development of fundamental issues of Colloid and Interface Science by well-known physicists and chemists at the first half of the 20th century, the practical use of systems containing interfaces like emulsions, foams and sols was constantly expanding based on empirical rules without rigid scientific foundation. Regarding sols the convergence of technological practice to fundamental scientific principles came along with a specific event: the development of DLVO theory that explains sols stability based on first principles. The corresponding development for the case of emulsions and foams did not proceed by a huge step like the DLVO theory but it followed a gradual advancement in small steps, like the hydrophilic-lipophilic balance (HLB) in the case of emulsions. Literature on these classical subjects that attempts to relate applications with scientific foundation in order to extend the fundamental knowledge and to improve the applications is extensive today. In parallel, new technological issues appear (such as smart or biomimetic interfaces) that call for fundamental backing and technologies to control them. One of the reasons for the rich

literature during the last decade on analyzing applications based on first principles is the vast increase in computational power and the development of sophisticated numerical methods. These tools render possible quantitative analysis that was not accessible before. Further to the above interface-centered issues there are many applications from the medical (diagnosis, controlled drug release), energy (boiling, evaporation), industrial (flotation, extraction) domains that use interfaces as a device to achieve certain goals.

Developing Smart & Green interfaces requires major scientific and technological advances that need considerable interaction among groups experienced in manufacturing, advanced characterization and modeling of interfaces in order to identify and implement best strategies and means to produce S&G interfaces. Literature survey reveals several topics in the field where substantial effort is undertaken. A tentative selection refers to (a) new eco-friendly materials or processes that increase the efficiency, selectivity and adaptability of interfaces, (b) innovative industrial methods for producing and dispersing B&D of well-controlled size, population and stability, (c) pioneering instrumentation and diagnostic systems, (d) performance enhancement of multiphase industrial processes.

The research on S&G interfaces is very broad and covers many fields of fundamental and applied science. The present work has therefore to be rather selective and we have to restrict ourselves on only few examples which are logically linked with each other. To categorize formally the research activities that have been performed in recent years in the field of colloids and interfacial science one can identify the following four distinct domains:

(1) **Fundamentals.** This domain refers to improvement of the fundamental understanding of the general interface structure and evolution dynamics. This is achieved by a combination of theoretical development, the implementation of numerical techniques for solution of the governing equations and the exploitation of experimental techniques. The work performed in this domain can be divided in three length scales: one concerning single interfaces (e.g. an isolated bubble or droplet), one that concerns multiple interfaces (e.g. multi-bubble/droplet systems like clusters, aggregates or clouds) and one concerning combination of multiple interfaces at industrial scale (e.g. foams, emulsions) including also the effects of the container wall, external fields and surroundings. The influence of surface properties (addition of surfactants, modified substrates) on the fundamental behavior (hydrodynamics and heat/mass transfer) of single bubbles and drops is also analyzed. Theories for bubble formation and growth and bubble motion in external fields (e.g., electrical, magnetic, temperature fields), are advanced based on new experimental data. New computational techniques (e.g. capturing the shape evolution of an interface based on the superposition of fundamental solutions of the fluid dynamics equation) and analytical approximations are employed. Also, systems further to those typically treated in colloid and interface science like the high energy impact of jet droplets on modified surfaces are theoretically and experimentally examined. The most important issue being the holy grail of the interface science is the quantitative relation of the intrinsic properties of interfaces (dynamic and static surface tension, rheological properties, micro-geometry of solid surfaces, electric potential etc) to the macroscopic properties of complex interface systems (e.g. emulsion and foam stability, inception of boiling, spreading of paints). A sound advancement in this direction is pursued by combined theoretical, experimental and numerical efforts employing scientists from the chemistry, physics and engineering disciplines.

(2) **Materials.** This domain contains all the efforts for the development and tailoring of new materials meant for Green and Smart interfaces. This refers globally to several different issues like: (i) development and characterization of new surfactants, macromolecules and nanoparticles that modify the gas-liquid interface towards enhanced energetic and rheological properties. The above includes also mixtures of materials. (ii) Chemical and physical (morphological) design of superhydrophobic and superhydrophilic solid surfaces. The most challenging task is the development of complex mixed surfaces e.g., patterning hydrophilic areas in superhydrophobic surfaces to control droplet deposition and spreading. Manufacturing of patterned and structured surfaces was achieved by employing lithography, chemical vapor deposition, etching or other contemporary techniques. (iii) Development of smart nanostructured interfaces controlling heat transfer upon drop impact. (iv) Foam polymerization to produce new foam structured solid materials. (v) Preparation of aerosol particles with specific surface properties. Special care will be paid that all new materials are eco-friendly (biodegradable, reusable, more durable, less energy consuming for their production). Popular topics within this domain are: synthesis, purification, separation, modification, characterization and classification of surfactants, macromolecules, particles and solid surfaces.

(3) **Diagnostics.** This domain refers to development of diagnostics, this including identification of systems' most representative parameters, measuring principles and techniques, and reaching accuracy/sensitivity, conditions and range of applicability, data analysis and interpretation. Diagnostics can be also categorized according to the length scale of measurement. The first category refers to diagnostics for the characterization of single interfaces. On this account, existing techniques for measuring static and dynamic interfacial tension, interfacial rheological properties and film thickness, propagation and rigidity are revised or improved. The second category includes determination of bubble/droplet size distribution in clusters improving classical optical techniques or developing modern techniques based on electrical resistance, differential scanning calorimetry, acoustic wave modification etc. The key point for all these diagnostics is how to convert the crude experimentally measured data to valuable results. The transformation is not in general easy and is known as an inverse problem. The study of the direct problem (necessary as prerequisite to the inverse) is included performed in the domain Fundamentals but the inversion procedure belongs to Diagnostics. Diagnostics that can be examined for the analysis of small and meso-scale interfaces are digital holographic interferometry, infrared thermography to register the motion of evaporating contact lines, particle image velocimetry, holographic tomography, high speed holography. The last category of diagnostics refers to techniques exploiting the properties of bubbles/droplets to monitor states of industrial, environmental, or medical interest. Industrial applications include estimation of gas holdup in adsorption/desorption towers, refinery and flotation equipment and in pipelines transporting liquids, e.g., crude oil. Modern environmental applications include fast estimation of pollutants in drinking waters by measuring rising bubble velocity in it and the use of optical and spectroscopic nanotechnological Quality Control in beverages. Diagnosis of diseases using patterns from blood droplet evaporation, monitoring the motion of carrier droplets for controlled drug delivery, detection of bubbles in the bloodstream during open heart surgery are examples in the medical domain.

(4) **Technology.** This domain concerns marketed industrial technologies and end-user applications. These technologies include specific products, processes or even computational tools for modeling and optimization that can span from small to large length scales. Applications span a broad range from typical large scale industrial processes to food, cosmetics and detergent production and to medical applications. Emphasis is given to industrial methods of generating and dispersing bubbles and drops, control of their population, size and stability. Bioactive encapsulation and controlled release, design of carriers for drug delivery by inhalation, active and passive control of drop formation are also issues of interest in this domain. Moreover, classical industrial processes such as boiling, evaporation, condensation, flotation and more modern ones such as molecular flotation (separation of molecular level entities by bubbles) also belong to this domain. Additional issues dealt in this domain are optimization of oil recovery, green use of emulsifiers, application of natural surfactants in pharmacy/cosmetics/foods, technologies for creation of foams and emulsions with tailor-made properties, surfactant/enzyme mixtures for food digestion and cleaning. All relevant technologies follow the principle of least energy and material consumption to minimize environmental impact. Integrated large scale software tools of the technological processes necessary for the optimization of their efficiency also belong to this domain. These tools simulate the complete process based on mean field approaches like multiphase computational fluid dynamics and population balances. Popular topics within this domain are: industrial methods of generating and dispersing bubbles and drops, control of population, and size, stability and processing

Within each domain one can easily identify three length scales: micro-scale, meso-scale, and large-scale. Green (eco-friendly) aspects and concerns are found in all domains.

This review, although not exhaustive, shows clearly that the advancement of individual domains and disciplines (e.g. colloid science, interface science or environmental engineering) has not been concerted. Unfortunately, research activities have been largely fragmented into several groups without a really interdisciplinary approach. The absence of an integrated approach appears to be detrimental to the achievement of major breakthroughs. This has been the motivation for setting up a dedicated scientific network, COST Action MP1106ⁱ, supported by the European Science Foundation. A COST action is the ideal mechanism for the integration of efforts and for developing a common language between scientists of different fields to allow cross-fertilization and exchange of knowledge across fields and develop expertise to resolve critical scientific problems and improve applications.

The structure of the work below follows the aforementioned four domains: Fundamentals, Materials, Diagnostics and Technology. Information is presented for each domain separately. A brief discussion is made in parallel. Finally, a conclusion section is provided along with foreseen future perspectives.

The structure of the work below follows the aforementioned four main domains of research on S&G interfaces: Fundamentals, Materials, Diagnostics and Technology. Selected examples are presented for each of the domains in order to give some insight into the topic. A brief

ⁱ COST Action MP1106 “Smart and green interfaces - from single bubbles and drops to industrial, environmental and biomedical applications”

http://www.cost.eu/domains_actions/mpns/Actions/MP1106

discussion is made in parallel between the sections in order to demonstrate the logical link between the domains. Finally, a conclusion section is provided along with future perspectives.

