

The Physics of Foams, Droplets and Bubbles.

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Brief description of the article (Max 30 words)

The physics of foams, droplets and bubbles describes and explains the intricacies of the materials we see all around us, which range from a sugary meringue to an opal.

Abstract (Max 100 words)

Foams or bubble dispersions are common to milk-shakes, bread, champagne froth, shaving mousse, shampoo, crude oil extraction systems, upholstery packing and bubble-wrap. Whereas, the term droplet is often synonymous with either a small drop of water or a drop of oil - a type of coarse dispersion. The latter are seen in butter and milk, household paint, nicotine patches and medical ointments or creams. Both common forms of coarse dispersion are constituted from nanoparticles or nanostructures. The zone joining the dispersed spheroids is known as a thin (liquid) film or TLF. The science of dispersions sits squarely in the subject area of nanotechnology or colloid science.

Keywords: dispersion, constituted, bubble

Introduction

Surface tension, the ‘elastification’ of a surface and surface activity, permit the formation of foams and emulsions [1] and has been studied for centuries. Notable eminent scientists looking at foams, foam films [1], emulsions [2], soaps and bubbles include, President Benjamin Franklin (detergents and surfactants), Young (detergency/wetting), Laplace (bubbles), Oswald (droplets and dispersions, emulsions), Newton (foam films/texture), Hooke (capillarity/texture), Brown (particle motion), Einstein (nanoparticles/motion), Langmuir (surface activity), McBain (micelle aggregates of surfactants) and Schulman (microemulsions). This science centres on the use of a surface active species or surfactant (emulsifier, tenside). These molecules or solid particles [3] themselves (surfactants) are attracted to the intersection (interface) of distinctly composed incompatible materials or phases such as oil and water [2, 4].

Table 1 - Products based on coarse dispersions

Dispersed phase	Dispersion medium	Example
Foams		
Air	Soapy water	Bath foam

Air/carbon dioxide	Gluten/starch matrix	Bread
Air	Sugary egg albumin	Meringue
Air	Frozen 'custard'	Ice cream
Air	Aluminium	Metal foam
Carbon dioxide	Beer	Beer froth

Emulsions

Olive oil	Vinegar + lecithin	Mayonnaise
Lipoproteins	Plasma/serum	Lymph
Perfluorodecalin	Water + lecithin	Artificial blood cell
Liquid paraffin	Buffered water	Emollient cream
Liquid paraffin + drug	Buffered water	IV anaesthetic
Water	Butterfat	Butter
Butterfat	Water	Milk
Sand	Bitumen/tar	Asphalt
Oil	Solid	Opal
Pigment	Oleaginous matrix	Lipstick/mascara
Chalk	Silicone oil	Anti-corrosion engine oil

