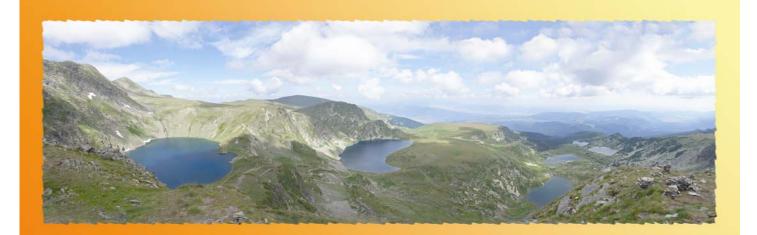


## **COST P21 "Physics of Droplets"**

Final meeting and WG meetings Borovets 14–15 July, 2010

## **BOOK OF ABSTRACTS**







#### **Welcome Address**

Dear Colleagues,

You are very welcome at the final meeting of our COST P21 action "The Physics of Droplets" which is held in the beautiful resort Borovets in Rila Mountain, Bulgaria (1400 m above the see level). This event combines presentations of the three Work Groups of our action with the Final meeting of the Management Committee. Thus we expect to see the last results of our studies and a general overview of the action. We have received applications by around 40 participants from 15 countries which reinforces our expectations for interesting and useful meetings, representing well our research output during the last four years.

The sessions of our meeting will be run in parallel with sessions of the Eufoam'2010 conference. There will be also two common morning sessions (on 14<sup>th</sup> and 15<sup>th</sup>) for these events, as well as common poster sessions for all participants. We did everything possible to avoid the overlap of topics in the parallel sessions, thus giving to everyone the opportunity to choose the most interesting presentation for him/her. We believe that these combined meetings will boost the exchange and cross-fertilization of ideas between the researchers.

The venue of the meeting is the congress center at Hotel "Samokov" in Borovets. The hotel rooms, meeting halls, restaurants, bars, relaxing facilities are all located there, which (we hope) will make you to feel very comfortable. We wish you a pleasant and useful stay!

The organizing committee

#### **Scientific Committee:**

Nicolas Vandewalle (Chair COST P21) – GRASP, Belgium

Michelle Adler (Vice Chair COST P21) – University Paris-Est, France

Frieder Mugele (Leader WG1) – University Twente, The Netherlands

Libero Liggieri (Leader WG2) – CNR - IENI, Italy

Edvard Govekar (Leader WG3) – University of Ljubljana, Slovenia

Thodoris Karapantsios (Leader STSM) – Aristotle University, Greece

Nikolai Denkov (Local organizer) – Sofia University, Bulgaria

## **Local Organizing Committee:**

Nikolai Denkov - Sofia University, Bulgaria

Peter Kralchevsky – Sofia University, Bulgaria

Krastanka Marinova – Sofia University, Bulgaria

Slavka Tcholakova – Sofia University, Bulgaria

Krassimir Danov - Sofia University, Bulgaria

Theodor Gurkov - Sofia University, Bulgaria

## **Program**

### Tuesday, July 13th

14:00 - 20:00 Registration

Registration desk in hotel Samokov

#### Wednesday, July 14th

7:30 - 19:00Registration Registration desk in hotel Samokov

Opening ses	<u>sion</u> : Eufoam Conference, COST P21 Meeting, COST D43 Symposium Hall A (Bulgaria) Chair: D. Langevin
8:30 - 8:50	P. Kralchevsky – Opening
8:50 – 9:30	F. Graner Plenary lecture: Foams as model systems: of complex fluids, of grain growth, of biological tissues
9:30 – 10:00	N. Kristen, N. Schelero, R. von Klitzing Invited lecture IL1: Control of foam film and wetting film stability by addition of (poly)electrolytes: electrostatics vs. ionspecifity (COST D43)
10:00 – 10:30	S. Hutzler, M.E. Möbius, D. Weaire Invited lecture IL2: Foam mechanics (COST P21-1)

#### Coffee Break

Session COS	T P21: Presentations WG2; Chair: L. Liggieri	Hall B (Rodina)
11:00 – 11:30	<ul> <li>A. Javadi, N. Mucic, J. Krägel, R. Wüstneck, V.I. Kovalchuk, E.V. Aksenenko,</li> <li>G. Loglio, L. Liggieri, R. Miller,</li> <li>P21-2: Oscillating and growing drop studies for characterizing the dynamics of adsort</li> </ul>	oed layers
11:30 – 11:50	I. Blute, R.J. Pugh, J. van de Pas, I. Callaghan P21-3: Silica nanoparticles as foam stabilizing surfactants	
11:50 – 12:10	S. Tcholakova, Z. Mitrinova, K. Golemanov, N. D. Denkov, A. Lips P21-4: Ostwald ripening in foams and concentrated emulsions	
12:10 – 12:30	E. Georgiou, Th.D. Karapantsios, M. Kostoglou P21-5: Measurement of thin film drainage among neighbouring foam bubbles of unec	nual size

#### Lunch

Session COS	ST P21: Presentations WG1 & WG2; Chair: D. van den Ende	Hall B (Rodina)
14:30 – 15:00	<u>J. Zawala</u> , <b>D. Terwagne</b> , <b>S. Dorbolo</b> , <b>N. Vandewalle</b> , <b>K. Malysa</b> P21-6: On mechanism of the bubble and droplet bouncing from the liquid/gas interface	е
15:00 – 15:30	N.D. Denkov, I. Lesov, K. Golemanov, S. Tcholakova, S. Judat P21-7: Drop breakup in emulsions with high concentration of dispersed phase	
15:30 – 15:50	T. Gambaryan-Roisman, M. Budakli, I. V. Roisman, P. Stephan P21-8: Effect of surface topography on hydrodynamics and heat transfer during drop i onto a heated wetted wall	mpact

	onto a neated wetted waii	
Coffee Break	1	
Parallel Sess	ion Eufoam 2010: Foam Structure and Modelling; Chair: S. Hutzler	Hall A (Bulgaria)
16:20 - 16:40	C. Oguey	
	O5: Long range topological correlations in cellular assemblies	
16:40 - 17:00	M. Fátima Vaz, S.J. Cox, P.I.C. Teixeira	
	O6: Defects in bubble clusters: simulation and analytical approach	
17:00 – 17:20	M. Durand	
	O7: Statistical mechanics of two-dimensional cellular patterns	
Parallel Sess	ion Eufoam 2010: Ind. Proc. & Sustainable Development; Chair: L. Arnaudov	Hall B (Rodina)
16:20 – 16:40	A. Sher, J-C. Gumy, S. Livings, C. Jimenez-Junca, K. Niranjan	al whinning

O8: Bubble mechanics of milk foams generated by steam injection and mechanical whipping J. Merz, H. Zorn, B. Burghoff, G. Schembecker 16:40 - 17:00 O9: Purification of a fungal cutinase by adsorptive bubble separation: A statistical approach

17:00 - 17:20 W. Doelling, R. Poss, A.-S. Dreher O10: System level definition for deep-bed filtration using open pore nickel and iron-based alloy metal foams

17:30 - 19:30 **Poster session** 

## Thursday, July 15<sup>th</sup>

Common Ses	ssion: Eufoam Conference, COST P21, COST D43; Chair: L. Liggieri Hall A (Bulgaria)
9:00 – 9:40	O. Velev Plenary lecture: Foam superstabilization and functionalization by particles with engineered structure and properties
9:40 – 10:10	T. Horozov Invited lecture IL6: Solid particles in thin liquid films
10:10 – 10:40	S. Stoyanov, E. Pelan, V.N. Paunov Invited lecture IL7: Foams stabilised by shape anisotropic particles

#### Coffee Break

## **COST P21: Final meeting of the Management Committee**

Hall B (Rodina)