2. Fundamentals

This domain is usually referred to as colloid and interface science and it still is. However, a wide variety of new research topics and corresponding new methods already emerged in this area and will emerge in the nearest future. The main feature of these methods is their extreme sophistication, work with very small objects/interfaces or even on a molecular level. Kinetics of adsorption on a molecular level is a fast growing area of research (see paragraph “Impact of adsorption layers on properties of thin liquid films”, “Polymer adsorption and electrokinetic potential of dispersed particles in weak and strong electric fields”, and “Foam, emulsion and wetting thin liquid films”). From this point of view these new areas of research include work with very “smart interfaces”. The latter requires new methods of investigations, and some of them are presented below: Electro-optics of colloid/polyelectrolyte complexes, Laser beam non-resonant and resonant interaction with single, suspended microdroplets, Phase transitions and chemical reactions in simple liquids in electric field gradients, Bubble bouncing and lifetime at undisturbed and vibrating water surfaces. Considerable progress has been made in the miniaturization and “smartness” of inject printing, and in combining CFD simulations with physicochemical models of bubble formation, flotation and flocculation. On the other hand scientists in this area are getting more and more involved in investigations directly or indirectly related to living organisms. This part of research must deal with “green interfaces” and the latter is of vital importance. This part of “green interfaces” research is presented below in Interactions of inhaled droplets and particles with human breathing system – in silico and in vitro approach, Smart systems and formulations with possible medical applications, and Pattern formation in drying of blood spots. Investigations in the above mentioned areas of “smart and green interfaces” require many new theoretical efforts. New methods of deposition of materials on “smart interfaces” using tiny evaporating droplets demanded considerable theoretical efforts, and the substantial progress in this area is presented also below.

2.1. Colloids and their applications

2.1.1. *Electro-optics of colloid/polyelectrolyte complexes*

Significant changes in the conformation and electrical properties of the adsorbed polyelectrolyte chains were demonstrated in dependence on ionic strength in the solutions of oppositely charged polyelectrolytes [1]. Effect of ionic strength and molecular weight on the stability of adsorbed polyelectrolyte bi-layers was also demonstrated for oxide particles in stabilized suspensions [2]. The sensitivity of electro-optics to particle surface charge was used to clarify the role of charge distribution of pectin chains, adsorbing them on oppositely charged ferric oxide particles [3]. The electro-optical signal contains information also on the particle dimensions (through their rotational diffusion coefficients), which allows investigating colloid stability in presence of polyelectrolytes. Mixtures of polyelectrolyte chains and oppositely charged colloidal objects are of fundamental importance for biology and medicine and present great interest for applications in the field of water treatment, food

technology, cosmetics, ceramics, etc. Recently, electro-optics was applied for studying multilayer films on non-spherical colloidal particles at high concentration of low molecular salt [4, 5, 6].

2.1.2. Laser beam non-resonant and resonant interaction with single, suspended microdroplets

The interaction of a single laser pulse with a single microdroplet suspended in air without destroying the droplet is not yet comprehensively studied. The interaction of distilled water droplet (3-4 μl volume) with a pulsed laser beam at 532 nm was investigated; the water absorption is very low and the interaction of an aqueous droplet suspended in air with the laser beam is dominated by non-resonant phenomena so that one produces droplet deformations and mechanical vibrations [7,8]. It was shown that the droplets lost material as a consequence of the impact with a laser beam. During non-resonant interaction one may produce nanodroplets that propagate at supersonic speeds and microdroplets propagating at lower speeds. In a second set of experiments the behavior of the microdroplets of Rhodamine 6G in distilled water was recorded at high speeds. The laser induced fluorescence emitted by the droplet material was measured evidencing even lasting effects in the droplet. A correlation between the non-resonant and resonant effects on a droplet at interaction with one single laser pulse was made in function of the laser beam power and the laser dye concentration. Further investigations [9] have concerned the interfacial and wetting properties after laser irradiation of the micro-droplets containing cytostatics and Doxorubicin, in order to assess their compatibility with microfluidic devices. These studies open new perspectives for using optofluidics methods for applications in nanomedicine and nanotechnologies.

2.1.3. Interactions of inhaled droplets and particles with human breathing system – in silico and in vitro approach

Health effects from inhaled aerosols depend on the efficiency and the site of particle deposition on the surface of the respiratory system, where subsequent events are initiated by contact of particles with the biological interface. CFD simulations of flow of micro- and nanometer-sized particles carried with the air inhaled to the particular regions of the respiratory tract were used to assess the importance of particle properties and breathing dynamics on aerosol particle deposition in the breathing system [10]. Parallel experiments were made using anatomical models (*in vitro* approach) which allowed verifying the computational (*in silico*) results.

Particles deposited in the deep lungs settle down on the alveolar liquid film and interact with the pulmonary surfactant, which is adsorbed at the gas-liquid interface. Physicochemical aspects of particle-lung interactions can be revealed by analysis of interfacial effects at this barrier and they are reflected by alterations of dynamic surface tension in this system. Extensive studies were carried out, which indicate that interactions of micro- and nanoparticles (NP) of different origin (e.g. diesel exhaust particles, metallic dusts, nano-clays) impair the native surface activity of the pulmonary surfactant (PS) under dynamic conditions imitating area variation within the lungs during breathing cycles [11]. Further understanding of the interaction of NP with the PS have been obtained by the investigation of deposited mixed lipid-NP layers at the aqueous surface. Such surface science approach, utilizing a set of

different techniques (Langmuir trough, surface rheology, AFM, Brewster Angle microscopy, ellipsometry), allowed significant effects of the NPs on the structural and dynamic features of model PS to be identified [12, 13], such as, modifications of the linearity (see Fig. 1) of its surface tension response under surface area expansion-compression cycles and of the 2-D phase behavior, which are potentially relevant for the impairment of the lung functionality. These effects suggest possible routes of toxic action of inhaled aerosol particles and may help to define new therapeutic strategies. In addition the above approach could be extended to provide a basic understanding of the interaction of NPs with other biological membranes, which is a fundamental step for the advancement of nanomedicine.

Fig. 1: Effect of different nanoparticles on the linearity of the surface tension response of phospholipid layers to surface area expansion-compression cycles.

2.2. Foam, emulsion, flotation

2.2.1. Impact of adsorption layers on properties of thin liquid films

Complex studies of adsorption-layer properties on air/solution interfaces and on foam films are performed with aqueous solutions of mixtures of proteins and soluble surfactants. This type of mixed systems has important applications in the food industry [14].

It has been clarified in [15,16] how the surfactant adsorption layer properties are related to the course of the drainage parameters of microscopic foam films in the special case of aqueous solutions of the ionic and non-ionic amphiphiles, containing premicellar nanostructures. It was established that in the premicellar concentration domain considerable irregularities of the adsorption layer properties are observed: plateau and kink regions are registered in the experimental surface tension isotherm along with unusual changes of the surface rheological characteristics. The systematic investigation of the drainage of microscopic foam films obtained from these solutions showed that the dependencies of basic kinetic parameters of the films on the amphiphile concentration run in synchrony with the changes in the adsorption layer properties. This fact is related to the presence of smaller surfactant aggregates (premicelles).

2.2.2. *Smart systems and formulations with possible medical applications*

Biocompatible and nontoxic poly(N-isopropylacrylamide) grafted with poly(ethylene oxide) chains pertain to the group of thermoresponsive smart materials. In aqueous solutions and at temperatures higher than the lower critical solution temperature the polymer molecules undergo coil-to-mesoglobule transition. Core-shell nanoparticles are obtained with predominantly hydrophobic core and hydrophilic corona. Surfactant- type drugs (e.g. non-steroidal anti-inflammatory drugs) are incorporated in these particles (in vitro, at lower temperatures) and released under controlled conditions at body temperature (mimicking conditions in vivo). These processes are finely tuned by temperature and the presence of specific additives. Combined investigations of bulk and interfacial properties of the polymer–drug–additive systems are performed.

Foam films of exogenous pulmonary surfactant preparations propose numbers of new parameters and dependences for description of their behavior and functional activity in vivo. These parameters are: film thinning times, critical concentration for black film formation, film stability in terms of probability for stable black foam film formation, film thickness and dependence of its change under applied external pressure, interactions with substances in the bulk, etc. They could be used to direction of optimization and improvement the production technologies as well as development of new generation of therapeutic surfactant preparations [16,17,18,19].

2.2.3. *Foam, emulsion and wetting thin liquid films*

Modern polymeric chemistry is capable of synthesizing “smart” polymers, i.e. macromolecules with a precisely controlled architecture that responds to the specific polymeric surfactant application’s purpose. These so-called “green” surfactants have been the subject of extensive research. Particularly interesting are the branch type ones, e.g. star-like polymers, grafted polymers, dendritic type polymers, ABA triblock copolymers, as well as natural graft ABn copolymers (A being inulin, a linear polyfructose backbone that has been modified by introducing several alkyl groups B).

Thin liquid films present in foams and emulsions (o/w/o and w/o/w) determine their respective properties. Understanding the interaction and behavior of thin liquid films is crucial in gaining some control over colloidal systems. In contrast to foam film studies, articles dedicated to oil/water/oil (o/w/o) and water/oil/water (w/o/w) emulsion films stabilized by natural and polymeric surfactants are scarce and their quantitative study is insufficient [20].

If the vast practical application of emulsions is placed on the one side of a balance and the articles exploring oil/water/oil and water/oil/ water emulsion films stabilized by natural and polymeric surfactants on the other, it will be outweighed by the former. Detailed information derived from quantitative studies of such films is still surprisingly scarce. It may be said though that certain steering in that direction is on the verge of becoming noticeable, evidenced also with the new methods and techniques developed in recent years [21, 22].

