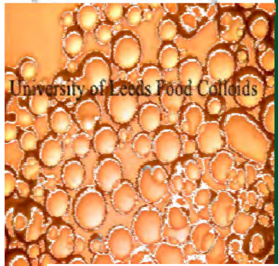

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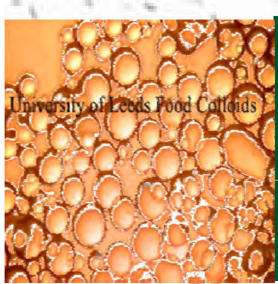
Physico-chemical basis of fat structure and function

Malcolm Povey

Physical Principles of Lipids for Food Products and Health

Weetwood Hall, University of Leeds

5th and 6th September 2013



Lecture 13: LIPID FUNCTIONALITY

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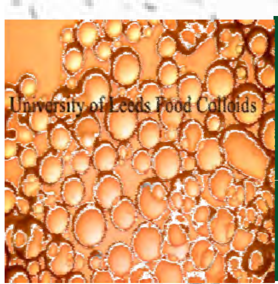
- Lipids, especially fats are an important component of our diet and are frequently consumed in colloidal form in products such as mayonnaise, yoghurt, margarine and butter.
- Products such as margarine and butter contain a high proportion of fat (>= 80%) and the properties of the lipids are central to the perceived properties of the product.

Important Properties

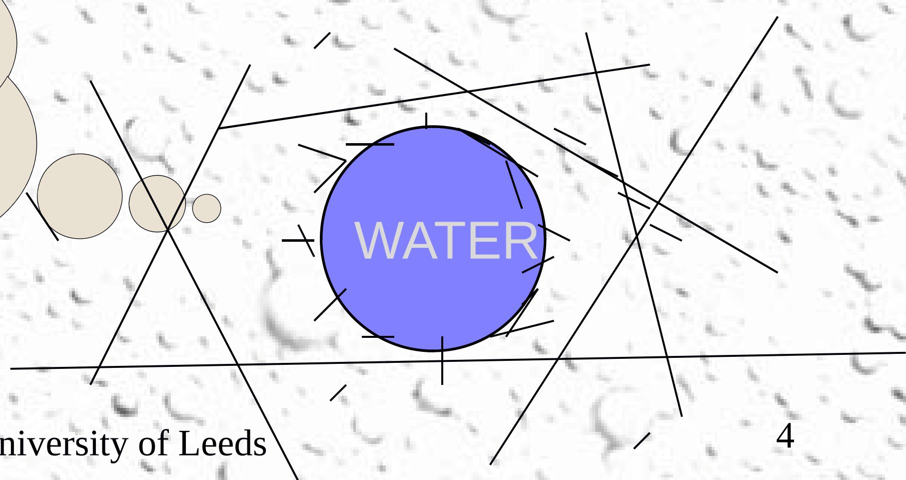
– Important properties include colour, spreadability, hardness, mouthfeel, taste, microbiological stability, consistency, stability and segregation. All these properties are profoundly affected by the properties of the lipids.



Why do we like fatty spreads?

On melting in the mouth, the disappearance of the fat crystal network allows the water-in-oil emulsion to revert to the more stable oil-in-water emulsion. This releases the water soluble flavours in the mouth and gives a ‘watery’, rather than an ‘oily’ mouthfeel.

Fat crystals form a space filling network which behaves like a gel. Small fat crystals aggregate on the water surface, stabilising it (This is called Pickering stabilisation)



Recrystallization

Recrystallization may cause a rearrangement of triglyceride molecules between different crystals. This can result in undesirable changes in the product, such as the appearance of 'bloom' on chocolate.

http://www.esrf.eu/news/pressreleases/chocolate/

Solid Fat Content

The solid fat content (SFC) and the associated crystal polymorph and crystal habit have a profound effect on the properties of margarines, shortening, chocolate and other fatty products. These crystal properties are an important factor in our partiality to fatty products.

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Melting

Melting of crystals produces a cooling effect which is perceived by the mouth and adds to the desirability of lipids in food products.

‘Spreadability’

SFC affects the spreadability of a fat. By blending a mixture of triglycerides, a consistent rheological behaviour may be engineered over a wide range of temperatures, achieving the expected ‘spread straight from the refrigerator’ behaviour.