Foyer of Hall A (Bulgaria)

11:00 - 13:00

#### Lunch

Session COS	ST P21: Presentations WG3; Chair: M. Adler	Hall B (Rodina)
14:30 – 15:00	E. Varka, <u>Th.D. Karapantsios</u> P21-9: Forest fire fighting foams: Foam drainage dependence on interfacial properties of fire retardant solutions	3
15:00 – 15:30	A. Britan P21-10: Aqueous foam barrier against blast waves	
15:30 – 15:50	V. Nastasa, I. R. Andrei, A. Militaru, M.L. Pascu P21-11: Interaction of micro-droplets with laser beams	

### Coffee Break

17:30 – 19:00 **Poster session** 

<b>Parallel Sessi</b> 16:20 – 16:40	on Eufoam 2010: Foam Rheology; Chair: M. Dennin <u>C. Raufaste</u> , S.J. Cox, P. Marmottant, F. Graner  O16: Orientational effects in the flow of liquid foams	Hall A (Bulgaria)
16:40 – 17:00	I. Irausquin, J.L. Perez-Castellanos O17: Finite element model for the analysis of a closed-cell metal foam under compre	ession
17:00 – 17:20	E. Ashoori, D. Marchesin, W.R. Rossen O18: The roles of dynamic foam behavior in enhanced petroleum recovery	
Parallel Sessi	on Eufoam 2010: Physical Chemistry of Foams, Thin Liquid Films; Chair: T. Horozov	Hall B (Rodina)
16:20 – 16:40	A-L. Fameau, B. Houinsou-Houssou, F. Cousin, F. Boue, J-P. Douliez, B. Nova O19: Impact of the structure of fatty acids supramolecular assemblies on the interface properties	
16:40 – 17:00	A. Salonen, M. In, J. Emile, A. Saint-Jalmes O20: Solutions of surfactant oligomers: A model system for tuning foam stability by the Structure	ne surfactant
17:00 – 17:20	H. Petkova, Khr. Khristov, D. Exerowa, J. Beetge, J. Venter O21: Molecular structure of "star-like" diethylenetriamine-based polymeric surfactant properties of foam films	s and the

## <u>List of Poster Presentations at the COST P21 Final MC and WG Meetings in Borovets</u>

P1	<u>C. Oʻ Donovan</u> , D. Weaire, S. Hutzler, M.E. Möbius	Spatial correlations in a wet foam
P2	S. Dorbolo, D. Terwagne, N. Vandewalle, N. Denkov	Antibubbles: confined air flow dynamics
P3	<u>I. Lesov,</u> S. Tcholakova, K. Golemanov, N. Denkov, S. Judat	Drop Size in Concentrated Emulsions, Obtained by Rotor-Stator Homogenization
P4	S. Limage, M. Schmitt, C. Dominici, E. Santini, M. Antoni, J. Krägel, R. Miller, F. Ravera, <u>L. Liggieri</u>	Cryo-SEM investigations of emulsions stabilised by associations of nanometric silica and CTAB
P5	M. Liverts, A. Britan and G. Ben-Dor	Acoustic/shock wave mitigation by particulate foam barriers
P6	G. Loglio, P. Pandolfini, J. Krägel, A. Javadi, R. Miller, A.V. Makievski, B.A. Noskov, <u>L. Liggieri</u> , F. Ravera	Interfacial properties of water/hydrocarbon systems: Experimental study of high-frequency drop oscillations
P7	A. Maestro, E. Santini, F. Ravera, L. Liggieri, R. Miller, F. Ortega, R. G. Rubio	Dynamics of nanoparticle-surfactant interfacial mixed layers
P8	M.Ferrari,L.Liggieri, F.Ravera, <u>E.Santini</u>	Liquid-air and liquid-liquid surfactant systems in contact with superhydrophobic surfaces
P9	V.Nastasa, K.Samaras, E.Dafnopatidou, T.Karapantsios, M.L.Pascu	Studies on the generation of micro/nano droplets of oil in mixtures of Tween 80 surfactant and water
P10	V. Starov, <u>S. Semenov</u> , R. Rubio	Kinetics of Evaporation of Droplets
P11	M. Sexton, M.E. Möbius, D. Weaire, S. Hutzler	Shear-induced bubble fluctuations in the soft disc model
P12	H. Shapiro, A. Britan, G. Ben-Dor	Advances in the numerical simulations of blast wave/foam interaction
P13	M. Simjoo, H. Guo, P. L. J. Zitha	Rheological transition of foam in porous media
P14	A.Testouri, C. Honorez, A. Barillec, D. Langevin, A. Ponton, V. Leroy, W. Drenckhan	Highly structured foams from chitosan gels
P15	Z. Vinarov, S. Alatova, Y. Atanasov, Y. Petkova, S. Tcholakova, N. Denkov, S. Stoyanov, A. Lips	Effect of surfactants on lipase activity under conditions mimicking the human digestive tract
P16	D. Kosior, <u>J. Zawala</u> , M. Krasowska, K. Malysa	Air at hydrophobic surfaces and the three-phase contact formation
P17	E. Wajnryb, B. Cichocki, J. Bławzdziewicz, J.K.G. Dhont, P. Lang	The intensity correlation function in evanescent wave scattering
P18	J. Bak, T.R. Sosnowski	Droplet characteristics of aerosolised liquid drugs
P19	J. Blawzdziewicz, M. L. Ekiel- Jezewska, <u>E. Wajnryb</u>	Motion of a spherical particle near a planar fluid- fluid interface: the effect of surface incompressibility
P20	D. Kosior, <u>J. Zawala</u> , M. Krasowska, K. Malysa	Air at hydrophobic surfaces and the three-phase contact formation

#### P21-1 / IL2

#### Foam mechanics

S. Hutzler, M.E. Möbius and D. Weaire

Foams and Complex Systems, School of Physics, Trinity College Dublin, Dublin 2, Ireland stefan.hutzler@tcd.ie

Foams offer a number of intriguing problems (and solutions) related to the mechanics of "matter with granularity" [1] and may be a better tested than systems of hard grains for which they have been intensively debated. How do static properties such as shear modulus or yield stress vary with packing density as a rigidity loss is approached? How does foam flow? Can it be described as a Herschel-Bulkely fluid and what is the exponent of the strain-rate dependence of stress? Under what conditions does shear localize in two-dimensional foams? Is nonlocality of its dynamics key to its understanding? What can a continuum description offer and what are its limits [2]? This presentation will address the above questions and try to offer answers, definitive or speculative.

Research supported by the European Space Agency (MAP AO-99-108:C14914/02/NL/SH and AO-99-075:C14308/00/NL/SH) and Science Foundation Ireland (08/RFP/MTR1083).

- [1] P. Schall and M. van Hecke, "Shear Bands in Matter with Granularity", Annu. Rev. Fluid. Mech. 42, 67-88 (2010).
- [2] D. Weaire, J.D. Barry and S. Hutzler, "The continuum theory of shear localization in two-dimensional foam", J. Phys.: Condens. Matter (Topical Review), submitted (2010).

## Oscillating and growing drop studies for characterizing the dynamics of adsorbed layers

A. Javadi<sup>1</sup>, N. Mucic<sup>1</sup>, J. Krägel<sup>1</sup>, R. Wüstneck<sup>1</sup>, V.I. Kovalchuk<sup>2</sup>, E.V. Aksenenko<sup>3</sup>, G. Loglio<sup>4</sup>, L. Liggieri<sup>5</sup> and <u>R. Miller</u><sup>1</sup>

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The aim of this presentation is a discussion of experimental tools available for measuring the short time dynamics and two-dimensional dilational rheology at interfaces between two liquids. This includes experiments performed with growing and oscillating drops based on profile analysis tensiometry as well as capillary pressure tensiometry, an overview of which is given in [1]. It is shown that at shorter adsorption times, i.e. faster drop formation, the hydrodynamic characteristics become more and more important and have to be taken into consideration quantitatively [2].