2.2.4. *Particles in emulsion and foam technology*

The large development of nanomaterials fostered during the last decade the use of micro/nanoparticles as additives in the formulation and for the control of the stability of emulsions and foams [23, 24, 25]. The subject presents several “smart” and “green” aspects. A proper design of the particle properties (size, hydrophobic/hydrophilic character, morphology, surface charge) can be utilized either to obtain ultrastable foams and emulsions, or as efficient de-emulsifiers or de-foaming agents, reducing in both cases the energy demand. Particles presenting partial wetting are able to segregate at the droplets interface hindering coalescence via a steric mechanism. A destabilising effect can be instead achieved by particles which after incorporation in the emulsion/foam film compete for the adsorption of the stabilising surfactant molecules or causes a bridging of the opposite film interfaces.

The effective mastering of the above mechanisms requires a fine control of the particle hydrophilic/lipophilic balance (HLB). Several methods to modify such feature have been proposed, based on specific chemical or chemico-physical treatments of the particle surface. However, these treatments are in general too complex and expensive for practical applications on an industrial scale. Surfactant adsorption onto the particle surface is a smart alternative to obtain such modifications. In fact that can be simply obtained by adding surfactants to the nanoparticle (NP) dispersions. Tuning the surfactant concentration can bring in a simple way to achieve different HLBs. In spite trivial from the operative point of view, using such strategy in practical applications requires a deep understanding of the complex physico-chemical interplay between particles and surfactants in the bulk phase and at the liquid interface [26 , 27].

In this respect NP-surfactant complexes can be seen as surface-active species, similar in some aspects to protein-surfactant complexes, but showing peculiar features in respect to their capability to modify basic interfacial properties. The latter's have been investigated for dispersions of NPs in the presence of common surfactants [28, 29], such as Cetyl trimethylammonium bromide (CTAB), octadecylamine (ODA), or palmitic acid (PA). In particular, some formulations are extremely effective in achieving large reductions of the surface tension or to obtain large increases of the dilational elasticity [30, 31].

While a picture of the effects for aqueous-air surfaces is relatively clear, how these NP-surfactant mixtures behaves in water-oil systems is still to be explored in detail. The presence of oil soluble surfactants, such as ODA or PA opens, in fact, a variety of different scenarios, depending on the initial surfactant distribution among the two liquid phases [31, 32]. That opens interesting scenarios for the utilization of NPs as surface-active species, alternative to classical surfactants in a vast number of products and technologies.

2.2.5. *Inkjet printing*

Inkjet printing has evolved into a technology which plays an important role in the graphical printing industry and in many emerging new industrial and medical applications [33]. The piezo inkjet technology has unique capabilities due to its ability to deposit a wide variety of materials on all kind of substrates in well-defined patterns. The physics behind the chain of

processes comprise the two-way coupling from the electrical to the mechanical domain through the piezo electric actuator, the coupling to the acoustic domain inside the ink channels, and finally the coupling to the fluid dynamic domain with free surface flow, i.e. the drop formation and the drop impact, spreading and solidification. Main challenge of this research is to prevent satellite drop formation.

The modeling of the physical phenomena is an essential part of research and contributes to the fundamental understanding of the underlying processes [33].

Measurements and simulations of the final stage of the inkjet printing process involves a number of various physical phenomena [34]. Main challenge is to cover the wide range of time scales, from ns for processes on molecular level until years for processes which determine print robustness.

2.2.6. Bubble bouncing and lifetime at undisturbed and vibrating water surfaces

When a rising bubble in a liquid column arrives at the liquid/gas interface its lifetime can vary from fractions of second up to hours. Stability of liquid films formed at various interfaces by the striking gas bubble is considered to be one of the most important factors determining the outcome of collision. The probability of bubble bouncing or film rupturing depends on many different factors such as bubble size, impact velocity, liquid viscosity and surface tension as well as presence of surface active substances. In the presence of even traces of impurities in the system the bubble lifetime can be significantly prolonged by changing the kinetics of the film drainage [35]. It has been recently reported that only 0.6% of adsorption coverage over the bubble surface can prolong the bubble lifetime at the interface by over 2 orders of magnitude – from milliseconds to seconds [36].

It has been shown that spectacular prolongation of the bubble lifetime at a liquid surface is possible without the presence of surface-active substances. When the energy dissipated during the bubble collisions was re-supplied from the interface vibrating with a proper acceleration [37] then the bubble lifetime was prolonged almost indefinitely at free surface of high purity water.

2.2.7. Combining CFD with physicochemical models bubble formation, flotation and flocculation

Numerical study of the formation of mini-bubbles in a 2D T-junction by means of computational fluid dynamics (CFD) and experimental study were presented in [38, 39].

Traditionally, the design of drinking water treatment processes is based on empirical or semi-empirical approaches. Nevertheless, efficient process design and optimization calls for advanced mathematical modeling of the processes. An approach of combining CFD with physicochemical models for the simulation of large scale processes concerning the removal of solid particles from slightly polluted waters has been developed. A new methodology has been proposed to simulate the performance of flotation [40] and flocculation tanks [41] of a drinking water refinery. In both cases the developed models were validated against experimental data and an extensive parametric analysis was performed, (Figure 2). The proposed methodology can be used to simulate and optimize the operation of large scale water purification installations.

Fig. 2: (a) Velocity flow field created by the impeller inside a flocculation tank, (b) contour map of the mean flocs diameter taken from [41].

2.3. Wetting and spreading phenomena

The effect of multi-scale roughness on the Lotus effect was found to be helpful, especially for the mechanical stability of super-hydrophobic surfaces, but not necessarily essential [42]. Because of the multitude of terms used for wetting of rough and heterogeneous surfaces (some of which are linguistically inaccurate), a complete terminology scheme was suggested in [43], which adheres as much as possible to existing, classical terminology. The meaning of measured contact angles has recently been strongly debated. In addition to the advancing and receding contact angles, for which there is no theory yet for interpretation, it has been advocated measuring the most stable contact angle. This is the angle that is predicted by the Wenzel and Cassie equations. As an example, this approach was applied to amphiphilic polymer films [44]. Surface-tension-induced motion is a classical, yet developing field. Recent work was done on vapor-driven Marangoni propulsion [45]. Disorder-induced hysteresis and nonlocality of contact line motion in chemically heterogeneous microchannels was investigated in [46].

2.4. Kinetics of Evaporation

2.4.1. Stages of evaporation: universal behaviour

Recently a considerable progress in theoretical and experimental studies of simultaneous spreading and evaporation of liquid droplets on solid substrates has been achieved [47,48,49,50,51,52,53,54] in the case of both complete wetting [47] and partial wetting [48, 49, 50, 51]. A universal behavior has been predicted and experimentally verified for both cases. For complete wetting the spreading/evaporation process proceeds in two stages [47]. A theory was suggested for this case and a good agreement with available experimental data was achieved [47]. In the case of partial wetting the spreading/evaporation of a sessile droplet of pure liquid goes through four subsequent stages [48]: (i) the initial stage, spreading, is

relatively short (1-2 min) and therefore evaporation can be neglected during this stage; during the initial stage the contact angle reaches the value of advancing contact angle and the radius of the droplet base reaches its maximum value, (ii) the first stage of evaporation is characterized by a constant radius of the droplet base; during the first stage the contact angle decreases from static advancing to static receding contact angle; (iii) during the second stage of evaporation the contact angle remains constant and is equal to its receding value, while the radius of the droplet base decreases; (iv) at the third stage of evaporation both the contact angle and the radius of the droplet base decrease until the drop completely disappears. It has been shown theoretically and confirmed experimentally that during the first and second stages of evaporation the volume of droplet decreases to the power $2/3$ with time. The universal dependence of the contact angle during the first stage and of the radius of the droplet base during the second stage on the reduced time has been derived theoretically and confirmed experimentally for pure liquids [48]. The theory developed for pure liquids is applicable also to nanofluids [54], where a good agreement with the available experimental data has been found. However, in the case of evaporation of surfactant solutions the process deviates from the theory predictions for pure liquids at concentration below critical wetting concentration and is in agreement with the theory predictions at concentrations above it [52, 53]. It was found that evaporation for microdroplets is considerably different as compared with macrodroplets: These deviations are caused by an increasing influence of the kinetic effects at the liquid-gas interface (Hertz-Knudsen-Langmuir equation) and this theory should be applied together with the diffusion equation of vapor in the air if the droplet size is less than $1\ \mu\text{m}$.

The drop evaporation causes movements of liquid inside it, in particular, Marangoni instability can develop inside the droplet driven by gradients of surface tension due to inhomogeneity of the surface temperature [49]. The comprehensive review on thermocapillary flows in evaporating droplets is given in [55]. High-speed microparticle image velocimetry [56] was used to study velocity profiles in the droplet and infrared thermography was used to study temperature profiles at its surface [57]. It was found that the flow rate inside the pinned drop increases dramatically (on one order of magnitude) toward the end of evaporation [56]. The local measurements of the interface temperature allowed deducing the local evaporation rates and their evolution in time, for which a theoretical description of droplet evaporation was proposed in [58].

The evaporation of sessile drops on substrates can be isothermal in which case there is no significant evaporative cooling. In this regime, throughout evaporation the drop's temperature is at, or very close, to ambient temperature. The phenomenon can also be non-isothermal with a substantial evaporative cooling. In this regime, the drops can experience various degrees of cooling, which can be significant. The transition between isothermal and non-isothermal regimes is well described by using the dimensionless Sefiane-Bennacer number, SB , as detailed in [59]. The dimensionless number, SB regroups all thermophysical properties of the three phases involved in the process, *i.e.* liquid, solid and gas. Furthermore, it includes geometry parameters and also offers a new expression for the evaporation rate which is valid for both regimes. The validation of SB number for describing the transition from isothermal to non-isothermal regimes and evaporation rates is illustrated in Fig. 3.