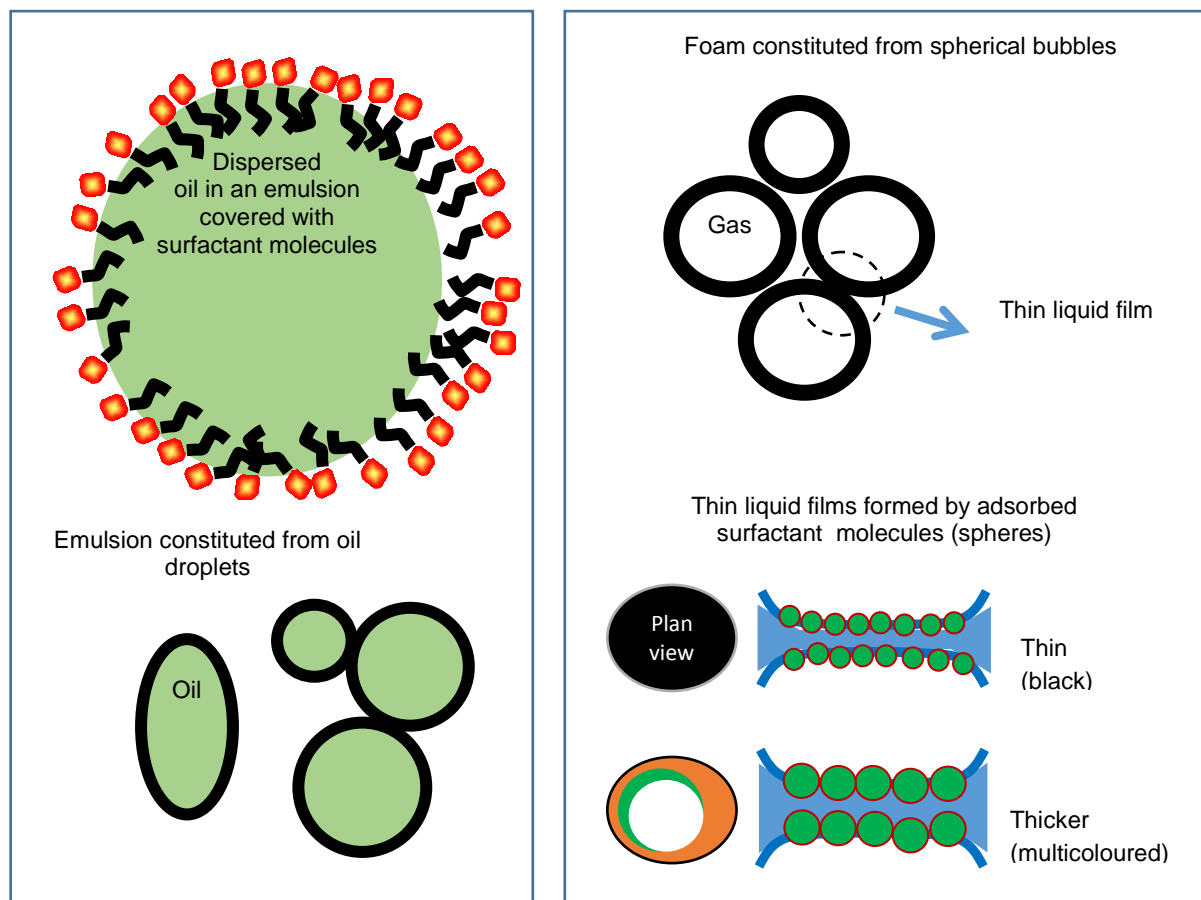
Suspension/sol/gel

Paracetamol	Buffered water	Calpol analgesic
Silicates	Water	Silt
Cocoa mass	Tristearin/cocoa butter	Chocolate
Chromium	Aluminium Oxide	Ruby
Water	Pectin	Jam/jelly

IV is intravenous injection; lecithin is the natural emulsifier present in egg yolk or soya bean

Foams are complex dispersions of bubbles (gas) in a liquid or solid matrix or phase [1]. They are ubiquitous in the world of manufactured goods (Table 1) such as bread, meringues, beer froth, hair mousse and upholstery packing [1, 3]. They are also used in ore and crude oil extraction processes to undertake a form of distillation. Medical shampoos are also based on foams [4] as are lightweight metal particle-based alloys used in aeronautics.