The dilational visco-elasticity can be determined from the amplitude and phase shift of the interfacial tension response to harmonic area perturbations. While the technique based on the Laplacian shape of a drop or bubble provides data for frequencies below 0.2 Hz, the capillary pressure tensiometry gives access to experimental values up to 100 Hz [3]. The limitations of both methodologies are determined by the hydrodynamics of the involved liquids: in the first case the experiments are limited due to the shape relaxation, and in the second the hydrodynamic contribution to the measured total pressure becomes significant and dominates the signal at higher frequencies.

- [1] R. Miller and L. Liggieri, Bubble and Drop Interfaces, Progress in Colloid and Interface Science, Volume 2, Brill, Leiden, 2010
- [2] A. Javadi, J. Krägel, P. Pandolfini, G. Loglio, V.I. Kovalchuk, E.V. Aksenenko, F. Ravera, L. Liggieri and R. Miller, Short Time Dynamic Interfacial Tension as Studied by the Growing Drop Capillary Pressure Technique, *Colloids Surfaces A*, (2010) in press
- [3] R. Miller, L. Liggieri (Eds.), Interfacial Rheology, Progress in Colloid and Interface Science, Vol. 1, Brill, Leiden, 2009.

## Silica nanoparticles as foam stabilizing surfactants

Irena Blute <sup>1,2</sup>, Robert J. Pugh <sup>1,2</sup>, John van de Pas <sup>3</sup>, Ian Callaghan <sup>3</sup>

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Nine different types of industrially manufactured silica nanoparticle dispersions (particles sizes ranging from 5–40 nm) were characterized with respect to size, shape, charge, surface area, surface tension, etc. In addition, the foamability and foam stability performance was evaluated using the Bikermann foaming column [1]. It was shown that the particles were only weakly surface active and surprising, the differences in surface tension reductions between the hydrophilic and partially modified hydrophobic suspensions was found to be small [2]. However, it was shown that the hydrophobic modified particles gave superior foaming performance which improved with reduction in pH and concentration of particles. Finally, Langmuir–Blodgett films were prepared at the air/water interface from dispersions of hydrophilic and partially hydrophobically nanoparticles and it was found that the hydrophilic particles featured expanded, fairly easily compressible, surface pressure–area isotherms with loosely structured agglomerates which contrasted with the hydrophobically modified particles which were more difficult to disperse and appeared to be in the semi-agglomerated state [3]. The results indicated that the mechanism of foaming with the hydrophobically modified particles involved the formation of an aggregated particulate film at the air/water interface which provides a physical barrier and prevents bubble coalescence.

- [1] I. Blute, R.J. Pugh, J. van de Pas, I. Callaghan, J. Colloid Interface Sci., 313 (2007) 645
- [2] I. Blute, R.J. Pugh, J. van de Pas, I. Callaghan, *Colloids Surf. A, Physicochem. Eng. Aspects*, **337** (2009) 127.
- [3] I. Blute, R.J. Pugh, J. van de Pas, I. Callaghan, J. Colloid Interface Sci., 336 (2009) 584.

## Ostwald ripening in foams and concentrated emulsions

S. Tcholakova, <sup>1</sup> Z. Mitrinova, <sup>1</sup> K. Golemanov, <sup>1</sup> N. D. Denkov, <sup>1</sup> A. Lips<sup>2</sup>

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Systematic experiments are performed, with the aim to determine the effects of (1) type of used surfactant, (2) presence of glycerol in the aqueous phase, and (3) air volume fraction, on the rate of Ostwald ripening (bubble size evolution, due to molecular transfer of gas between neighbouring bubbles) in foams. The experimental results are interpreted by using original theoretical model, which allows us to determine the overall gas permeability of the foam films between the neighbouring bubbles. Further, this overall gas permeability of the foam films can be decomposed into two contributions – permeability of the aqueous core of the foam films and permeability of the surfactant adsorption layers. For verification of the theoretical model, the determined values from the experiments with bulk foams are compared with values determined by model experiments with single bubbles, attached to air-water interface. Very good agreement is found for all sets of experiments. The theoretical interpretation of the experimental data show clearly that the rate of Ostwald ripening in the foams depends significantly on all three factors studied: (1) When surfactants with high surface modulus are used for foam stabilization, the rate of Ostwald ripening diminishes about one order of magnitude, compared to foams stabilized by surfactants with low surface modulus. This effect is explained with the lower gas permeability of the adsorption layers of these surfactants; (2) The presence of glycerol changes the gas permeability of the aqueous core of the foam films between the bubbles which also leads to slower Ostwald ripening; (3) The increased air volume fraction leads to faster rate of Ostwald ripening in all studied systems, due to the larger area of the foam films between the bubbles. The theoretical model and the main factors discussed above are equally relevant to Ostwald ripening in concentrated emulsions.

## Measurement of thin film drainage among neighbouring foam bubbles of unequal size

Eva Georgiou<sup>1</sup>, Th.D. Karapantsios<sup>1</sup>, <u>M. Kostoglou<sup>1</sup></u>

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Recently, a new device has been proposed for registering the drainage of thin films around a small foam bubble based on the non-linear escalation of the electrical resistance of the draining film [1]. The measuring concept calls for a small bubble being expanded inside a vertical liquid bridge up to the point that a thin film forms between the bubble and the outer surface of the bridge. This configuration resembles the situation in a foam where large bubbles surround and confine a much smaller bubble in the space among them. Then the liquid of the bridge is withdrawn at a variable, but constant each time, flow rate. On-line measurement of the bubble pressure allows monitoring and control of the bubble size during drainage. In addition, video recording yields the evolving geometrical characteristics of the liquid bridge (total height, neck axial location and width, etc). Since the electrical resistance during film thinning increases by more than an order of magnitude recording is switched between coarse (low gain) and fine (high gain) mode during measurement.

The present work reports results for liquid withdrawal rates between 20 and 200  $\mu$ l/hr which correspond to total drainage time from ~3 minutes to ~25 minutes. Experiments are performed with aqueous solutions of SDS having concentrations between 50 and 2000 ppm, inside a temperature and humidity regulated chamber. An independent set of foam drainage experiments have been conducted with the same SDS concentrations in a cylindrical test vessel where Electrical Resistance Tomography (ERT) has been employed to measure the evolution of the local liquid fraction at four different heights along the foam column. Static and dynamic surface tension is measured by the Wilhelmy plate and maximum bubble pressure technique, respectively.

A simple theoretical model is used to describe the evolution of the liquid bridge-bubble system. The model is based on the assumptions of a spherical bubble which influences the shape of the liquid bridge just as a volume constraint. A simple approach for the electric resistance computation is used in order to present the evolution of the resistance of the bubble film. A parametric study of the model is presented. The experimental results from the new device and ERT are compared to each other and discussed in view of the findings of the theoretical model.

[1] Kostoglou, M., Karapantsios T.D., Zamanis A. and Evgenidis, S.P."A new device for measuring thin film drainage around single foam bubbles" EUFOAM 2008 Conference, ESTEC, Netherlants, 8-10 July, 2008.