Fig. 3: Transition from isothermal to non-isothermal regimes as described by SB dimensionless number, modified and adapted [59]

2.4.2. Pattern formation in drying of blood spots

Investigations of the appearance of pattern after evaporation of blood serum are an analytical tool to identify diseases. The specific regular pattern characterized by dried drops of the blood serum is different for healthy person and person with blood disease. Therefore, experimental investigation of dried droplets of biological fluid had been performed [60, 61].

It is important to know not only the final pattern after evaporation of blood but also the mechanism and the driving forces of the whole process. Brutin et al. [62] show that the main mechanism of blood droplet evaporation and pattern formation is the motion of red blood cells at the edge of droplet. Formation of spots and cracks after evaporation has been investigated mostly in relation to polymeric and colloidal suspensions (physical systems) but similar mechanism has been observed for drying of other biological fluids [63, 64].

Pattern formation is a non-equilibrium process influenced by many factors such as concentration, ionic strength, the presence of surfactant, the thickness of the system, deformability, the size of particles and environmental conditions. Sobac and Brutin [65] found by investigating the concentration of solid mass in the drop during the evaporative process that crack nucleation is driven by a critical mass concentration of solid. They demonstrated that two regimes of evaporation occur during the drying of drops of blood. The first stage is driven mainly by convection, diffusion, and gelation, the second stage is only diffusion controlled. Between these two stages a transition phase occurs with the complete gelation of the system. This phase is correctly predicted by means of a model of diffusion through the liquid evaporating into the air.

The relative humidity is one of the most important factors in the evaporation process. In [66] it was proved that the evaporation rate and the morphological evolutions are clearly influenced by the relative humidity levels. Also the influence on the spreading behavior and

pattern formation of whole human blood was investigated. Their experimental results show that independent of the relative humidity the transition between the purely convective evaporation phase and the gelation phase occurs always at 65% of the total drying time and the contact angle decreases as a function of the relative humidity which influences the final deposition pattern at the end of the evaporation process. The influence of surface forces acting in the vicinity of the three phase contact line during evaporation was investigated in [67].

2.5. Selected phenomena in electric fields

2.5.1. Phase transitions and chemical reactions in simple liquids in electric field gradients

When a mixture of two simple liquids, or a pure liquid in coexistence with its vapor, are under the influence of spatially uniform electric field, the critical temperature may change by a small amount, typically in the mK regime. A different scenario occurs when the external fields has gradients. In this case the change to the coexistence temperature is 2-100 times larger than the change in uniform fields. The phase separation is reversible: when field gradients are turned off, the mixture becomes homogeneous again. This new “electro prewetting” by pursuing analytical calculations, extensive computer simulations and experiments have been undertaken [68].

Preliminary experiments have revealed several interfacial instabilities, occurring as a competition between surface tension and electrostatic forces. In addition, as the size of the electrodes is reduced, surface tension becomes more dominant; at the scale of 50 μm it was possible to achieve a large array of small drops of one liquid embedded in a matrix of a second liquid. This array of droplets of one solvent embedded in a second solvent is the basis of the idea of how to control the rate and extent of chemical reactions: if two reagents undergo a reaction, when the solvents are mixed the reaction will take place everywhere. When they are demixed, however, the reaction will be accelerated and will take place only in a small droplet which serves as a micro-reactor.

The phase transition may have various applications in nanotechnologies, since it benefits from field gradients near small conducting objects. Some of the promising directions studied by us are demixing in microfluidic channels, Micro-Electro-Mechanical-Systems and electro lubrication.

2.5.2. Polymer Adsorption and Electrokinetic Potential of Dispersed Particles in Weak and Strong Electric Fields

Adsorbed polymers, depending on their structure, molecular mass, added amount and (for polyelectrolytes) their charge density, can dramatically change the value and sign of the electrokinetic potential of dispersed particles. Also electrokinetic data provide valuable information about the effect of adsorbed polymers on the parameters of the electrical double layer, about the polymer layers structure at the surface as well as mechanisms of stabilization and destabilization of colloids by polymers.

The complexity of the problem is due to the fact that adsorbed polymers change different properties of the liquid adjacent to the surface and practically all parameters of the particles' electric double layer. This requires a complex approach, i.e. integrated investigation of polymer-containing particles using different methods, which usually includes the study of the

effect of adsorbed polymers on the surface charge density, electrokinetic potential and surface conductivity of dispersed microphases. The influence of polymer adsorption on the ζ -potential has been studied till recently in weak electric fields only (few or several dozen V/cm). Recently investigations have been started on the electrophoresis of polymer-covered particles in strong electric fields (several hundred V/cm).

It was shown in [69,70] that adsorption of poly(ethylene oxide) and poly(vinylpyrrolidone) as well as poly(vinyl alcohol)/polyacrylamide grafted copolymers decreases strongly, by an order of magnitude or more, the electrophoretic velocity (V_{ef}) of polystyrene, graphite and aluminium-oxide as well as correspondingly silica particles in weak electric fields (6 V/cm). This decrease is larger the higher the adsorbed amount or the molecular mass of the polymer is higher. This is explained by the shift of the shear plane toward solution due to polymer adsorption. It is shown also that the adsorption of poly(ethylene oxide) onto SiC, TiC and Si₃N₄ surfaces has no effect on the surface charge density and causes a considerable decrease in the electrokinetic potential of the particles. The calculated “electrophoretic” thickness of PEO adsorbed layers are in good agreement with the dimensions of the end of tails of adsorbed macromolecules estimated from the Scheutjens-Fleer theory of polymer adsorption.

Pioneering studies have been performed on the effect of polymers on the electrophoresis in strong electric fields using polystyrene latex, graphite and aluminum oxide particles having adsorbed poly(ethylene oxide) and poly(vinyl) pyrrolidone non-ionic polymers. To determine the high electrophoretic mobility (mm/sec) in strong fields a new method has been developed based on measurements of the deviation of the particles’ movement from the normal sedimentation trajectory by using short electric field pulses and image analysis technique, the main features of which were summarized in [71,72].

In conclusion we can say that the research on the fundamentals of colloidal systems and interfaces is increasingly complex and the complexity of problems to be solved is not only caused by our improved insight into details but also due to the challenge of taking more and more additional aspects into consideration, such as S&G aspects. This is often not simply one more aspect but entails completely new strategies and consideration of new materials. Many traditional products for example in food or cosmetics contain components which have to be replaced by green ones, which must be done not in a traditional way, i.e. empirically as in many earlier formulations, but with professional knowledge such that the new products are of better quality, excellent performance or healthier, or all at the same time. The next two sections will discuss some details of green materials to be used instead of traditional but unwanted ones, and smart diagnostic methods available to verify the proper replacement of components in known products or the optimum composition of new ones.

3. Materials

3.1 *What do we mean by ‘green and smart’ materials*

Material science has evolved from studies of inert building materials to designing functional materials. Many functional materials, such as piezoelectric materials, shape memory alloys, optical fibres, electrorheological fluids, have a unique ability to respond to stimuli, displaying ‘smart behavior’. Stimuli may be stress, strain, temperature, pressure, an electric field,

incident photons etc. Smart behavior occurs when a material can sense some stimulus from its environment and react to it in a useful, reliable, reproducible and usually reversible manner, i.e. thermochromic behavior. Smart materials have been the focus of much attention as researchers seek ever more functionality in materials [73]. Since many reactions occur at surface and interfaces, surfaces and interfaces play a crucial role in the development and use of smart materials. New technologies exploiting smart interfaces include reversibly adherent polymer melts, removable inks, healable surfaces and interfaces, contact adhesives etc. At liquid/solid interfaces, for example, lab on chip technologies, biomaterials and sensors require tunable interfacial dynamics in layers physically adsorbed at liquid/solid interfaces [74]. For more details on available techniques see Section 4 further below.

On the other hand, there is a strong need for redesigned manufacturing processes, so-called green manufacturing. Green manufacturing is based on the substitution of raw materials and the design of processes to either eliminate waste streams or ensure that they are non-toxic and environmentally friendly. Such green manufacturing techniques include, for example, synthetic catalysts, bio-base processes, non-chlorine-based water purification, biodegradable polymers [75]. In the past three decades, scientific advance in chemistry, biology, physics, engineering and medicine have altogether revolutionized drug delivery [76]. Smart drug delivery systems have been developed to provide highly controlled drug release rates in response to stimuli, such as pH or temperature changes, small molecules, enzymatic reactions, light, magnetic fields or radio frequencies. The example of smart drug delivery shows the intimate relationships between developments in biotechnology, nanotechnology and materials technology. These relationships have continued to grow and mature over the past decade to an extent that integration and cross-functionality of advanced technologies has become the rule rather than the exception.

As the subject of “smart and green” is very broad, we will restrict ourselves here to (i) smart dispersions – materials with liquid/liquid and liquid/solid interfaces with a green aspect (manufacturing or applications); (ii) smart foams – materials with air/liquid interfaces displaying smart behavior, and (iii) encapsulation materials such as micro-/hydrogels, and (iv) their combinations. Additionally, some ‘green’ processes for manufacturing smart materials are mentioned briefly.

3.2 *Smart emulsions*

Solid particles have been identified as a new type of emulsifying agents in addition to surfactants and amphiphilic polymers, going back to the pioneering studies by Ramsden [77] and Pickering [78] more than a century ago. Such emulsions are known as Pickering emulsions, where solid particles of intermediate wettability in the size range from several nanometers to several micrometers attach to liquid-liquid interfaces and provide emulsion stability. If solid particles with additional functionality are used [26], the emulsions are considered as smart materials – they have additional functionality (UV protection) and change their behavior depending on external conditions. It was demonstrated, that emulsion, stabilized by both – nanoparticles and emulsifiers – showed a different behaviour in dependency on external strain, i.e. sometimes it exhibited thixotropy or antithixotropy and sometimes both of them.