FUNDAMENTALS OF CRYSTALLIZATION

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- Triglycerides (Triacylglycerols) undergo a process called crystallization as their temperature is lowered. A crystal is a solid substance showing some marked form of geometric pattern, to which certain physical properties, angle and distance between planes, refractive index etc., can be attributed (Chambers Science & Technology

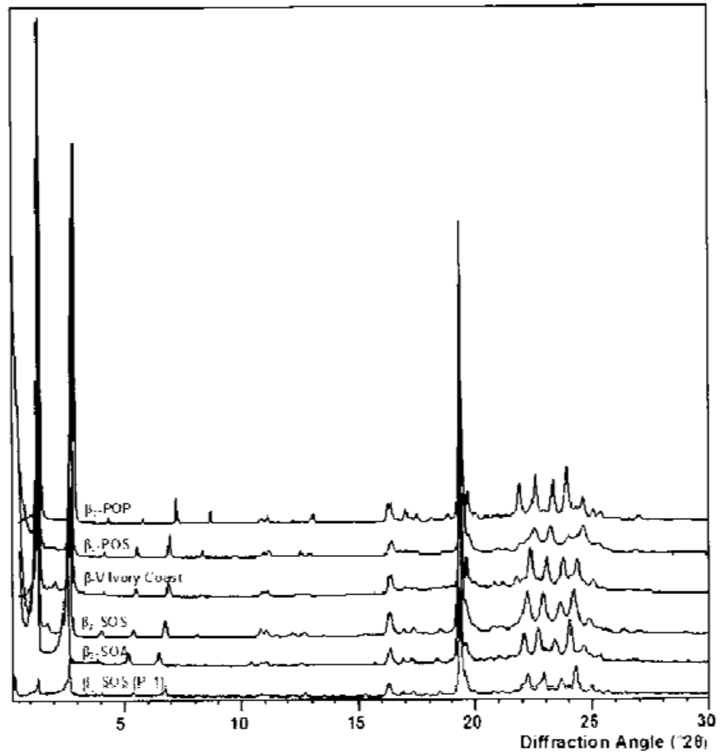

Fig. 3.2: Overview of β- diffraction patterns with 2θ-scale converted to Cu $K\alpha_1$ radiation. The bottom pattern was used for the structure determination of the $P\bar{1}$ model (Peschar et al., 2004).

Crystallisation

- Crystallization is the slow formation of a crystal from melt or solution. In the case of triglycerides, the process of crystallization may be very slow, taking hours, days or even months.

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Crystallization

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- There are two physically distinct stages to crystallization - crystal nucleation and crystal growth.
- Nucleation requires a degree of supercooling below the melting point.

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…crystal nuclei

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Nuclei may form by the chance coming to together of molecules in melt or solution, releasing heat to their surroundings because the crystal form must be a lower energy state than that of the melt or solution if nucleation is to occur. This is called *homogeneous* nucleation. It rarely occurs in practical fats.

Usually nucleation occurs because another material (Catalytic impurity, nucleation site, surface) acts as a nucleator. (This role may be played by small quantities of trans fats in practical processing). This is called *heterogeneous* nucleation.

Crystal growth

Crystal growth may continue at the melting point since at this temperature the release of heat associated with the transformation of liquid to solid exactly balances the removal of heat from the melt or solution which is necessary for crystallization to continue.

...crystal growth

Crystal growth is a complicated process which exhibits some or all of the following features - habit, defect, polymorphism, melting point

A defect is an interruption in the regular arrangement of the crystal.

...crystal polymorphism

Polymorphism is the ability of triglycerides to exist in two or more distinct crystal forms, usually at least three. Each polymorphic form has a different melting point and a crystal may transform from one form to another, not necessarily through melting and recrystallization.

Polymorphs of triacylglycerols

The polymorphic forms of triglycerides are called alpha (α), beta-prime (β') and beta (β). The β form is the most stable and has the highest melting point. β' is intermediate in stability and has a lower melting point and α is the least stable with the lowest melting point.

TAG Molecule, Polymorphism, Subcell and unit cell

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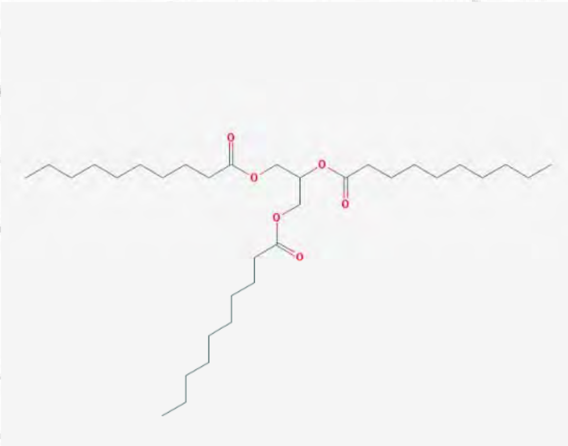