## On mechanism of the bubble and droplet bouncing from the liquid/gas interface

J. Zawala<sup>1</sup>, D. Terwagne<sup>2</sup>, S. Dorbolo<sup>2</sup>, N. Vandewalle<sup>2</sup>, K. Malysa<sup>1</sup>

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Formation and rupture (coalescence) of dispersed system (foams, emulsions, suspensions) occurs always under dynamic conditions and the process outcome can be strongly affected by magnitude of the external forces acting and velocity of the system reaction. It was showed that when a bubble (or droplet) collides with liquid/gas interface, the time of their coalescence with the bulk phase depends on their impact velocity and can be prolonged by applying additional external force causing vibration of the interface. Bouncing of the bubble and/or droplets can be considered as an outcome of the "competition" between the velocities of: i) the thinning of the liquid film separating the colliding object from the liquid/gas interface, and ii) the increase of the free energy of the system resulting from the increase of the bubble (droplet) surface area. Using bubbles of different sizes and impact velocities we found that in water the bubble bouncing increases with the kinetic energy of collision. The increased tendency for bouncing with bubble kinetic energy was due to enlargement of the radius of the intervening liquid film being formed between the colliding bubble and liquid/gas interface. Higher kinetic energy means larger deformation of the bubble shape during the collision and consequently the larger radius of the film formed leads to the increase of the time of the film syneresis. This conclusion was confirmed by the experiments with bubble colliding with silicone oil/gas interface, when the system was under action of external vibrations of different frequencies. It was found that the number of bounces on the oil/gas interfaces depended on frequency and amplitude of the interface vibrations. For example when the interface is at rest, the bubble bounces three times before the bubble rupture, and simultaneously the bubble deformation degree (ratio of horizontal and vertical diameters) decreases at each bouncing. At the vibration frequency v = 40 Hz the bubble deformation degree is practically constant, i.e. the liquid film formed had always similar radius, and the number of the bounces increased up to 30.

## Drop breakup in emulsions with high concentration of dispersed phase

N. D. Denkov, <sup>1</sup> I. Lesov, <sup>1</sup> K. Golemanov, <sup>1</sup> S. Tcholakova, <sup>1</sup> S. Judat <sup>2</sup>

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Systematic emulsification experiments were performed to determine the mean volume surface diameter,  $d_{32}$ , and maximal drop diameter,  $d_{V95}$ , as functions of: (a) Oil volume fraction,  $10 \% \le \Phi \le$ 90 %; (b) Interfacial tension,  $\sigma$ ; (c) Viscosities of the continuous phase ( $\eta_C$  between 1 and 50 mPa.s) and dispersed phase ( $\eta_D$  between 3 and 10000 mPa.s); and (d) Rotor speed in the rotor-stator homogenizer. In addition, the rheological properties of the formed emulsions were measured to analyze the relation between the shear stress during emulsification and the size of the formed drops. The experimental results showed that: (1) For viscous oils with  $\eta_D > 20$  mPa.s, the drop size and polydispersity decrease significantly upon increase of Φ above 40 %; no such effect is observed for the less viscous oil with  $\eta_D = 3$  mPa.s. (2) At  $\Phi \le 50$  %, the mean and the maximum drop diameters significantly increase with the increase of oil viscosity, whereas at  $\Phi \ge 85$  %, these diameters are almost unaffected by oil viscosity. The interfacial tension and speed of rotation affect significantly the final drop sizes, for all oil volume fractions studied. The obtained results are explained by considering two different regimes of emulsification, corresponding to low and high drop volume fractions, respectively. The experimental data for the semi-concentrated and concentrated emulsions ( $\Phi \ge 40$  %) are described by a simple scaling dependence. These results are important for optimization of the experimental conditions when viscous oils are to be emulsified into small (micrometer and submicrometer) droplets.

## Effect of surface topography on hydrodynamics and heat transfer during drop impact onto a heated wetted wall

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<sup>3</sup>Chair of Fluid Mechanics and Aerodynamics, Technische Universität Darmstadt, Darmstadt, Germany

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Spray cooling is a very effective means of heat removal from hot surfaces [1-3]. Its efficiency can be further improved using structured wall surfaces [2]. One of the fundamental processes governing spray cooling is an impact of a single cold droplet onto a heated wetted wall. The hydrodynamics of drop impact governs the transient heat transport in the film and in the wall. We have studied hydrodynamics and heat transfer during the impact of a single drop onto a thin liquid layer on smooth and structured heated plates. The splash dynamics and the evolution of liquid-gas interface temperature distribution have been visualized using high-speed infrared thermography. The film thickness evolution in the inner region has been measured using chromatic confocal imaging technique.

A self-similar analytical solution of the full Navier-Stokes equations and of the energy equation is obtained for the velocity and temperature fields in the spreading film. The theory allows a prediction of the contact temperature and the residual film thickness.

At the initial stages of the drop spreading the film thickness evolution follows a law which is typical for inertia-dominated flows, whereas at later spreading stages the film thickness is nearly constant (residual film), and the flow is affected by viscous forces. The theoretical predictions for the residual film thickness are compared with the experimental data. The dimensionless residual film thickness is determined only by the Reynolds number. The agreement is very good.

Experimental investigations on the cooling effect of the drop impact show a significant influence of the impact velocity and of the initial film thickness. The cooling effect of the drop impact onto a grooved plate is stronger compared to the cooling effect of the drop impact onto a smooth plate. In this study we explain this heat transfer enhancement by the generation of the additional fast wall flow along the grooves.

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## Forest fire fighting foams: Foam drainage dependence on interfacial properties of fire retardant solutions

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Chemical fire retardants are widely used against forest fires all over the world. These substances have the ability to reduce flammability of fuels by physical or chemical action [1]. Fire retardants improve water's capability to wet and cover fuels by reducing its surface tension. Moreover, they create a foam blanket which clings to vertical and horizontal surfaces without run off. Foam bubbles create larger surface area than plain water droplets and so increase dramatically the ability to absorb heat. In addition, a foam blanket has a smothering action with vapour displacing oxygen (air), leaving the fire with not enough combustive agent [2].

The aim of this work is to study whether the drainage of a fire fighting foam depends on the surface properties of the foam agent (fire retardant) solution against air. Tests have been conducted with a very popular fire retardant that has been extensively used against forest fires in Greece the last years. Experiments were conducted at three different fire retardant concentrations (0.1%, 0.5% and 1.0% w/w) which are within the range recommended for different fire suppression strategies i.e., direct attack, indirect attack, exposure protection, mop-up. Three different types of water, sea (salt) water, fresh (mineral) water and Millipore water were employed in making the solutions. To understand the effect of temperature rise as the fire retardant solution approaches a fire, dynamic surface tension measurements were carried out at three different temperatures (20, 35, 50°C).

Foams were produced by an air-aspirating nozzle which is a common type of discharge device in fire fighting vehicles. Foam drainage versus time was monitored non-intrusively by a 3D Electrical Resistance Tomography technique. Equilibrium and dynamic surface tension data were obtained by the Wilhelmy plate and the maximum bubble pressure technique. The results show significant differences among different conditions stressing the strong role of interfacial properties on retardant effectiveness.

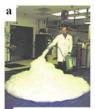
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### Aqueous foam barrier against blast waves

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Detonation of conventional explosives in open environment generates a flow field that is dominated by an unsteady shock wave (usually called blast wave) in the surrounding air. For many applications where solid and heavy protections against the blast are non-applicable, the blast wave mitigation in a cost-effective manner could be achieved using aqueous foams barriers [1]. Pictures (a) to (c) show simple examples of such barriers. Picture (d) demonstrates significant effect of the unprotected explosion on the van situated 10 m away from the charge. In picture (e) this effect is negligible because the explosive charge was covered with the foam barrier [2].











Typical arrangements of the foam barrier (a –c) and effect of 44 kg C-4 explosions on van (d,e).

When this barrier is compressed by the blast wave and then expands back to ambient pressure, the part of the energy spent by blast wave is returned to the emergence shock. The residual energy which is left inside the foam could be transferred into the foam shattering, evaporation and acceleration of the resulted droplets. Whereas direct relationship between these mechanisms and the blast wave mitigation is not specified yet, significant uncertainty to this knowledge is introduced by the structural instability of the foam due to decay. This paper reviews various aspects of this complex field of research over the past thirty years, with main focus on the experimental methods and the results explaining the physical pattern and the involved mechanisms.