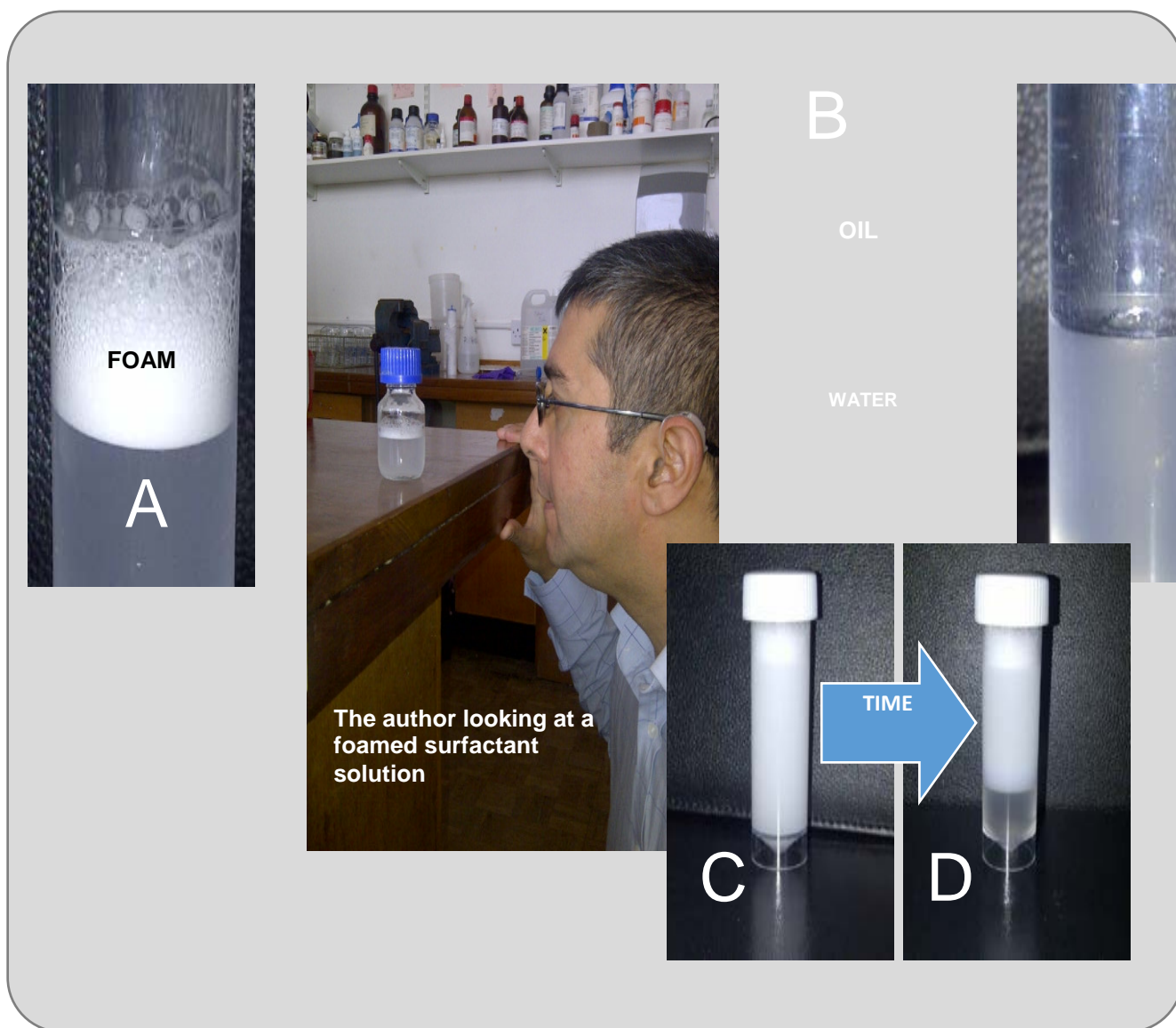
A droplet is a spherical entity composed of numerous aggregated or collective molecules, which may or may not be coated with a "stabilising" surface coating (surfactant/emulsifier). Droplet size ranges cover several mm to sub-micron (micrometers) of many nanometers in diameter [5, 6]. Most coarse dispersions e.g. bubbles, oil droplets, fat crystals and solid dispersions or sols are often synonymous with industrial products such as fire-fighting foams, crude oil and photographic film coverings, respectively but may also include food (ice-cream, soufflés) and cutting-edge medicaments (injections, antibiotic creams) [7]. Unlikely dispersions of oil droplets include hormone replacement [8] and nicotine skin patches and gemstones such as the opal.

Figure 1 - Bubble and droplet physics and form

Where two dispersed particles (solid spheroids, bubbles or spherical oil droplets) meet an interstitial film called a thin liquid film (TLF) exists [1, 3]. It is the surface structure (physico-chemical characteristics) and mechanical behaviour of this TLF that determines dispersion stability according to a theory called DLVO theory [7, 9]. At the margins of the TLF is a region called the Plateau border [1]. The intersection of several thin liquid films is called a node. Entrained liquid drains out of the TLF to the Plateau margins due to capillarity (suction) and gravitational forces [1, 9]. The escaping liquid then percolates through the foam to the base of the foam column. In a foam this leaves single surface spheroidal cells (*ederschaum*) becoming polyhedral (*polyederschaum*) in nature. Recent mathematical predictions [9] give the average number of faces to be just over 14. Many factors determine the texture of the foam [10] such as the chemistry of the surfactant, contaminants, solubility, vibration, droplet phase density and viscosity, particle size, temperature and internal Laplace pressure *versus* atmospheric pressure [1, 9].

Both common forms of coarse dispersion are constituted from nanoparticles or nanostructures that constitute the surface layering of the droplet [11-13]. The surface layer can be in the form of a self-assembled or spread monolayer. Emulsions, for example that are stabilised by surface adsorbed particles are known as Pickering Emulsions [14-16]. The structure of the TLF and its physics has been the topic of considerable interest. The mechanism of dispersion destabilisation has also captured the imagination of scientists (Figure 2). The main mechanisms are creaming, sedimentation and compaction, coalescence, flocculation, disproportionation [6, 8] and chemical change; this is of crucial importance in oil-based products such as engine oils, make-up, butter and cream substitutes (Figure 2). The science of dispersions sits squarely in the subject area of nanotechnology or colloid science.