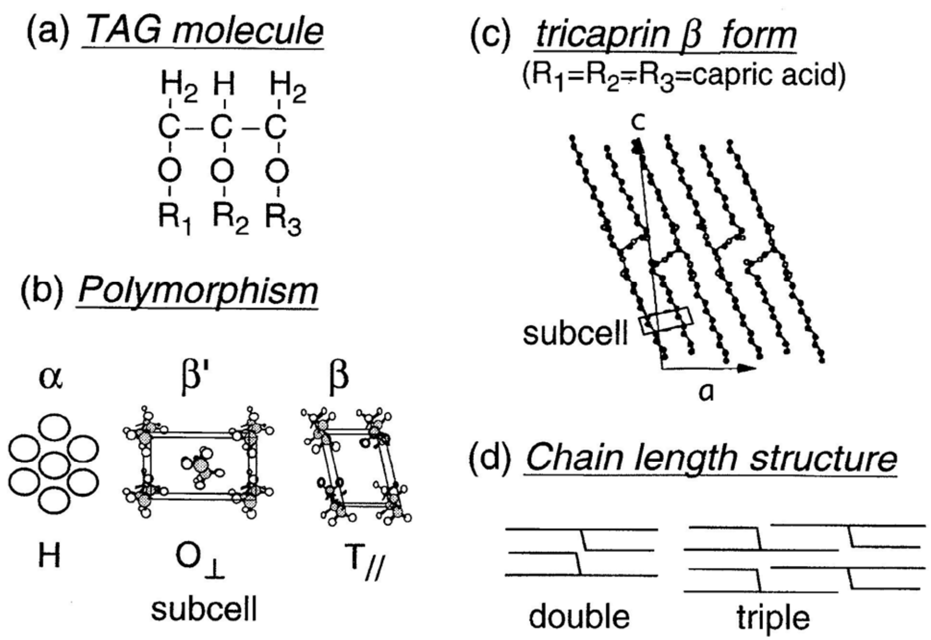

Fig. 1. A triacylglycerol molecule, polymorphism and subcell structures, chain length structure and unit cell structure of tricaprin β form.

Structure models and *G-T* relationships for PPP

; Science 56 (2001) 2255–2265

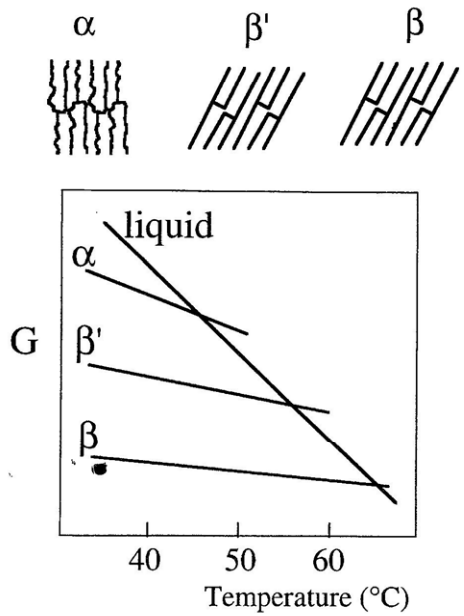

Fig. 2. Structure models and Gibbs energy (*G*)–temperature relationship of three polymorphs of PPP.

An exceptional case

The six so-called polymorphic forms of cocoa butter may be explained in terms of the three basic polymorphic forms combined with a bi-layer or tri-layer stacking of the triglyceride molecule.

Structure models and G-T relationships for SOS

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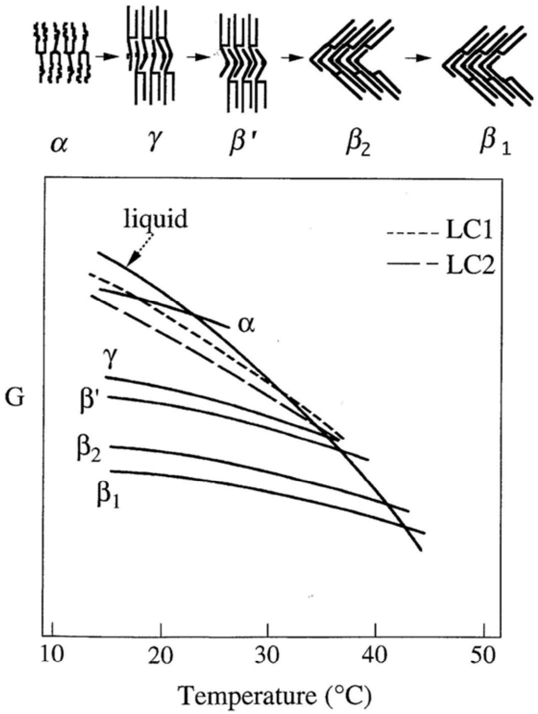

Fig. 3. Structure models and Gibbs energy (*G*)–temperature relationship of five polymorphs of SOS.

Mixtures of triacylglycerols

Mixtures of triglycerides can affect crystallization and polymorphism in complex ways. This is because a ‘guest’ molecule may fit into a crystal, modifying its structure in some way. Certain mixtures may form compound crystals, in which two or more triglyceride molecules form part of the crystal structure, producing a crystal possibly unlike the crystal produced by either pure material.