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### **Interaction of micro-droplets with laser beams**

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The interaction of the laser radiation with the micro-droplets may be unresonant when the beam is not absorbed by the molecules (of solvent or solutes) present in the micro-droplet or resonant, in which case the radiation leads to excitation of molecules confined in the droplet, on electronic and/or molecular vibration—rotational states. The experimental set-up allowed the exposure of the micro-droplets generated in hanging/pendant position to laser radiation emitted in ultraviolet and visible by a tunable Nd: YAG laser system which included an Optical Parametric Oscillator. The laser emission was pulsed, at a repetition rate of 10Hz with an average energy adjustable between 0.2mJ and 30mJ; the laser pulse time width at half maximum was 5ns and the spectral range along which the laser radiation wavelength can be tuned was 400nm—750nm.

The micro-droplets contained laser dye solutions in ultra-pure water or ethyl alcohol at typically 10 <sup>-3</sup>M and cytostatics/ antibiotics solutions in ultra-pure water.

The ultrapure de-ionized water was delivered utilizing a sterile filter; its bacterial content was <1 CFU/ml and the particle content <1 (TKA Smart2Pure UV); the water resistivity was  $18.2M\Omega xcm$  at  $25^{\circ}C$ , and its conductivity,  $0.055\mu S/cm$ .

The unresonant interaction leads mainly to mechanical effects on the droplet: deformations, vibrations, damped oscillations in the pendant positions, emission of micro and nano-droplets which lead to loss of material.

The resonant interaction of the micro-droplets that contain solutions of Doxorubicin/Daunorubicin, Vancomicin and Dextran in distilled water, at concentrations between 10<sup>-3</sup>M and 10<sup>-6</sup>M was studied.

For both types of interaction between the laser beam and the micro-droplet the effects depend on experimental parameters such as: laser beam wavelength and intensity, micro-droplet content, dimension and shape, position of the laser beam focus with respect to the droplet's center and even with the surface exposed directly to the laser beam, dimension of the beam focus.

If the laser beam wavelength is tuned on an absorption line of the solute, the photons are absorbed by the solute's molecules which become excited; when the wavelength of the absorbed radiation is in the visible spectral range, the excited state is an electronic state and in some cases this leads to irreversible modifications of the molecular structure of the absorber. In most cases the absorbing molecules fall in some nanoseconds back on the electronic fundamental state by emission of fluorescence radiation. In our case the molecules exhibited significant modifications after exposure at laser radiation (the pH remained all the time neutral) which were studied by measuring the UV-Vis absorption and fluorescence spectra. The measurements of the modifications of the solutes in microdroplets of solutions have shown that the modification process is more rapid in droplets than in bulk irradiation of solutions.

## Spatial correlations in a wet foam

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Two-dimensional dry foams and other cellular structures possess spatial correlations that obey the Aboav-Weaire law [1,2]. This law relates the average number of sides, m(n), of the neighbouring cells of an n-sided cell and has the form: m(n) = A + B/n. Many-sided cells tend to be surrounded by cells with few sides and vice versa. We investigate if such a law also holds in the wet limit where the foam can be viewed as a disordered packing of soft discs. Instead of cells with n sides, we look at discs with n contacts. We employ the soft disc model to simulate packings of a two-dimensional wet foam and investigate how the m(n) changes as a function of packing fraction. Do correlations persist down to the packing fraction where the discs loose contact? Do the correlations in a wet foam obey the same functional form as in a dry foam?

Research supported by the European Space Agency (MAP AO-99-108: C14914/02/NL/SH and AO-99-075: C14308/00/NL/SH) and Science Foundation Ireland (08/RFP/MTR1083)

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## **Antibubbles: confined air flow dynamics**

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An antibubble is a spherical air shell that is immersed in a water-surfactant mixture. This air film thins with time because the air is drained from the bottom to the top of the antibubble under the action of the hydrostatic pressure difference. The lifetime of the antibubble is thus governed by the characteristic time of the drainage. The lifetime has been measured for two different mixtures in order to evidence a coupling between the air flow and the surfactant walls of the shell. We show that the air flow is influenced by interface properties of the liquid used to form the antibubble. The slipping conditions of the air flow on the interfaces are discussed.

Acknowledgements: SD thanks FNRS for financial support.

## **Drop Size in Concentrated Emulsions, Obtained by Rotor-Stator Homogenization**

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Emulsions are disperse systems with important applications in various industries. One of the main requirements for practical emulsions is to contain small and well defined (monodisperse) droplets. The usual industrial methods for emulsification are typically energy consuming and often lead to high polydispersity of the drops. Previous study showed that concentrated emulsions with high volume fraction, containing small and relatively monodisperse drops, could be easily obtained if appropriate surfactant is used [1]. The major aim of the current study is to clarify the main factors affecting the drop-size distribution in such concentrated emulsions (of oil-in-water type), obtained by rotor-stator homogenization. Systematic experiments were performed at different oil volume fractions,  $10 \% \le \Phi \le 90 \%$ . The effect of oil viscosity was studied within the range of 3 to 150 mPa, with three different mineral oils. Series of anionic, nonionic and mixed surfactants were tested to find appropriate emulsifiers. The main results could be summarized as follows: Most appropriate are the nonionic surfactants with HLB  $\approx$  13. The drop size increases with the increase of oil viscosity and interfacial tension for diluted and semi-concentrated emulsions,  $\Phi \le 70$  %, and does not depend on these factors for concentrated emulsions,  $\Phi \ge 80\%$ . Increase in the viscosity of the continuous phase leads to smaller drops in the entire range of volume fractions studied. The concentrated emulsions are particularly appropriate for emulsifying highly viscous oils and for obtaining small (and relatively monodisperse) droplets. The experimental results for the average volume-surface diameter and the maximal diameter of the drops, formed in the emulsification process, are described by (still empirical) master curves.

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## Cryo-SEM investigations of emulsions stabilised by associations of nanometric silica and CTAB

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The stabilisation by associations of nanometric particles and surfactants is being investigated as an interesting route to obtain emulsions with outstanding stability features.

Among these systems, associations of nanometric colloidal silica and the cationic surfactant CTAB have been extensively investigated during the last year. Both ingredients are in fact easily available and well characterised. In addition, since CTAB adsorbs to a large extent on the silica particle surface, tuning the ratio between CTAB and silica content represents an effective way to control the particle hydrophobicity, which is the driving force for particle segregation at the liquid-liquid interface.

Here we present an extensive study on the morphological and structural properties of these emulsions performed by utilising CryoSEM techniques. The study was performed in the framework of the project ESA-MAP FASES (Fundamental and Applied Studies in Adsorption Stability) in preparation of experiments onboard the International Space Station.

The results show that the ratio between CTAB and silica content can be utilised to control the stability of the emulsion and its structure, as determined by the shape of the disperse phase droplets. It has been found in fact that a sharp transition from spherical to irregular droplets can be achieved by decreasing the CTAB/silica ratio.

Cryo-SEM investigation also allowed for the investigation of the CTAB-silica nanostructures which form at the liquid interface and in the bulk. Substantial differences were observed depending on the oil utilised (hexane and paraffin oil) and on the emulsification procedure.

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## Acoustic/shock wave mitigation by particulate foam barriers

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Barriers of aqueous foam can serve as a good protection against sound/blast waves. The damping capacity of these barriers arises due to the cellular foam structure which scatters and disperses pressure waves and causes viscous and heat transfer losses. Compressibility of foam cells and/or bubble disruption enhances mitigation effect. Now it is well established that particulate additives of appropriate properties (size, shape, hydrophobicity, etc.) slow down the foam decay, i.e. drainage and coarsening and therefore enhance foam stability. Whereas stability is an important factor of the protection design a particle related stabilization of the foam barriers has not been analysed yet.