Figure 2 - Photographs of lab-prepared foams, emulsions and films. The Figure shows a frothy foam (A) formed from soapy solution, two immiscible phases - oil and water (B) that when shaken form a homogeneous emulsion (C) and which with time separate to form a creamed oil-rich upper layer and a oil-depleted lower layer.



Contemporary and future use of suspensions, foams and emulsions is an element of immense recent growth [13, 17]. Current research is looking at blood substitutes using perfluorocarbons, optical anaesthesia and numerous cancer chemotherapeutic particles [8]. When linked to a targeting agent that can give a nanomedicine product superior penetration into the diseased tissue.

Methodologies and tests

You will need:

Several 100 ml stoppered measuring cylinders

Several 10 cm diameter Petri-dishes

20ml glass beaker

A wine glass and 20 ml of strong red wine (>11% alcohol) or cognac

100 ml of beer (e.g. bitter)

A 'rectangular' bath sponge

Washing up liquid (soap)

Olive oil

Raw egg white

Clean tap water

Matchsticks

Drinking straw

Rubber gloves

Test 1. Coalescence of bubbles and droplets

a) Shake i) 30 ml 0.5% v/v soapy water and ii) 30 ml beer vigorously; watch bubbles form and then burst - which sample bubbles burst the most easily?

b) Shake 20 ml of olive oil in 20 ml of tap water, watch the droplets fuse. Why do we need a surfactant [1]?

Test 2. Disproportionation and Ostwald ripening

c) Take 60 ml 0.5% v/v soapy water (soap in water) and divide into two portions. Shake one with air. Using a straw blow stale breath into the liquid to achieve comparable foam volume. Which samples become irregular in form first? Why is this behaviour seen?

Test 3. Drainage from the foam

Consult a) and b) just after formation. What are bubble shape and the percentage liquid (of the total volume) after 1 minute and 10 minutes?

Test 4. Marangoni effect [1] - tears

d) Pour 30 ml of strong red wine (or cognac) into a wine goblet and watch the sides of the glass. What is happening and why?

Test 5. Competitive adsorption [1, 3-5] - the surface canoe

e) i) dip a matchstick into washing up liquid and then into a Petri-dish with 20 ml of pure water, ii) dip a matchstick into egg-white and then into a Petri-dish with 20 ml of pure water. Using gloved hands drop a clean matchstick into each Petri-dish. Nudge each of the floating match sticks with a clean pencil. Which matchstick moves most freely and smoothly? Why is this behaviour seen?

Test 6. Emulsification [2] - imposed shear

f) Vigorously shake 20 ml of olive oil in 20 ml of tap water containing one drop of washing liquid (oil dispersant) for 3 minutes. After 1 minute standing do you see two distinct phases or one? Can you see the bigger oil droplets? Is the oil dispersed in water (O/W) or water dispersed in oil (W/O)? How might you tell the difference?

Test 7. Creaming [2] - Stokes' Law

In sample f) after 10 minutes standing do you see different layers in the sample? Why would oil float to the top?

Test 8. Bicontinuous network and phase volume [2] - bath sponge

g) Take a bath sponge (a continuous network) and estimate its volume (length x height x depth). Dip the sponge in a bucket of water, let all possible water absorb into the sponge. Squeeze out all possible water from the sponge and measure the volume of entrained water. Volume of water/volume of sponge indicate the phase volume of spaces or air voids in the foam. Spheroids can pack together to a ratio of 0.74 (Ostwald maximum). At values higher than this the spherical droplet assumes a polyhedral form. Why is the water-filled sponge analogous to a bicontinuous liquid foam network?

Test 9. Spreading monolayer [1, 11]

h) Pour into a Petri-dish 20 ml of pure water, and sprinkle the crumbled cinders of an ignited matchstick over the surface. Dip a matchstick into washing liquid and then gently into the water; watch the rapid clearance of floating soot to the margins of the dish. Why does this happen?

Trial 10. Topology and the TLF - Newton's interference fringes [1, 3-5, 12]

i) Dip an inverted 20ml glass beaker into a solution of 0.5% v/v soapy water (soap in water) and examine the colours in the resulting TLF.