Mutual solubility

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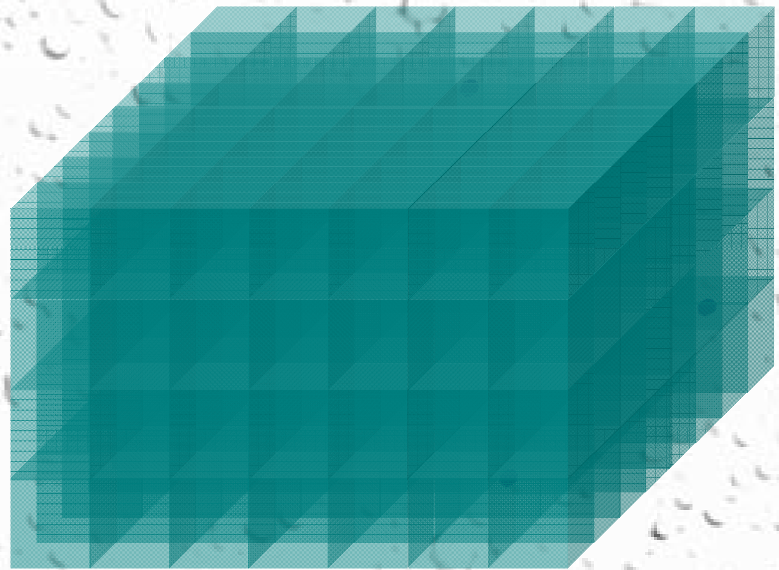
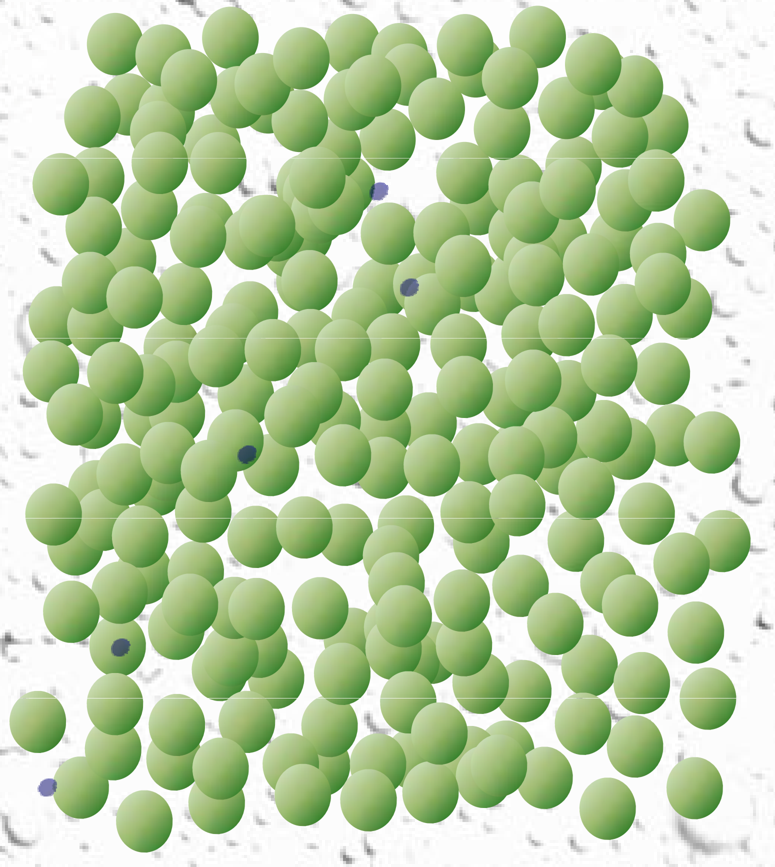
Crystal melting points may be affected by solubility in liquid triglycerides present in the same mixture.