The primary goal of the present work is to study how coal ash additives affect both, the mitigation performances and stability of the particulate foam barrier. Using a shock tube tests three typical cases of the wave/foam interaction were investigated:

- 1. **Sound wave/foam interaction:** weak pressure waves propagating with sound velocity allow the foam sustain the impact and maintain it initial cell structure. These tests are evidently focused on the influence of concentration of the particulates on sound velocity inside the intact foam.
- 2. **Shock wave/foam interaction:** shock waves of step-wise pressure profile when approaching the foam is partially reflected from the foam face and partially transmitted inside the foam. The main objectives are influence of particles on the flow pattern and amplitude, rise time and velocity of the resulted shock waves.
- 3. **Blast wave/foam interaction:** propagation of shock waves of blast-shape pressure profile over the particulate foam barrier, the role of the shock wave intensity and duration on the mitigation performances were investigated.

Conducted experiments clearly show that added particles enhance mitigation, increase wave scattering, viscous and mechanical losses. As a result, the wave's velocity slows down, the rise time increases and the peak pressure reduces. At the maximal tested particles concentration about 40% by weight, the most significant effect was observed for the blast profiled shock waves. When compared to the conventional (no particles) foam, the propagating velocity reduced by 25%, the rise time increased twice and the peak pressure decreased by 40%. On contrast, the step-wise shocks and the sound waves demonstrate much less sensitivity to the particles presence.

## Interfacial properties of water/hydrocarbon systems: Experimental study of high-frequency drop oscillations

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The study of the dynamic properties of interfacial layers at liquid-liquid interfaces is an important topic due to its relevance for many technological processes involving multiphase multicomponent systems, such as emulsions, liquid films and foams.

Our purpose is taking a step toward the advancement of the knowledge on the stability and evolution of the above-mentioned complex systems. To this end we pursue reliable measurement values for the physical interfacial properties of single liquid-fluid interfaces [1].

In the presentation, we show the progress concerning the design, realisation and features of a capillary-pressure tensiometer for the measurement and for the visual observation of nanolitre-sized water drops in a hydrocarbon matrix. Measurements results are illustrated for drops oscillating up to 150-Hz frequency [2].

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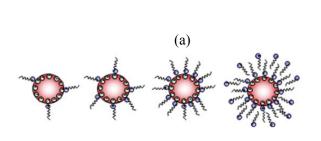
### Dynamics of nanoparticle-surfactant interfacial mixed layers

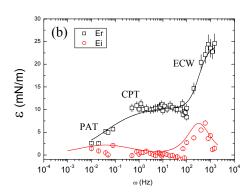
A. Maestro<sup>1</sup>, E. Santini<sup>2</sup>, F. Ravera<sup>2</sup>, L. Liggieri<sup>2</sup>, R. Miller<sup>3</sup>, F. Ortega<sup>1</sup> and R. G. Rubio<sup>1</sup>

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Foams and emulsions can be created and stabilised in presence of tailored particles, according to the well-known principle of Pickering. By the addition of surfactants, the properties of the particles' surface can be modified, and as a result the free energy of their attachment to a liquid interface could change. Thus, we could control the behaviour of a particle/surfactant system to get further improvement of insight in the generic mechanisms of foam and emulsion stabilisation. When surfactants are added, the hydrophobicity of the particles change, as it is schematically shown in Figure 1.a where a cationic surfactant is adsorbed onto a negatively charged particle surface providing additional hydrophobicity to the particle.

We have studied the interaction between nanoparticles of silica and fluid interfaces in relation to the surfactant adsorption on the particle surface, and we have quantified its effect on the macroscopic interfacial dynamics. In fact, *interface viscoelasticity* is expected to play an important role in the stability of films, foams and emulsions. We experimentally studied the interfacial tension and the dilational viscoelasticity of two mixtures of silica nanoparticles with two cationic surfactants (Alkyl trimethylammonium bromide,  $C_nTAB$ , with DTAB for n=12 and CTAB for n=16). Concretely, the measurements have been performed on the whole range of frequencies experimental accessible combining three different techniques; i.e. *Drop Profile analysis tensiometer (PAT)*<sup>1</sup> from 0.01 to 0.2*Hz, Capillary pressure tensiometer (CPT)*<sup>2</sup>, from 0.5 to 100*Hz and Electrocapillary waves device (ECW)*<sup>3</sup> from 25*Hz* to 1.5*kHz* (see Figure 1.b). All the results can be fitted to the theoretical model proposed by Ravera et al.<sup>4</sup>





**Figure 1.** (a) Change of the hydrophobicity of a particle due to interactions with surfactants. (b) Dilational elasticity,  $\varepsilon$  of the CTAB (10<sup>-5</sup>M)- Silica nanoparticles mixture in the whole frequency range studied. Solid line corresponds to the theoretical model used to describe the experimental dates.

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## Liquid-air and liquid-liquid surfactant systems in contact with superhydrophobic surfaces

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In this work the effect of surfactant solutions on the wetting in air-water and oil-water systems on superhydrophobic surfaces has been studied.

Low energy surfaces that exhibit water-contact angles (CA) greater than 150° with low hysteresis (< 5°) are known as superhydrophobic (SH) or ultrahydrophobic surfaces and have raised great interest in both fundamental and applied research fields and in commercial devices/materials. Superhydrophobic surfaces (water-contact angle greater than 150°), due to the small contact area shown when in contact with water, strongly reduce interactions with aqueous environment inhibiting adhesion phenomena and enhancing liquid drainage.

The nature of the amphiphilic molecules and the solid substrate topography have been found to play important roles in influencing the surface properties.

Partition coefficient between immiscible phases then the solubility of the surfactants in the oil phase show a strong influence on the behaviour in liquid-liquid environment.

Preliminary results related to foam and emulsions stability in presence of high water repellent coatings are shown.

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## Studies on the generation of micro/nano droplets of oil in mixtures of Tween 80 surfactant and water

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The generation of emulsions of vitamin A diluted in sunflower oil and a solution of Tween 80 surfactant in distilled water is examined with respect to the volumetric distribution of the two phases. The concentration of surfactant in water was typically 5\*10<sup>-3</sup> %. We have studied in a batch stirred tank system the dependence of the droplet dimensions in emulsion function of the mixing rotation speed, agitation time and components ratio.

In order to study the dependence of droplets dimensions on the rotating speed we have varied the speed of the rotor for the same ratio oil/water. We have noticed that by increasing the speed we obtain droplets with smaller diameters. We have also varied the ratio between the oil component and the water volume in order to measure the dependence of droplets dimensions on it. The used ratios were: 10% - 50% oil in respectively 90% - 50 % water. In each case the total volume of the mixture was 270 mL. At rotation speed of 600 rpm we have generated droplets with diameters between  $20~\mu m$  and  $500~\mu m$  noticing that 90% were in the  $20~\mu m$  -  $100~\mu m$  range.

The final goal was to obtain droplets of diameter in the nanometres range. To do this we have used an Ultra Turax T25 homogenizer providing up to 25000 rpm and a high pressure homogenizer APV with a  $\Delta P = 800$  bar. The surfactant concentration in water was: 0.32%. The droplet diameters were measured using a microscope system type Axiostar plus and a Malvern type light scattering instrument type Mastersizer Hydro 2000M. We have obtained droplets with diameters smaller than 100 nm; the diameters distribution exhibited a peak at 65 nm. It appears that the presence of the Vitamin A molecules in sunflower oil does not affect the oil droplets behaviour in surrounding distilled water. It also appears that the surfactants' concentration is essential in obtaining the nano droplets and keeping them stable in the emulsion for at least 7 days.