Pickering emulsions can be used to synthesize core-shell nanocomposite particles, where the polymer serves as the core and inorganic particle serve as the shell [79]. Such materials provide a new class of supramolecular building blocks, exhibiting unusual, unique properties with potential applications in drug and gene deliveries, enzyme immobilization, colloidal nanocatalysts, chemical sensing, functional coating. Emulsion-based synthetic strategies for preparation of amphiphilic core-shell particles were recently reviewed in [80].

In [81], nonporous adhesive latex coatings and inkjet deposited latex microstructures, containing concentrated viable but non-growing microorganisms were presented. Such non-toxic (low biocide or biocide-free) latex emulsions with carbohydrate porogens which were used for generating nanopores can be used for smart coatings. When rehydrated, these bioactive coatings can be used for multi-step oxidations, reductions, as biosensors, in biofuel cells or high intensity industrial biocatalysts. Another application of smart emulsions in biotechnology was described in [82]. The authors functionalized biotinylated oil-in-water emulsion droplets with biotinylated single-stranded DNA oligonucleotides using streptavidin as a linker. It was shown the components of this linking systems to be stable and to induce sequence-specific aggregation of binary mixtures of emulsion droplets.

In recent years, environmental awareness has increased dramatically leading to a quest of new surfactants with biodegradable and biocompatible properties. Non-conventional, eco-friendly surfactants have attracted attention for personal care products acting as a new class of emulsifiers. New eco-friendly surfactants, e.g. glycerol ethers, have been synthesized [83, 84] attaining very low critical micelle concentrations and low surface tensions. In addition, they combine the advantages of glycerol ether surfactants and amino acid lipopeptides and due to their ether bond they are very stable at high temperatures and can endure pH variations.

Finally, a smart design of oil-water interfaces and their behaviour in food science and technology was recently reviewed [85]. The development of nutrition and healthy food products requires specific microstructures for improved dispersability and bioavailability of bioactives and probiotics. As an example, the generation of microstructure for fat-reduced ice-cream is shown in Fig 4.

Fig. 4: Generation of microstructure for fat-reduced ice cream, taken from [85].

Food microstructures are also useful for chemical stability and for protecting probiotic bacteria during drying, shelf life and application. Suitable microstructures based on emulsions are needed for foods with increased amount of fibres, whole grains, vegetables, fruits and proteins to minimize negative sensorial effects.

3.3 *Smart foams*

Liquid foams are of outstanding importance in materials chemistry and daily life. They can be used as precursors for the production of solid foams [86, 87] or as sacrificial templates for macroporous materials, in food and cosmetics or for a large variety of other applications [88]. In [89], switching reversibility between ultrastable and unstable foams is described. Foams produced using multi-lamellar structure (12-hydroxy steric acid and the counterions ethanolamine and hexanolamine for dispersing) were shown to be outstandingly stable over months (ultrastable). Interfaces were optimally and extremely rapidly covered as in the case of low-molecular-weight surfactants. After heating, the multi-lamellar tubes melt into micelles depending on the nature of the counterions. The authors offer a versatile and simple way to produce temperature-tuneable foams, which are completely reversible.

Another example of the fabrication of smart foams with temperature-tuneable stability was shown in [90]. The authors provided direct evidence of catanionic monolayer formation from catanionic vesicular dispersions. The mechanical behaviour of the layers resembles that of soft glass materials. The foams made from vesicle dispersions are very stable against Ostwald ripening and coalescence due to the extremely high compression rigidity of the catanionic monolayer. Their temperature behaviour is similar to that of the vesicle bilayer, melting at 55°C. When the dispersion surface is well-covered, successive layers at vesicles are jammed underneath, yielding a very thick surface layer.

3.4 *Microgels, hydrogels and other carrier materials*

One of the first applications of microencapsulation was dedicated to carbon-free self-copying paper that was commercialized in 1968. Nowadays, encapsulation is used in pharmaceuticals, cosmetics, food, and agriculture, and for chemical trapping and delivery. Microencapsulation involves encapsulating liquid or solid substances in tiny thin-walled natural or synthetic drops. Encapsulation allows moisturisers, therapeutic oils or insecticides to be incorporated into textiles and is also used in thermo-chromic and photo-chromic fabrics, which change colour with changes in temperature and light.

Methods of encapsulation based on emulsions – colloidosomes – as well as their release mechanisms are reviewed in [91]. An alternative to sustained release of microcapsules by shell rupture or their dissolution is to employ swellable shells, which are formed by incorporating responsive materials into the shells. Such materials undergo reversible transitions when stimulated by external conditions such as pH, ionic strength, light or temperature. Shell swelling initiates the release of microcapsules.

The colloidal behaviour of microgels with switchable properties is strongly affected by interparticle interactions. In [92], smart microgels focusing on Janus and oscillating microgels were described. Janus microgels show anisotropic shapes and chemical/physical properties. Oscillating microgels show autonomous swelling/deswelling behaviour.

Green synthesis of a temperature sensitive hydrogel in supercritical carbon dioxide (sc-CO₂) was described in [93] for possible applications in drug delivery, tissue engineering, smart membranes with tunable permeability. Over the last decades, a class of smart hydrogels exhibiting unique biomimicking functions was discovered and demonstrated by the authors of [94] – thermoresponsible volume phase transitions similar to sea cucumbers, self-organization into core-shell hollow structures similar to coconuts, shape memory as exhibited by living organisms, and metal ion-mediated cementing similar to marine mussels. It was demonstrated how the concept of balancing hydrophilic and hydrophobic forces could be exploited for designing chemically cross-linked hydrogels with self-healing properties.

Lung diseases are commonly treated by inhalation of aerosolized medicines. To achieve pharmacological action, micrometer-sized drug particles – after their deposition on the surface of bronchial mucus – have to penetrate the viscous layer and reach cells of the lung tissue. Mucus is often overproduced and more viscous in the disease what significantly reduces the rate of drug migration to the cell surface. Some concepts of new inhalation powders acting as carriers of pulmonary medicines were tested and, finally, special functional carrier particles have been designed and obtained by a spray drying technique [95]. Another smart medical application is described in [96], where modifications of medicines with laser beams in bulk and droplets is suggested in order to identify new ways for fighting multiple drug resistance acquired by bacteria. It is a promising alternative to modify existing medicines by exposing them to laser radiation and to obtain photoreaction products which may have bactericide effects. Phenothiazines are such candidates and when exposed to laser beams undergo reactions that result in the degradation of the parental compound and the formation of new species.

In recent studies [97, 98] the properties of pH/thermo-responsive polyelectrolyte microgels were investigated with regard to a surface functionalization of textiles. Microgels were prepared to have their pH/thermo-responsiveness expressed within the physiological pH and temperature range. They consisted of pH/thermo-responsive microparticles of poly(N-isopropylacrylamide-co-acrylic acid) (PNIAA) either alone or complexed with the pH-responsive natural polysaccharide chitosan (see Fig. 5).

Fig. 5: Cryo-SEM images of cross-sections of PNIAA microparticles (a) and complexes of PNIAA microparticles and chitosan (b) in freshly prepared microgels; taken from [98].

The studies revealed that the studied thermo-responsive microparticles and their complexes with chitosan undergo a volume-phase transition from swollen and hydrophilic to de-swollen and hydrophobic at temperatures close to the average human body temperature. Kinetics measurements showed that this transition is completed in approximately 15 min. Furthermore, the polyelectrolyte complexes exhibit a change of surface charge from positive to negative values at pH 6, i.e. within the physiological pH range. The size difference between chitosan/PNIAA complexes and PNIAA microparticles alone is decreased from ca. 45% to less than 20% as microgels passed from a hydrated to a dry state below their lower critical solution temperature. The PNIAA thermo-responsiveness kinetics was found to be both temperature- and pH-dependent. Finally, complexes were found to be surface active, with their surface activity lying in between those of chitosan and PNIAA. The information obtained about hydrophilicity/hydrophobicity aspects of the studied systems is considered essential, as these systems are intended to be used for surface functionalization of polyester textiles (see Fig.6).

Fig. 6: Poly(N-isopropylacrylamide-co-acrylic acid)/Chitosan polyelectrolyte complexes for fabrication of pH/thermo-responsive microgels intended for surface functionalization of textiles. Microgels were prepared to have their pH/thermo-responsiveness expressed within the physiological pH and temperature range (skin); taken from [97]; LCST is the lower critical solution temperature.

Other examples of improved microstructures for textile functionalization were shown in [99, 100, 101]. The target was the design, synthesis, evaluation and characterization of environmentally friendly bactericide composites on textiles like polyester and on flexible thin low cost polymers like polyethylene. The long-range operational stability of films and surfaces like glass, metal was to be uniform and able to disinfect and preclude pernicious biofilm formation under mild conditions. Innovative composite anti-pathogenic films were prepared involving nano-particle preparation and optimization to obtain improved microstructures leading to a more effective bactericide action than the materials available today using green chemistry, i.e. no residues.

In the review [102], the most commonly used polymers for the preparation of aqueous-based soft and core-shell responsive particulate systems are summarized. For example, depending on targeted applications, researchers achieved ways of controlling particle adsorption at air/water or oil/water interfaces, or transport of particles across the respective interface. This holds large potential for formulating smart emulsion and foam products in cosmetics and food industries. Furthermore, these nanoparticle properties can be extremely useful in biological

membranes/barriers and in the design of drug delivery vesicles.