Crystallization in bulk fat



Dispersion of bulk fat as a colloid



Contact angles and surface energy

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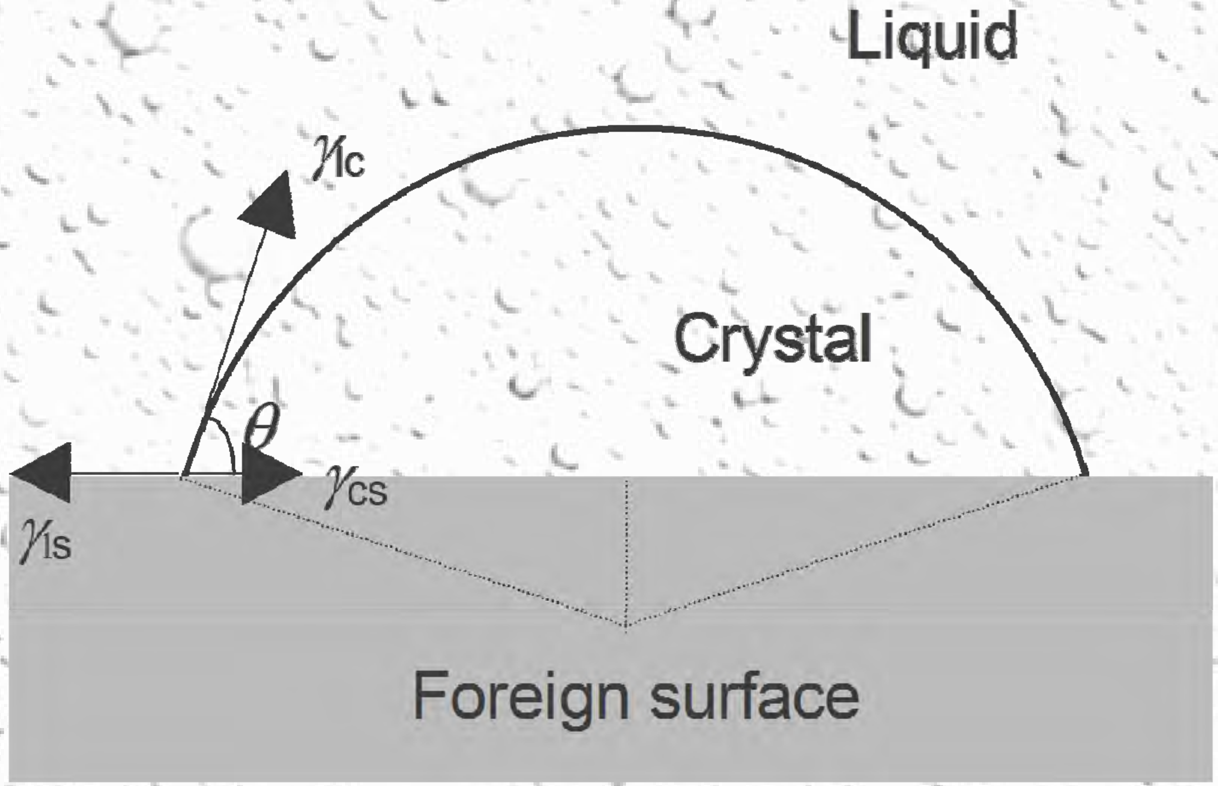