## **Kinetics of Evaporation of Droplets**

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It was shown experimentally earlier, that the rate of change of the volume of an evaporating droplet depends linearly on the radius of the droplet base [1]:  $\frac{\mathrm{d}V(t)}{\mathrm{d}t} = -\alpha L(t)$ , where t is time, V(t) is the droplet volume,  $\alpha$  is a proportionality constant, L(t) is the radius of the droplet base. The latter means proportionality of total flux of vapour from the surface of a droplet, J, to the radius of the droplet base, L.

Computer simulations were carried out to investigate an influence of the geometry of a sessile droplet of volatile liquid on the distribution of normal vapour flux density j along the droplet surface, as well as the total flux of liquid vapour, J, from the surface.

The following phenomena were taken into account in our simulations: a heat conduction in the substrate, liquid droplet and surrounding air; the latent heat of vaporisation; vapour diffusion in the surrounding air; viscous flow in a droplet caused by thermocapillary tangential stress.

Convection in the air was neglected because experiments [2] have shown that there is no influence of a forced convection in the surrounding air on the evaporation rate.

The simulation revealed that the distribution of the normal vapour flux density, j, substantially depends on the contact angle,  $\theta$ . Those distributions are determined by the distributions of the surface temperature and by the diffusion of vapour into the air.

It has been found that such variations in the distribution of vapour flux density do not affect the linear dependence of total vapour flux, J, on the radius of the droplet base, L. In all cases we found the linear dependence of the total vapour flux on the radius of the droplet base,  $J \sim L$ . The latter result is in a good agreement with the theoretical prediction [3], where the latter phenomenon was related to the evaporation rate in a transition zone between the droplet and the thin adsorption films in front.

This research is supported by MULTYFLOW project EU, and Engineering and Physical Sciences research Council, UK.

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#### Shear-induced bubble fluctuations in the soft disc model

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Recent experimental work [1] has shown non-trivial bubble fluctuations in sheared two-dimensional foams. The shear-induced diffusion constant and corresponding relaxation times showed a non-trivial dependence on the shear rate. We employ the soft disc model [2] for wet foams to investigate shear induced diffusion through simulations of a linearly sheared two dimensional foam. Our simulations confirm the non-linear dependence of the diffusion constant with the shear rate. Furthermore, we discuss the link between dissipative bubble rearrangements and bulk rheology.

Research supported by the European Space Agency (MAP AO-99-108: C14914/02/NL/SH and AO-99-075: C14308/00/NL/SH) , Science Foundation Ireland (08/RFP/MTR1083) and IRCSET Embark.

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#### Advances in the numerical simulations of blast wave/foam interaction

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The objective of this paper is a critical overview of available approaches to the numerical simulation of the flow pattern resulted by blast wave/foam interaction. Different models from the simplest, dusty-fluid to more complex models accounting the real behaviour of explosively produced blast wave in foam are discussed with the main focus on:

- (i) mathematical formulation of the problem;
- (ii) equations of state for air/water mixture;
- (iii) similarity and/or difference in description of the relaxation processes.

The main purpose of the analysis presented herein is eventually to answer the question to what extend the state of the art theory can give explanation to the shock dispersion, the pressure growth and the increased mitigation of the blast wave with distance observed in the tests.

## Rheological transition of foam in porous media

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Foam has numerous applications including various processes of interest for the oil and gas production. The behaviour of foam in porous media is notoriously complex due to its non-Newtonian character which depends on porous media properties and foam microstructure [1, 2]. The Herschel-Bulckley type model combining power law behaviour with a yield stress has been used to describe foam rheology in porous media [2]. The resulting foam viscosity is a strict function of the bubble density in the flowing foam.

Resent CT scan experiments where  $N_2$  and surfactant solutions are co-injected in granular porous media showed an even more intriguing picture [3]. At short times there seems to be no significant gas trapping suggesting that the yield stress tends to zero. At long times instead a sharp increase in the pressure indicates the development of a yield stress. From various experiments we found that the transition from zero to high yield stress occurs at a characteristics gas fraction of about  $0.65\pm0.05$ . We provide an interpretation of these observations based on the concept of jamming [4].

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## Highly structured foams from chitosan gels

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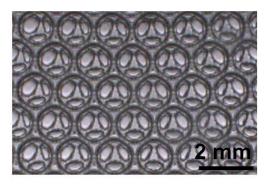
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Solid foams are composed of closely-packed air bubbles integrated into a continuous solid phase. They have very versatile properties (lightness, low density, compressibility, high surface-to-volume ratio...) and are therefore used in several applications (thermal and acoustic insulation, liquid absorption...). These properties are very closely related to the density and the structure (bubble size and size distribution) of the foam and hence need to be controlled with sufficient accuracy. We show here, how this accuracy can be provided using aqueous polymer solutions in milli-fluidic flow-focussing techniques to generate equal-volume bubbles which spontaneously organise into highly ordered (hexagonally close-packed) liquid foam structures. Once formed, these structures are solidified through the cross-linking of the polymer by an appropriate agent.

The polymer which we use is chitosan, a widely used, biodegradable polysaccharide, known for its ability to form stable hydrogels in the presence of aldehyde groups (cross-linker). Foamed chitosan gels are already used in some applications such as wound bandage or tissue engineering. The cross-linker, which we employ, is glyoxal.

Reliable foam generation and solidification are complex physico-chemical processes, which are governed by a range of inter-dependent parameters, such as the (non-Newtonian) viscosity and gelification time of the polymer solution. We therefore performed a number of foaming and rheological studies to choose appropriate chemical compositions and experimental conditions which provide sufficient foam stability before solidification. This included the calibration of the milli-fluidic cross-flow device for non-Newtonian solutions. We present here our results obtained concerning the generation, the stability, solidification and some properties of the obtained chitosan foams in the liquid and the solid state.



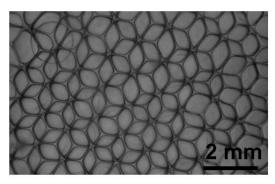


Figure 1: Highly structured, gellified chitosan hydrogel foam before (left) and after (right) removal of excess water.

## Effect of surfactants on lipase activity under conditions mimicking the human digestive tract

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In the human digestive tract, the pancreatic lipase is an enzyme which catalyzes the hydrolysis of water insoluble triglycerides into partially soluble fatty acids and monoglycerides. As all lipolytic enzymes, the pancreatic lipase is water soluble. However, its action is accomplished after adsorption on the water-lipid interface (e.g. the surface of an oil drop) and, hence, the presence of surfactants could significantly affect the lipase activity. In the current study we present systematic experimental results, aimed at the clarification of the mechanism of pancreatic lipase inhibition by surfactants, in presence and in absence of bile salts. We studied the influence of the type and concentration of surfactant and the concentration of bile salts on the enzyme activity of the pancreatic lipase. For determination of the degree of hydrolysis of the triglycerides we used Thin Layer Chromatography (TLC), for studying the morphology of the reaction products we used optical microscopy, and the surface activity of the various components in the reaction mixture was characterised by interfacial tension measurements. The performed experiments show clearly that the inhibition of the enzyme in absence of bile salts is due to the inability of the enzyme to adsorb on the oil-water surface, due to the formed dense adsorption layer by the surfactant. The addition of bile salts in the reaction mixture leads to a significant increase in the enzyme activity. The analysis of the experimental results shows that the bile salts (if their concentration is sufficiently high) displace the surfactant molecules from the surface of the oil drop and form an adsorption layer which does not prevent the access of the enzyme to the surface of the drop – thus the enzyme activity is restored.