Nanoparticles were used in a recent study [103] to create pH-sensitive switchable interfaces based on a layer-by-layer film formation of haemoglobin. Smart interfaces were created which are switchable between the state ‘on’ and ‘off’ controlled by the pH value of the solution. The films were fabricated by alternately adsorbing haemoglobin and silver nanoparticles on the surface of a chitosan modified glassy carbon electrode.

In another study [104], the synthesis, characterization and film-forming properties of two-component polymer nanoparticles that undergo a reversible morphology transformation in water as a function of pH was described. The authors found a remarkable and reversible morphology transformation from a core-shell structure in basic to a uniform blend in acidic solution. It was also shown, that the protonated form of the oligomer accelerates polymer diffusion in latex films. These materials are intended for coating applications.

The growing request in innovative materials with low environmental impact and high performances often finds interesting solutions in multiphase systems, whose properties are strongly dependent on their microstructure. Flow induced microstructures of multiphase fluids were investigated in [105, 106, 107]. The non-Newtonian behavior of one of the phases can strongly influence the deformation of the droplet of the disperse phase or induce the migration under simple shear flow of the inclusions leading to flow focusing and to the formation of ordered micro structures. Even in the simple case of an emulsion of two Newtonian immiscible fluids in a simple parallel plate shear flow cell, the formation of alternating regions of high and low volume fraction of dispersed phase droplets can be observed. A similar experimental approach, based on flow visualization, has been used to investigate the deformation under shear of surfactant multilamellar vesicles which play a key role in the formulation of many industrial products, such as detergents, foodstuff, and cosmetics.

3.5 *Combination of smart materials*

Stimuli-responsive emulsifiers that allow controlled stabilization and destabilization of emulsions could strongly enhance the opportunities for enzyme-catalytic reactions in biphasic media. It was recently shown [108] that smart microgels respond to changes in external stimuli such as temperature and pH value by changing their size. Softness and hydrophobicity can be used as stabilizers for emulsions, also called ‘Mickering’ emulsions. Compared to Pickering emulsions, which are stabilized by rigid nanoparticles, microgels are soft gel particles that deform at an oil-water interface. The authors demonstrated a proof-of-concept that smart emulsions prepared by stimuli-responsive smart microgels provide unique opportunities for biocatalysis in two-phase systems. Furthermore, microgels can be tailored to enable reversible stabilization and breakage of emulsions under conditions that meet the requirements of enzymatic reaction and allow simple product separation and recycling of biocatalysts and emulsifier.

In another study, the structure of microgel packing at an oil/water interface was investigated by using cryo-SEM [109]. It was shown, that the structure of interfacial microgel layers strongly depends on pH of the microgel dispersion. It is an evidence that emulsion stability is independent of the particle-packing density. Some structural changes induced by the interface

were observed, leading to interconnections between individual interfacial microgels. These findings showed that microgels behave at oil/water interfaces quite differently compared to solid particles used for Pickering emulsions.

A combination of two concepts – Pickering emulsions and sol-gel chemistry – was demonstrated in [110] in order to elaborate for the first time stable wax and silica core-shell capsules. These capsules can be stored and used in both – dispersed and dried – states. The fabrication procedure can be generalized and applied to various oils – alkanes, block paraffin, triglycerides. This generalisation opens a large field of applications in pharmaceuticals, cosmetics, food since triglycerides are biocompatible and eatable oils. It was shown, that the temperature of release can easily be controlled by the choice of the oil and that the way the oil is released can be tuned by the choice of the continuous phase. And the kinetics of release can be accelerated by an external hydrodynamic field. More complex capsules comprising multiple compartments with a high potential as pharmaceuticals for facilitating multitherapies can be elaborated.

The following section is meant to give some examples of experimental tools which appear to be smart from a historical or present point of view but will be seen as standard procedures in the very near future once the S&G philosophy has been established properly. Then such methods do no longer appear like smart but just routine and we will look out again for even smarter methodologies.

4. Diagnostics tools

4.1. Overview of available interfacial methodologies

Most of the very modern methodologies in interfacial science are based on single drops and bubbles. In a recent book [111], the state of the art of most of the existing methods was presented and the various aspects of each method described in detail. The target of this book, however, was not to analyze the methods with regard to their “intelligence and color”, i.e. if they are smart and green, however, from the working principles and the possible fields of application one can easily draw conclusions in this direction.

In profile analysis tensiometry (PAT) is based on the shape of single drops and bubbles, having a gravitational force (weight) that is of the order of the respective surface tension force. The fundamentals of the modern profile analysis tensiometry were laid down by Rotenberg et al. [112] in the first important paper on ADSA – axisymmetric drop shape analysis. The most recent progress in this methodology was summarized by Hoorfar and Neumann in [113] and Loglio et al. [114]. The green side of this technique is the fantastically small amount of liquid required for experiments. Using proper experimental protocols, the liquid amount equal to that of a single drop, i.e. 20 μl of a liquid are sufficient to form a drop and study its surface properties, including change in surface tension as the consequence of adsorption of solved surface active molecules and the surface dilational rheology as a function of deformation frequency.

A second methodology is the capillary pressure tensiometry (CPT) [111,115], also for measuring the surface and interfacial tension of liquid surfaces and interfaces and of the

dilational rheology in a frequency range much broader than accessible by PAT. CPT provides in addition access to measure fast interfacial dynamic quantities as it was discussed by Javadi et al. in [116]. In particular for interfaces between two immiscible liquids CPT allows producing data for adsorption times as short as about 10 ms [117]. For interfaces between two liquids of similar density or in microgravity, this methodology is anyway the method of choice [118], as it is the only one not based on gravity effects.

Oscillating drops and bubbles were first proposed by Kretzschmar and Lunkenheimer [119] and not considered as an efficient tool for the determination of the dilational visco-elasticity of interfacial layers. Only with the routine use of piezo drives and electronic pressure sensors this method became the most frequently used technique now to study the relaxation behavior of various adsorption layers.

It is known for quite a while that rising bubbles are very sensitive to the presence of smallest amounts of surface active molecules in a liquid [120]. Recently, this phenomenon was proposed as indicator for the detection of surface active impurities in water [121]. The general state of the art of rising gas bubbles in pure liquids like water and in aqueous solutions of various surface active molecules was summarized recently Malysa et al. in [122]. With a further refinement of the theoretical background and an automation of rising bubble experiments, this method has the potential to become a smart methodology for green applications such as the control of potable water on one side and control of water treatment plants on the other side.

Incorporation of a fast video technique into classical tensiometry makes the methods much smarter. This does not only refer to the philosophy that things do not exist when invisible. The video recording gives access to completely new phenomena, such as oscillation phenomena at a certain eigenfrequency, as it was observed by McMillan et al. in [123]. Also, oscillations of remnant drops with an eigenfrequency result after a drop detaches from a capillary. The eigenfrequency itself is not only a function of the liquid properties like density and viscosity, but also of surface quantities, such as surface tension and dilational rheology. Deeper insight into such phenomena would definitely allow improving the physical background of the new smart field of microfluidics.

A special coaxial double capillary, first proposed by Wege et al. [124] is a smart system that allows completely new experimental protocols and the creation of scenarios in surface science not imaginable before. Ferri et al. [125], for example, demonstrated how this tool can successfully be applied for desorption experiments, i.e. to verify the reversibility of adsorption of surface active molecules or of attachment of particles. A broad overview was provided recently in [126] to show the potential of this double capillary methodology (DBMM) and also to demonstrate its capacity for smart and green applications. Here the experimental protocol of sequential adsorption of different compounds at the same interface has to be particularly mentioned. Also the possibility of mimicking the situation of multiple emulsions or of liquid spherical films with the option of measuring the capillary pressure of all interfaces, including the film tension is remarkable. In Fig. 7 the schematic of such a special design of the double capillary arrangement is shown, together with a photo of a drop in a drop formed in a liquid matrix.

Fig.7: Scheme of the DBMM (SINTERFACE Technologies, Berlin, Germany) coupled with a double capillary (left), drop in a drop arrangement model for a multiple emulsion (right).

4.2. Online control of technological processes and specific sensors

One of the targets in green interfacial technologies is the efficient use of surface active material. Washing machines in households and large industrial facilities are typically loaded with detergents such that the amount is estimated for the worst case. Intelligent machines, however, could optimize this amount. One of the strategies would be to equip the washing machines with a sensor such that the detergent is added in a minimum amount however sufficient to reach a maximum cleaning effect [127, 128].

This optimum amount of detergent can vary a lot, depending on the material to be cleaned, and it can change during the washing process, i.e. consumed detergent would have to be replaced. After cleaning, the detergent has to be removed by rinsing, and also this procedure can be optimized by on-line measurements using suitable sensors sensitive to detergents. The procedures proposed in [129], are first attempts, however, not smart and cheap enough for being used as routine on-line sensor.

A much more intelligent system that is certainly a smart methodology is the tensiography proposed by McMillan and co-workers and summarized in [123, 130]. Tensiography principal application is environmental monitoring in real waters and for simultaneously flagging solvent or surfactant discharges at ppm levels from the dynamic surface tension measurement of the drop-under-test, in which high quality optical dispersion measurements are obtained while simultaneously the bulk spectra is obtained. In optical tensiography, a method of measuring dynamic surface tension in a single drop based on monitoring a tensiotracermeasurand in a sample that does not detach from the measurement head can certainly be described as smart as it enables full tensiographic profiling capability on a drop under test [131].

On this first cuvetteless track, an early indication that tensiography could open up with new spectroscopic analysis approach came already in 1995 with the work of Liu and Dasgupta. They evolved drop analysis into a new and independent technique for gas analysis using the drop as a windowless optical cell for spectroscopic measurements in a flow system [132] and their system aimed to provide analytical chemistry in a drop [133].