Fatty acid ordering at oil droplet surface

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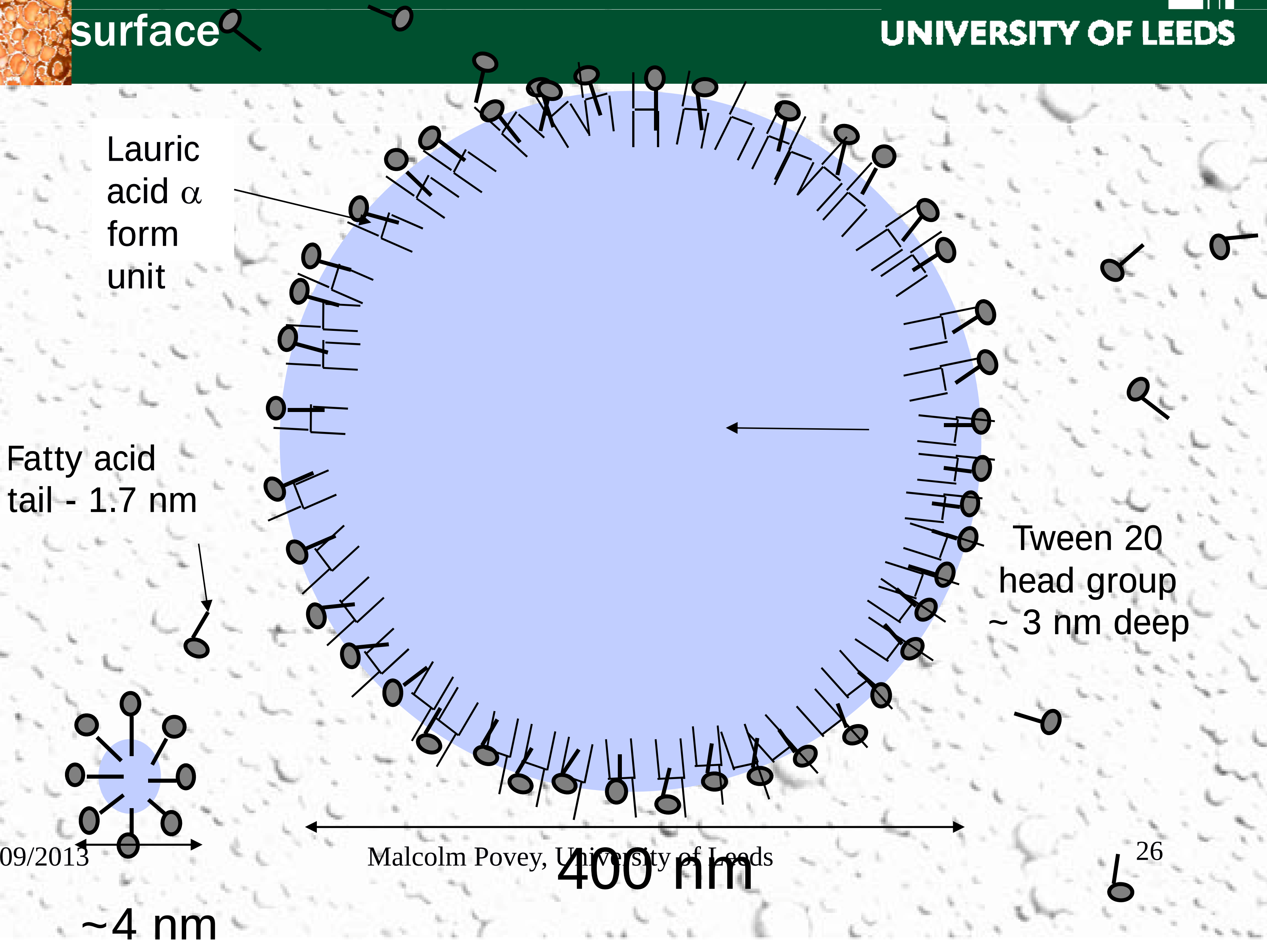
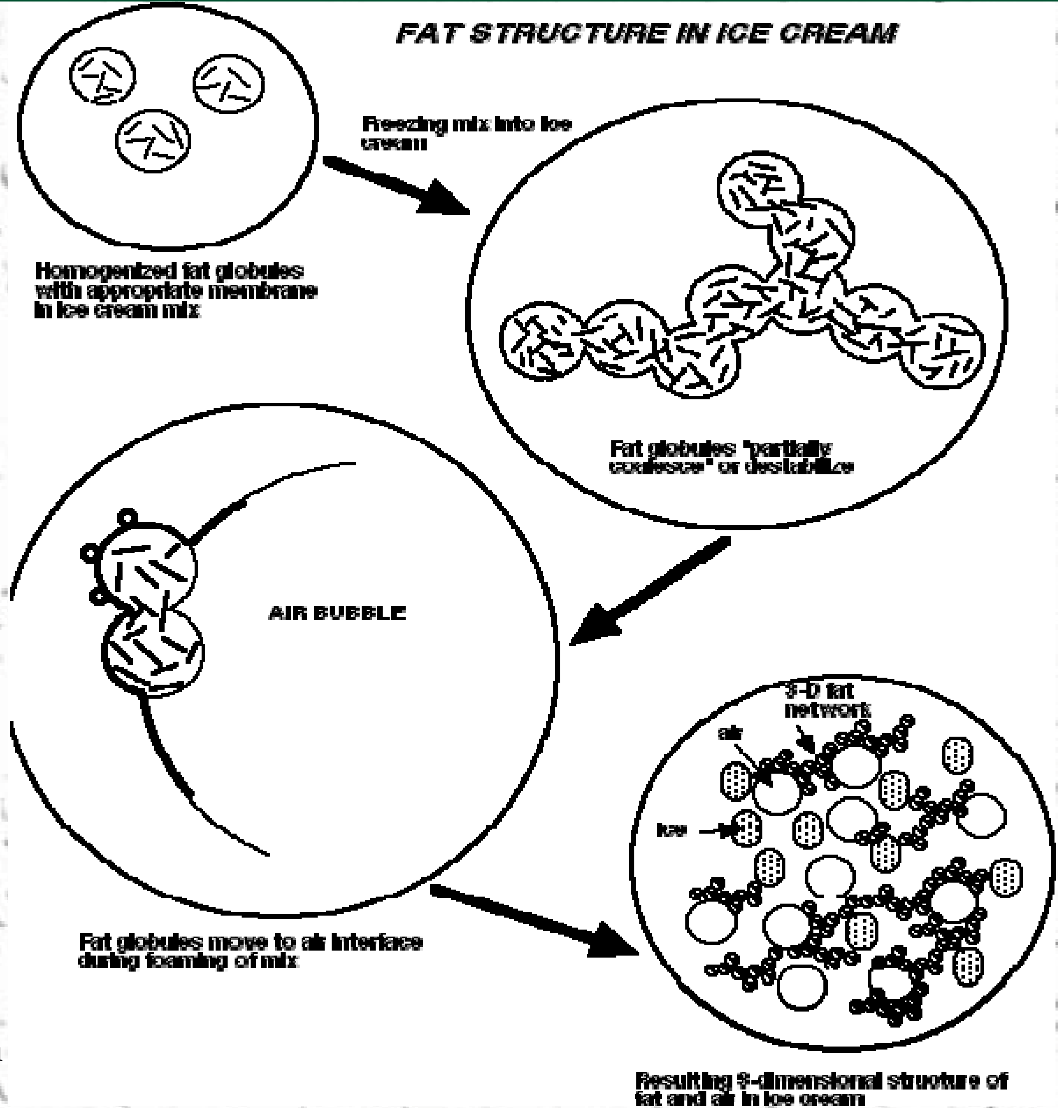
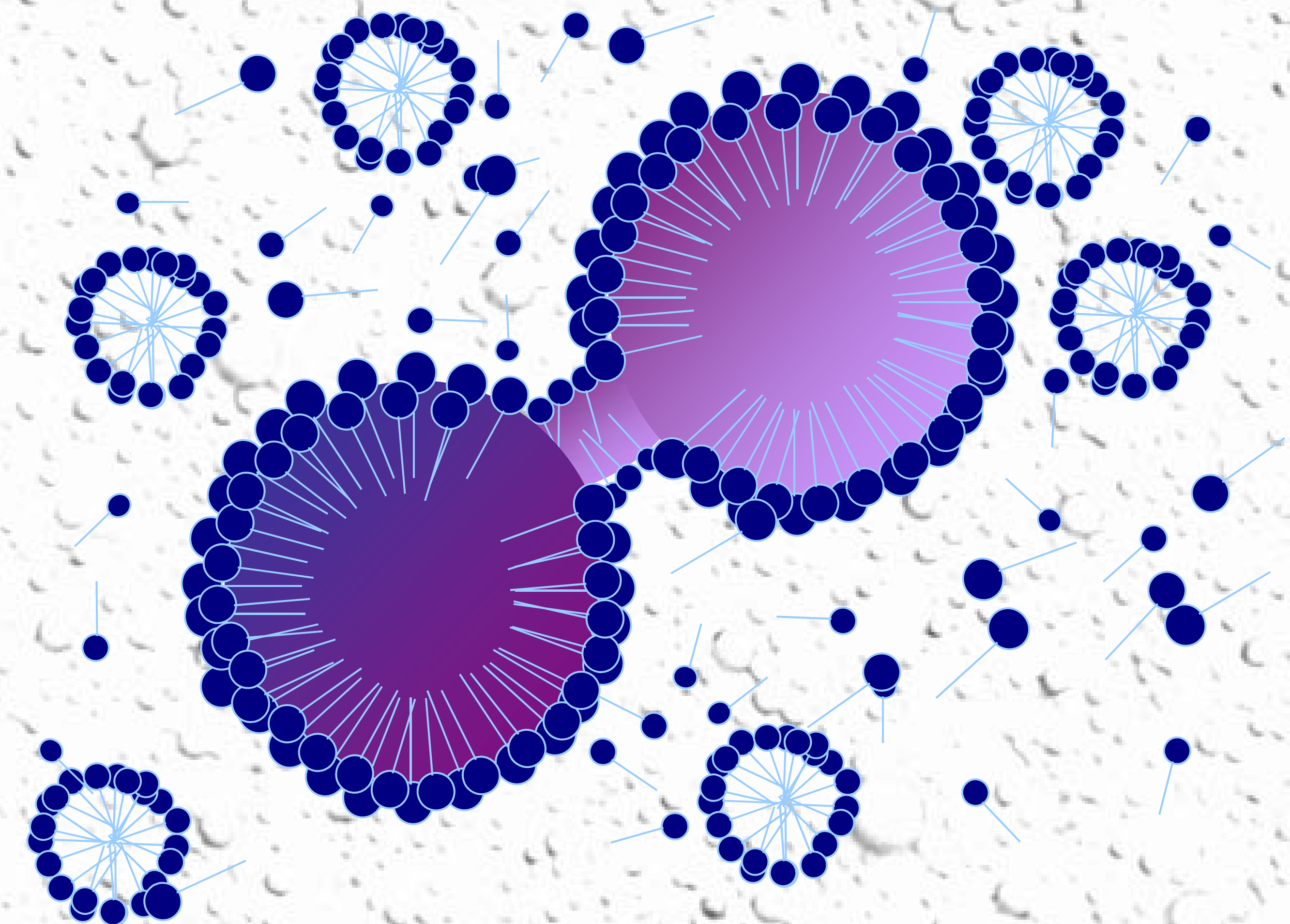