Discussion of what the results and demo mean

Test 1. Coalescence of bubbles and droplets

a) By shaking samples vigorously we form i) surfactant and ii) polymer (beer/barley polymeric peptide) coated bubbles, respectively. Polymers give more mechanically robust rigid bubbles, thus preventing bubble rupture and thicker interstitial TLFs because of their "wobbly" polymer shape [14], so they trap more water and are consequently, less delicate and less easily perturbed. This effectively renders the more coalescence resistant. Peptides also bind water to make a protective water cushion between bubbles [5]. Soap bubbles should burst the most easily [15]. Interestingly, if you wipe your nose then touch the beer foam it will collapse as the fats from your skin prefer to cover the bubbles [1, 3-5, 14, 16] in an incoherent manner but also do this in a piecemeal form. This effectively lowers bubble integrity.

b) Shearing olive oil and tap water together makes a transient dispersion. This dispersion has no significant longer-term stability as droplets collide, fuse and grow leading the emulsion splitting [2, 16] almost instantaneously. We need a surfactant to ensure that droplets do not fuse (coalesce) easily. The surfactant thus provides a protective sheathing. This can have a number of effects, such as preventing fouling and biofilm formation [13] in medical applications involving unbreached particle integrity[17], such as injected anticancer emulsions [6, 8, 13].

Test 2. Disproportionation and Ostwald ripening

c) Having taken soapy water and incorporated air in the first sample and in the other sample, air and carbon dioxide (CO₂) we see the effect of dispersed phase (Table 1) solubility on dispersed phase integrity and polydispersity. Stale breath contains lots of CO₂, which is very water soluble.

Laplace theory states the pressure inside small spherical objects is much larger than in larger ones. Solubility and high pressure permit dispersed phase to transfer from one cell to another [4] via the dispersion medium (Ostwald ripening or disproportionation, in foams). Consequently, foams and dispersions only get coarser (Figure 1) and irregularly honeycomb-like in structure as small spherical particles disappear (Figure 2) being reconstituted within larger ones [10]. This means fine bubbles and particles only get larger.

Test 3. Drainage from the foam

d) After a liquid foam is initially fabricated the bubbles or cells are symmetrical and spherical with a large surrounding layer of dispersion medium [1-5]. Upon standing liquid drains out of the foam by three processes. These are capillarity and capillary suction to the Plateau borders and nodes, the attraction for dispersed phase cells for one another and the consequent squeezing out of solvent from between the dispersed particles and gravitational forces pulling the drained liquid downward causing a percolation effect and out of the foam body (Figure 1). Consequently, thin liquid films (foam lamellae, foam films; also emulsion thin liquid films) always get thinner with time down to an equilibrium value [1, 9]. The equilibrium value is controlled by the size and water binding capability (see Trial 4) of the surface adsorbed surfactant molecule [14].

Test 4. Marangoni effect - tears

Strong red wine (or cognac) has significant quantities of ethanol. Ethanol is surface active and can be described as a very short chain surfactant with a polar hydroxyl group that binds lot of water. The ethanol diffuses across the glass surface [11] and this is enhanced as the molecule is also volatile. The lateral diffusing alcohol drags water with it until the mass of the water becomes too substantial to counteract gravity and "tears" appear which fall back into the drink. This is the Marangoni effect in action. In bubbles, emulsion droplets and TLFs surfactant molecules migrate dragging associated solvent with them to fill a void arising from inconsistent surface coverage by surfactant in response to environmental fluctuations [1, 3-5]. This means that TLFs (Figure 1) stay intact even when distorted vibrated or heated.

Test 5. Competitive adsorption - the surface canoe

e) A solution of washing up liquid and one with ovalbumin protein from egg-white have surfaces with differing chemical and mechanical properties just as the ovalbumin gives a rigid elastic network of insolubilised protein residing at the surface [1]. Each surface is "self-regulating" in respect of maintaining its own integrity because of nanosecond dynamics and molecular diffusion [1, 3]. A floating matchstick (surface canoe) is retained and trapped in the monolayer of adsorbed protein in the Petri-dish, however the matchstick can move easily in the fluid surfactant surface. Both forms are mutually incompatible, mixing surfactant and polymer (protein) means the fluid surface is rendered non-ideally fluid and the network of polymer lacks its pre-requisite lateral associations [1, 3-5, 14-16]. The process is defined by the preferential surface adsorption of small molecules, which has been called competitive adsorption or competitive displacement. This is seen when beaten egg white protein (polymer), with good foaming properties is inadvertently contaminated with fatty egg yolk (surfactant).