4.3. Gas bubbles rising in liquid as new methodology

The main feature of rising bubbles in pure liquids and solutions has been understood for quite a while and is presented in a comprehensive way by Levich in [134]. A further quantification of the hydrodynamics linked with the formation of a dynamic adsorption layer at the bubble surface was presented in [135], however, with limitations regarding the adsorption mechanism, the Marangoni and the Reynolds number. As one can learn from the most recent review to this topic by Malysa et al. [122], in particular the theoretical foundation still requires a lot more quantitative input in order to understand for example the velocity profile of a rising bubble quantitatively. Therefore, the capacity of this methodology has not yet been sufficiently utilized, although it has been applied already in the nineties in water treatment plants [120].

Fig.8: Mean velocity of a gas bubble in dependence of the concentration of two detergents; for further details see in [121].

However, based on a more qualitative/empirical approach this method was refined and applied as environmental sensor to quantify the purity of water [121]. An example is given in Fig. 8 for the mean rising velocity of a gas bubble of 1.5 mm in diameter. From a rather low detergent concentration on, about 2 mg/l, the mean rising velocity reaches a minimum value. For concentrations $c < 2$ mg/l the rising velocity is changing and in absence of any surfactant, it reaches the maximum value which is about twice as high.

4.4. Tensiometry and surface rheology as tool in medical diagnostics and therapy control

Overviews of developments on this subject during the last 15 years were given in [136, 137, 138]. The studies have demonstrated that dynamic surface tensions can provide very important information of the health state of patients, even when other much more established medical or biochemical diagnostic tools fail. In particular blood serum and urine carry information in form of specific surface tension values of which change specifically when a patient suffers from certain disease. Recently, it was demonstrated that the dilational rheology is superior to surface tension as it is more sensitive to the composition of surface active compounds in solution. As examples, in [138] biological liquids like cerebrospinal

fluid, expired air condensate and umbilical blood of newborns have been investigated for patients suffering from neurosyphilis. The measured visco-elasticity has shown that these parameters depend significantly on the disease, i.e. can be used as a sensitive diagnostic tool. These methods are also very valuable tools to control the success of medical therapies. The use of these physico-chemical methods like tensiometry and dilational rheology could develop into routine protocols in medical practice and could partly replace rather expensive biochemical methods.

4.5. Refinement of the theoretical background for dynamic experiments

Most of the modern technologies applying surface science principles are based on very dynamic conditions. Therefore, many experimental tools were adapted to the required interfacial dynamics. Although the functionalities of such often very sophisticated methods are rather advanced, a quantitative data analysis is often not possible because there is no adequate theoretical background.

As an example, we can go back again to the experiments based on a coaxial double capillary, as discussed in [126]. In order to allow for a quantitative analysis of the surface phenomena at such a drop, one would need to fully understand the flow pattern inside the drop. With the assumption of a fixed shape the inflow of liquid through a capillary was simulation with a CFD code in [139]. The resulting flow field (see Fig.9, right) is at least qualitatively identic with that observed in the experiments (Fig.9, left). Hence, this type of simulations can help understand rather complex experimental protocols and gives access to quantitative data happening at the drop/liquid interface.

There are many more situations in the fundamental and applied fields of surface science where simulations are required in order to develop smart experimental tools for various applications.

Fig. 9: Comparison of drop volume exchange in experiment (left, inflowing liquid colored by a surface active dye) and CFD simulations (right) with contours representing of the dye concentration; taken from [139]

4.6 *Electrical tomography technique for emulsion destabilization*

There are several techniques available for monitoring emulsions. The conventional global volumetric techniques offer a poor description of the destabilization process because the phase separation that leads to emulsion destabilization is not only a function of time but also of location. With regard to simplicity and fast response, electrical measurements offer a tempting alternative for determining the longitudinal phase distribution in emulsions/foams. A far more challenging application is electrical resistance tomography (ERT).

A two-dimensional ERT which uses ring electrodes (mounted around the circumference of vessels) at different axial positions to yield the instantaneous longitudinal phase distribution has been developed [140]. This technique is appropriate for real time measurement of foam/emulsion destabilization and separation of the constituted phases [141]. The estimation of the local oil volume fraction and of the dominant droplet size from ERT data is allowed based on appropriate theoretical tools [142,143].

4.7. *Devices for film stability in foams*

Foams are structured gas/liquid fluids in which gas bubbles are separated by liquid layers that can be relatively thick (wet foams) or thin (dry foams). Foams have many applications in food and cosmetic industry. There are three mechanisms of foams destabilization: (i) drainage (ii) coalescence (iii) ripening.

A procedure has been developed for the assessment of a surfactant's influence on coalescence in foams, based on an innovative experimental process governed by the same physical laws as film rupture in a foam [144]. The new process calls for the formation of a bubble inside a small liquid bridge formed between two rigid rods. The withdrawal of liquid from the bridge at a controlled flow rate generates drainage of the liquid layers between the small inner bubble and the outer bridge surface which is registered by electrical resistance measurements. The time elapsed up to film rupture is related to the foam stability with respect to coalescence.

4.8. *Sensors for smallest amounts of liquid*

For a number of application fields the measurement of specific interfacial properties is essential although smallest amounts of the liquid under test are available. In McMillan and co-workers [145] have shown how spectroscopy can be applied to small single drops dispensed by micro-volume pumps. It was demonstrated that this version of a drop analyzer has a number of advantages over standard UV–visible spectrophotometers. The technique has also been shown to be useful in a number of research fields, such as pharmaceutical applications, production of various beverages including beer and whiskey.

A further example is the development of a special measuring cell for the maximum bubble pressure tensiometry applicable to small liquid volumes of liquids, essential biological liquids [146]. Several human liquids are available in larger volumes, such as blood serum or urine, however, others are difficult to obtain in amounts of ml. The special cell developed for bubble pressure tensiometry allows measurements with few ml of a liquid. Even easier are experiments with smallest amounts of a liquid on the basis of single drops. Extensive studies

with a liquid volume of 50 μl , just sufficient to form 2-3 drops, are possible with the drop profile analysis tensiometry. Instead of forming drops by a dosing system filled with the liquid under study, only the tip of a capillary can be filled with this liquid while the rest of the dosing system contains pure water. Such an arrangement provides all possible experimental protocols, except measurements with a large series of drops, such as capillary pressure studies of fast growing drops [116].

Developing from smart microvolume pendant drop techniques there have been recent important developments of surface-science-based nanovolume sessile drop technologies [147] in which notably also as with tensiography [148] neither the source nor the detector fibers touch the drop; sample are placed on drophead with a pipette. The optimized design quartz drophead [145] does not suffer irreversible contamination and indeed cleaning solutions and cleaning tools in a kit have been developed for both the Transmitted Light Drop Analyser instruments [149] and spectrometer accessories. Real drop spectroscopy is a non-collimated-light method with claimed measurement advantage over traditional collimated approaches that are extended to microvolume techniques of typically samples of 1 microlitre but in the array of microvolume spectrometers the pipetted drop samples are squashed or sucked into a capillary. This system is not only a registration and documentation system but is already partially smart as some of the properties of the samples can be changed via respective feedback to the production line.

The importance of the development of NanoSpectroscopy was perhaps one the first ‘smart’ technology were those associated with photonics which is acknowledged as one of the key enabler technology for ‘smart and green technology’. The invention of the first mini-spectrometer by Ocean Optics in 1992, in fact made possible the development of the NanoDrop microvolume technology. This key commercial breakthrough came from the observation that the ratio of peaks in the DNA spectrum gives a measure of protein contamination of DNA or RNA and is both a rapid and reliable method to check the sample purity; this check on DNA and RNA purity is ‘*the smart key*’ to NanoDrop’s success as it avoids wasting money in putting a contaminated sample into a costly process of a DNA gene sequencer. The recent work by Smith, McMillan and O’Neill directly exploiting surface science in spectroscopy for the first time with the non-collimated light approach in microvolume analysis [149] has extended the dynamic range of UV-visible spectroscopy with confocal accessory for sample volume measurement from 65 to 85 A-units, lowered detection limits by at least one order of magnitude with three decimal absorbance measurements, produced a working system for sample volumes of 200nL but perhaps importantly has enabled sequential nanosample spectroscopic analysis with UV-visible then either Raman or NIR via fiber connectivity as seen in Fig.10. Indeed, the rotating loading system can be extended to allow a single microdrop sample to be analysed using all three molecular spectroscopic techniques with also a high quality fluorescence analysis in a four step analysis.

Fig.10: Dual Nanovolume Drop Extendable System for Molecular Spectroscopy.

The presented tools are only a small selection of the large variety. The following section shows a few examples for how scientific ideas and laboratory set-ups developed into routine methods to be used for producing green products in a smart way.

5. Technologies

The multidimensional nature of smart chemistry in complex biology has been the subject of an important editorial by Sawyer [150] but here optical innovations are emerging as the key enabling technologies. Analysis as always is key to smart instrumentation in our field of surface science. Bamfield [151] uses an interesting new approach to analytical classification of chromic phenomena according to whether they fall into five broad groups involving: reversible color change, absorption and reflection of light, absorption of energy and emission of light, absorption of light and energy transfer or conversion, and manipulation of light. Switching electrochromic materials offer the possibility of smart windows and indeed tailorable materials offer an infinite possibility of instrumental and sensor application. Micro-Electro Mechanical Systems research today is certainly full of such technological innovations. Such technological capabilities are but a small part of an expanding portfolio with enormous potential for surface science applications. There is a developing notion of ‘ambient intelligence,’ where technology, embedded into everyday processes and objects, can anticipate personal preferences, and adapt to different individuals and situations can be applied immediately to develop smart interfaces for smart technology and systems are most obviously always smart, but more often also green. Samples presented for chemical analysis are invariably mixtures, often very complex mixtures and the important new element in smart analysis is reacting. Smart surface science and kinematics is key here as interfaces where chemistry and biochemistry takes place and thus must inevitably move to the centre of these technological breakthroughs. The research and commercial opportunities of bringing together kinematics of surface science with new instrumentation are enormous as Hirshmugl [152] says in his review of IR at frontiers of interfaces and surfaces “In particular, super

opportunities are expected to develop in a broad range of scientific disciplines, e.g., biology, device engineering, chemistry, and physics.”