## Air at hydrophobic surfaces and the three-phase contact formation

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An affinity to air is a typical feature of all hydrophobic surfaces. When a hydrophobic solid is transferred from gas (air) atmosphere into an aqueous phase then some air can stay adhered to the hydrophobic surface. This fact has been overlooked quite often. A classic example of such negligence is the problem with understanding the nature of long range attractive interactions measured between hydrophobic surfaces in an aqueous solution. As has been reported recently these long range attractions were due to van der Waals interactions between two nanobubbles present at both interacting surfaces. The stability of nanobubbles is currently a hot topic. Even though from the thermodynamic point of view the nanobubbles shouldn't exist there are a lot of evidences that not only they do exist but also they can stay stable quite a long time at the hydrophobic surfaces. Most of approaches to prove presence and stability of nanobubbles involved invasive techniques. We have used a non-invasive technique to study kinetics of the three phase contact (TPC) formation on highly hydrophobic solid (Teflon) of different surface roughness. The surface roughness is a factor strongly affecting the time of the TPC formation  $(t_{TPC})$  by the colliding bubble, where the  $t_{TPC}$  is the time period from the first collision to the moment of the TPC formation. In the case of the roughest Teflon surface (scratches and crevices were of an order 100  $\mu$ m) the  $t_{TPC}$  was ca. 4-5 ms. At smooth Teflon surface (scratches and crevices below 1  $\mu$ m) the  $t_{TPC}$  was of an order 80 ms – longer by an order of magnitude. This significant difference in the t<sub>TPC</sub> values were considered to be not only due to differences in surface roughness, but also in amount of air entrapped at these hydrophobic surfaces - higher roughness affected larger amount of the air entrapped. Another evidence proving validity of this concept is prolongation of the t<sub>TPC</sub> by the bubble striking the rough Teflon plate in n-alkanol solutions. Since increasing n-alkanol concentration leads to increased stability of the foam films therefore these data indicate that some air in form of nano- and microbubbles was present at the Teflon surface and the TPC was formed as a result of rupture of the liquid (foam) film between the colliding bubble and air "pockets" at the Teflon surface.

## The intensity correlation function in evanescent wave scattering

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As a first step towards the interpretation of dynamic light scattering with evanescent illumination, in order to probe dynamics near walls, we develop a theory for the initial slope of the intensity auto-correlation function for suspensions of interacting spheres. An expression for the first cumulant is derived that is valid for arbitrary concentrations, which generalizes a well-known expression for the short-time, wave-vector dependent collective diffusion coefficient in bulk to the case where a wall is present [1]. Explicit expressions and numerical results for the various contributions to the initial slope are obtained within a leading order virial expansion. The dependence of the initial slope on the components of the wave vector parallel and perpendicular to the wall, as well as the dependence on the evanescent-light penetration depth are discussed. For the hydrodynamic interactions between colloids and between the wall, which are essential for a correct description of the near-interface dynamics, we include both far-field and lubrication contributions [2,3]. Lubrication contributions are essential to capture the dynamics as probed in experiments with small penetration depths. Simulations have been performed to verify the theory, and to estimate the extent of the concentration range where the virial expansion is valid. The computer algorithm developed for this purpose will also be of future importance for the interpretation of experiments, and to develop an understanding of near-interface dynamics, at high colloid concentrations.

## Droplet characteristics of aerosolised liquid drugs

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The effectiveness of drug delivery by inhalation of aerosolized liquids relies on aerosol concentration and droplet size distribution [1]. These parameters are influenced by liquid properties, especially viscosity and the dynamic surface tension (DST). Liquid medicines for inhalation are based on water and they contain beside drugs, which may exhibit no surface activity, also some surfactants as antimicrobials and stabilizers (e.g., benzalkonium chloride).

Within this work we measured DST of selected inhalation drugs and confronted the results against the size distribution of aerosol droplets produced in a commercial pneumatic inhaler (Pari). Count median diameter of droplets, CMD, was determined based on the aerosol spectrometer data (Palas).

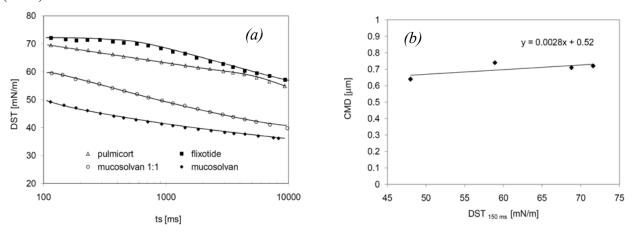


Figure 1. DST of selected inhalation medicines (a), and the relationship between DST (150 ms) and count median diameter (CMD) of aerosol droplets (b).

The results shown in Figure 1 suggest that the mean size of droplets released from the pneumatic inhaler is correlated with short-time (150 ms) DST of atomized liquid medicines. Similar correlation was found for aerosol generation rate (data not shown). Therefore, it can be concluded that the presence of surface-active components in the water-based inhalation medicines may influence the quality of therapeutic aerosol and the amount of medicines delivered to the lungs.

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## Motion of a spherical particle near a planar fluid-fluid interface: the effect of surface incompressibility

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Hydrodynamic coupling of a spherical particle to an undeformable planar fluid-fluid interface under creeping-flow conditions is discussed. The interface can be either surfactant-free or covered with an incompressible surfactant monolayer. In the incompressible surfactant limit, a uniform surfactant concentration is maintained by Marangoni stresses associated with infinitesimal surfactant redistribution. Our detailed numerical calculations show that the effect of surface incompressibility on lateral particle motion is accurately accounted for by the first reflection of the flow from the interface. For small particle--interface distances, the remaining contributions are significant, but they are weakly affected by the surface incompressibility. We show that for small particle-wall gaps, the transverse and lateral particle resistance coefficients can be rescaled onto corresponding universal master curves. The scaling functions depend on a scaling variable that combines the particle--wall gap with the viscosity ratio between fluids on both sides of the interface. A logarithmic dependence of the contact value of the lateral resistance function on the viscosity ratio is derived. Accurate numerical calculations are performed using our Cartesian representation method.

## Dynamic surface tension of pulmonary surfactant medicines

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Pulmonary surfactant (PS) medicines are administered to the respiratory system for restoring lung function when the innate PS is deficient or inactive [1]. PS should exhibit surface activity after adsorption at gas-liquid interface under dynamic conditions associated with surface area variations caused by breathing. In this paper we focus on comparative measurements of dynamic surface tension (DST) in solutions of three commercial PS medicines: Curosurf, Survanta and Exosurf, using maximum bubble pressure technique (BP2 – Kruss, Germany). DST was studied as a function of medicines concentration and temperature. Selected results shown in Figure 1 indicate that surface activity of studied medicines differ noticeably under dynamic conditions.

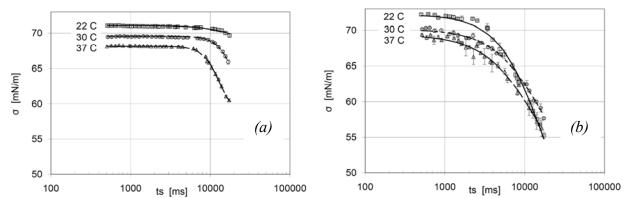


Figure 1. DST of Curosurf (a) and Exosurf (b) as a function of temperature. Concentration: 0.5 mg/ml.

The experimental points were fitted with the phenomenological Hua-Rosen equation [2] in order to estimate the characteristic adsorption time  $t^*$  and the meso-equilibrium surface tension value  $\sigma_m$ , which allowed for quantitative comparison of the PS medicines. Data obtained from the analysis of dynamic surface activity are useful in the evaluation of therapeutic value of PS medicines, but they are also important for the optimal design of surfactant delivery by inhalation, since DST is recognized as a parameter important for the quality of medicinal aerosols produced by liquid atomization [3].

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