Test 6. Emulsification - imposed shear

f) Combining olive oil, tap water and washing up liquid (detergent) creates blood cell-sized droplets if the sample has been shaken vigorously (Figure 2). Because of a large size range

distribution, coalescence and Ostwald ripening after a minute, creaming of the more buoyant oil (Figure 2) at the top of the sample is visible and inevitable [2, 5, 6, 8, 14]. This becomes very pronounced after some further time and to a point where the very large droplets are visible. Washing up liquid detergents generally disperse oil rather than water and this can be proved by taking a drop of the sample and smearing it on paper. Oil dispersed in water (O/W) emulsions do not produce a translucent streak mark in this case unlike water dispersed in oil (W/O) forms.

Test 7. Creaming - Stokes' Law

f) In the sample after 10 minutes creaming of the less dense oil (Figure 2) at the top of the sample is visible and inevitable [8]. This can be slowed but never prevented by reducing droplet size, making the droplets match the suspending solvent in terms of their density (density of water is 1.00 g/cm^3 ; density of most oils is 0.7 g/cm^3) by adding mineral solids that adhere to the oil fraction with a density greater than 1.00 g/cm^3 . The sample viscosity (water viscosity is 1.0 mPas but a thickened solution may be $>200 \text{ mPas}$) can also be increased and this slows down the buoyancy of oil droplets.

Test 8. Bicontinuous network and phase volume - bath sponge

g) With a bath sponge (a form of continuous network) a significant fraction of its volume is made of the solid foam material [10]. Water fills the voids and gives an indication of the volume of dispersed phase which may be incorporated in a dispersion of this type. Up to 74% of a sample (0.74 phase volume, ϕ) may be the dispersed phase when droplets are entirely spherical [2, 8]. Much higher phase volumes are possible but the cells and bubbles or droplets take on a polyhedral form. A ratio of 0.74 is more commonly known as the Ostwald maximum and at a value of 0.5ϕ the emulsion can be said to be loosely packed.

Test 9. Spreading monolayer

h) Dipping the matchstick laden with surfactant introduces a monolayer of surfactant, which spreads on the surface just as Benjamin Franklin discovered. The spreading speed is 'phenomenal' (approximately $>1 \text{ m/s}$) and so the sprinkled floating soot and cinders are pushed to the margins of the Petri-dish [11]. Identical spreading of surface active agent occurs during dispersion and permits the envelopment of oil droplets and bubbles in emulsions and foams, respectively [1-5]. The dimensions and mechanics of the spread monolayer are astounding [1-5, 11] (a monolayer is a single surface replica of the two surfaces found in an emulsion or foam TLF. One can tell students this is the same as a sheet of paper pushing a lorry out of its way. This highlights the very special nature of the surfactant or emulsifier (amphiphile; polymer) and its necessity many of the forms listed in Table 1.

Test 10. Topology and the TLF - Newton's interference fringes

i) An aqueous planar horizontal film is seen in the inverted glass beaker [1, 3]. The film has to be viewed from the side at a $20\text{-}30$ degree angle incident to the plane of the film to see internal scattered light. Newton's interference fringes (colours) are clearly visible and are analogous to the lines of a contour map, charting topological changes and the timescale of this fluidity and mobility [1, 3-5, 9, 10, 12]. The colours represent unique and discrete thicknesses in the TLF. Dark holes appear in the film at equilibrium the thickness of the foam film or TLF may be $5\text{-}25 \text{ nm}$ [3-5]. For comparative purposes an atom is approximately 0.07 nm so TLFs are truly nanostructures. Multiple versions of his planar film experiment are visible in a well-drained foam such as a glass

of beer head or the foam on the top of a washing bowl. Oil-based rather than bubble-based TLF exist but these are generally much more difficult to visualise, primarily because oil droplets are a hundred to a thousand times smaller than a bubble [2, 5, 9].

Summary and concluding remarks

Surface activity and thus surface composition have a profound effect on macroscopic form and the dynamic behaviour and both texture [10] and resistivity of dispersions (Figure 2), such as foam and emulsions [17]. This occurs by a modification of physical form. Foams and films are often used for study rather than emulsions but this is often based on ease of examination. To some extent the same general theories apply to dispersions of air-in-water, solid-in-water or oil-in-water. TLFs have also been used to model energetics [8] and thermodynamics. More recent approaches have helped the formulation and modelling of foods, diagnostic devices, in vivo medical devices, therapeutics and drugs [4, 13, 17].

Acknowledgements

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