The great Utopian dream of Lab-on-a-Chip has even been questioned by Rios et al. [153] for bulk analysis in what is an important recent review of the emerging field with such long-term revolutionary importance. This study identifies various reasons for Lab-on-a-Chip scarce implementation in routine analytical laboratories despite its high analytical potential, as well as identifying what they believe are probably main “niche” for successfully practical developments. On a positive note, this review points many ways forward and some are important for the future of surface science. Certainly, by way of a bridge to the future and a more practical option for today’s surface science in the laboratory is lab-on-a-valve [154] and are an essential component of smart and green framework in today’s analytical chemistry. Such developments are of absolute importance in the field of single drop and bubble analysis. Microfluidics are evolving rapidly to answer in commercial and economic ways the new and realizable objectives of surface kinetics. Microvolume sample programmable delivery systems make this approach to a step-by-step automation of processes very attractive with a ‘smart technology’ that already is established widely in today’s laboratory. Such technology is particularly attractive for microvolume analysis technologies as they are indeed the basis of the approach that has been developed for nearly twenty years for ‘smart analysis’. The current state-of-the art of mesofluidic systems include those of Lab-on-a-Valve for real-world applications that might not be at present tackled by Lab-on-a-Chip microfluidics approaches and can open up practical options that do not require fabrication capabilities.

It might be permissible given the importance for surface science applications to take a moment to review briefly the potential to develop the optical imaging and analysis systems as these are burgeoning in almost a boundless way at this point. Sealy [155] highlighted the combined advantages of nanowire waveguides and fiber-optic fluorescence imaging, we can manipulate light at the nanoscale inside living cells for studying biological processes with high spatial and temporal resolution. Fluorescence switching is key to single molecule methods [156]. The development of microscopic technologies are now not only combining ultramicroscopic measurements but also analytical technologies so quantitative and qualitative measurements can be undertaken at a molecular level. Drop and bubble methods are of course moving forward smartly to combine imaging and analysis systems. Spectroscopy today has so many more strings to its bow many of which are important for our field such as for measuring structural dynamics at interfaces using femtosecond time-resolved and two-dimensional vibrational sum frequency spectroscopy developed by Ghosh et al. [157]. The toolbox of optical technologies are there to be exploited providing new probes of complex molecular structures and their kinematics for example chiroptical spectrometers [158] that clearly will in the future be helping expand smart bio-applications. These few examples point the way forward hopefully in instrumentation as it moves to its smart future.

Smart instrumentation requires attention to materials, for example when Holzapfel et al. [159] ask “How smart do biomaterials need to be? ...”. Obviously lessons can be learned from the photonics/telecommunications revolution of the late 1980s for smart and green interface science. Already rather advances is the medical nano-smart science. Just one rather simple example will suffice to give some insight for recent developments in nano-smart diagnostics

and instrumentation. NanoDropfluorospectrometry has been applied for measuring enzyme activities using fluorogenic substrates such as the proteolytic activities of the 26S proteasome on 2 microlitre samples, and the amount of sample extract, substrate, and cofactors used for an enzyme assay can be further significantly reduced [160]. This work is a fairly obvious development from existing well-established technological base.

Instruments already exist to measure for example fluorescence from a single protein molecule [161]. Such instrumentally smart technology of single-molecule spectroscopy enables the analysis of exactly one molecule at a time and could of course be a targeted or labeled molecule. Standard spectroscopy yields an average of a given measurand for a large number of molecules based on an ensemble average. Single-molecule spectroscopy removes this averaging effect and variations of data characteristic of the sampled individual molecule can be studied. Sampling statistically relevant numbers of single measurands delivers a histogram of the respective measurement with a characteristic shape and width from which further insight into the photophysics of the analyzed sample can be obtained. This is a brave new world of chemistry and bioscience with massive new challenges for surface scientists to exploit. Nano-instrument engineering and nanophysics here requires the collaboration with application experts from other disciplines who must indeed lead the way forward for smart and green surface science applications.

The linked green paradigm is well developed aiming to provide direct analytical methodologies; a reduction of reagents consumption and/or waste generation; the recycling of used solvents; the replacement of toxic compounds by non-toxic or, at least, less toxic ones; low energy systems; multivariate/multi-dimensional analysis for several simultaneous measurements and finally and not least smart combinations of technologies to deliver green outcomes. New generations of compact fiber sensor smart node technologies [162] for example capable of interrogating a variety of multiplexed fiber sensors, processing the data, and communicating the results digitally are being developed to meet such emerging green and smart demands. The work of monitoring has progressed enormously in recent years and Prien's review is useful landmark and gives a wider view of the development of smart sensor technologies for oceanic monitoring [163]. Wireless is of great importance to such sensor network technologies [164] as indeed is microfluidics [165]. The use of electrochemical effects for actuation in microfluidic devices is developing in multiple directions for example in electrokinetic flow. Electrochemical microfluidic devices in analytic chemistry and biochemistry developed initially for separation and detection has led to the development of electrochemical microreactors exploiting synthesis and processing advantages that come from microscale operations. Microfluidic devices are, more than ever, serving as a platform for nanoscience and nanotechnology, with molecular scale manipulation and detection enabled by microfluidic control of the environment. In such developments "Complementors" are important in today's international instrumentation marketplace and recent years have exhibited a burst in the amount of collaborative activities among firms selling complementary products.

6. Conclusions and Outlook

We have given a review of smart and green applications of liquid interfaces. It is apparent how these interfaces are pervasive of a large mass of products and of natural and artificial processes, which makes their investigation already worth for the improvement of classical applications. In addition, since the area/volume ratio increases with decreasing the system volume, these interfaces are in practice always relevant when nanometric sizes are considered. Thus strengthening the above concepts is a mandatory step on the route of the development of sustainable nano-materials by nano-technologies.

The complexity of issues surrounding nanoscience and nanotechnology has been considered, effectively admittedly by Amall and Parr [166]. There is clearly an emerging new vision of instrumentation with the potential manufacture of molecular devices and machines that will surely transform in time our understanding of analytical instrumentation [167] but one that can only reinforce the importance of surface science in the future.

In this perspective it is more and more important also to develop a new theoretical understanding of the concepts related to nanosized interfaces. In fact, most concepts taken from the classical surface science (adsorption, interfacial tension, wettability, etc.) are ill defined on this scale, because of the lack of statistical meaning or because of the comparable size of liquid interfaces with interacting nanocomplexes (for example, particles at droplet interfaces in emulsions or foams). This aspect, probably underestimated so far, would open important perspectives in a more rationale design of liquid interfacial properties on that scale, supporting important applications, such as the development of nanofluidic devices or the use of interfaces to obtain nanostructured materials.

Finally, in spite of the large potential of many of the reported results, their implementation into effectively green and smart applications requires in many cases the optimum interplay between different disciplines. The energy-production and biomedical applications represent paradigmatic examples in that sense, where expertise in science and technology must match properly with economical, societal and ethical issues.

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Graphical abstract

SMART AND GREEN INTERFACES: FROM SINGLE BUBBLES/DROPS TO INDUSTRIAL ENVIRONMENTAL AND BIOMEDICAL APPLICATIONS

by V. Dutschk, T. Karapantsios, L. Liggieri, N. McMillan, R. Miller and V.M. Starov

Highlights:

- Improved understanding of interface structure by combining theoretical and experimental tools
- New vision for smart microfluidics and nanofluidics
- Best strategies and means to tailor Smart & Green interfaces
- New and improved diagnostic techniques and instrumentation.
- Improvement of smart & green consumer end-products
- Association of Smart and Green interfaces with nanoscience and nanotechnology

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Figure 1: Effect of different nanoparticles on the linearity of the surface tension response of phospholipid layers to surface area expansion-compression cycles.

Figure 2: (a) Velocity flow field created by the impeller inside a flocculation tank, (b) contour map of the mean flocs diameter taken from [41].

Figure 3: Transition from isothermal to non-isothermal regimes as described by SB dimensionless number, modified and adapted [59].

Figure 4: Generation of microstructure for fat-reduced ice cream, taken from [85].

Figure 5: Cryo-SEM images of cross-sections of PNIAA microparticles (a) and complexes of PNIAA microparticles and chitosan (b) in freshly prepared microgels; taken from [98].

Figure 6: Poly(N-isopropylacrylamide-co-acrylic acid)/Chitosan polyelectrolyte complexes for fabrication of pH/thermo-responsive microgels intended for surface functionalization of textiles. Microgels were prepared to have their pH/thermo-responsiveness expressed within the physiological pH and temperature range (skin); taken from [97]; LCST is the lower critical solution temperature.

Figure 7: Scheme of the DBMM (SINTERFACE Technologies, Berlin, Germany) coupled with a double capillary (left), drop in a drop arrangement model for a multiple emulsion (right).

Figure 8: Mean velocity of a gas bubble in dependence of the concentration of two detergents; for further details see in [121].

Figure 9: Comparison of drop volume exchange in experiment (left, inflowing liquid colored by a surface active dye) and CFD simulations (right) with contours representing of the dye concentration; taken from [139].

Figure 10: Dual Nanovolume Drop Extendable System for Molecular Spectroscopy.