Fat structure in ice cream

See and also



Transient partial coalescence



Hairy spherulites and partial coalescence

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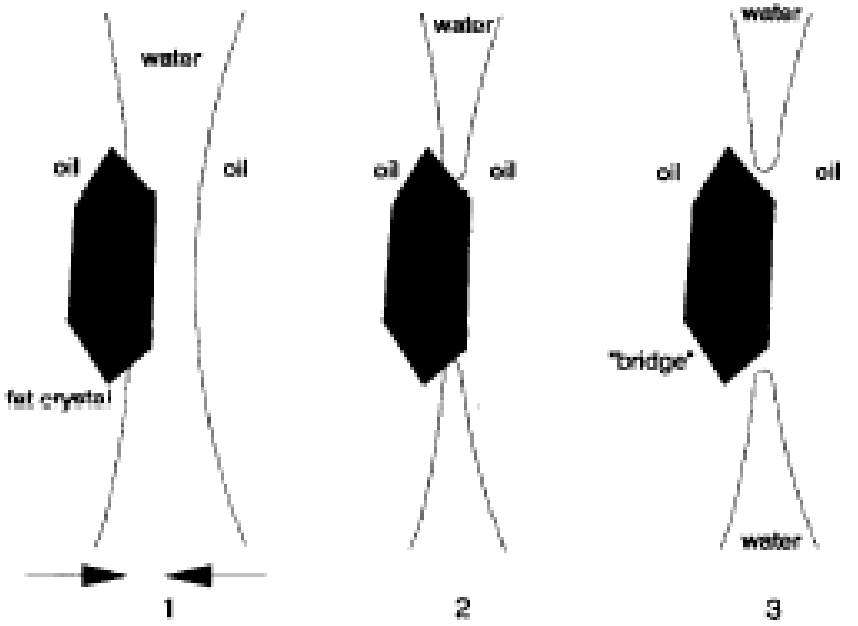

Fig. 1. Schematic drawing of the hypothetical (partial) coalescence mechanism induced by a protruding crystal: 1, approach of droplets; 2, crystal breaches water film; 3, water film breaks.

nearly always had such crystals. Although the

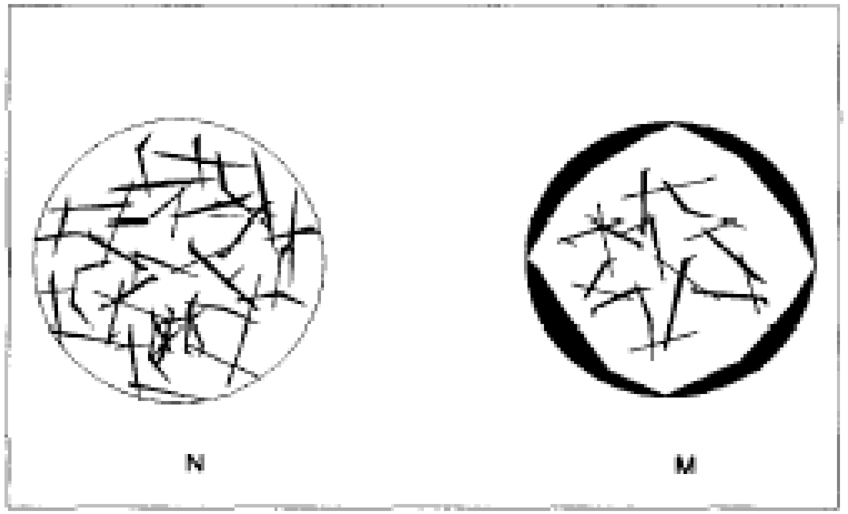

Fig. 2. Possible habits of emulsion globules containing fat crystals, as observed by polarized light microscopy: N, needle type; M, mixed type (needles and layers) (mainly after Walstra [31]).

Boode and Walstra (1993), Colloids and Surfaces A, **81**, 121-137 (this and the next two slides)

Partial coalescence

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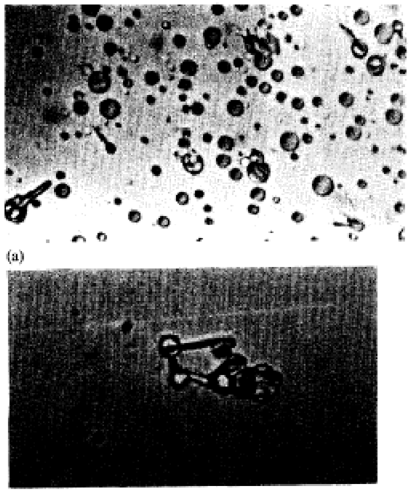


(a)

(b)

Fig. 7. Crystals grown out of the oil globules where crystal dimensions exceed the globule diameter (SDS (10 mM)–triglyceride blend B (0.5%) emulsion): (a) single globules; (b) clump formed by partial coalescence in the previously mentioned emulsion (magnification, × 800).

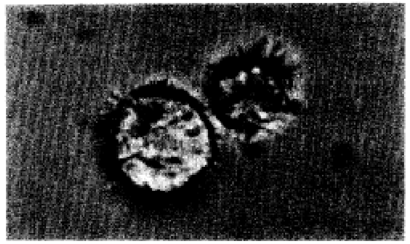
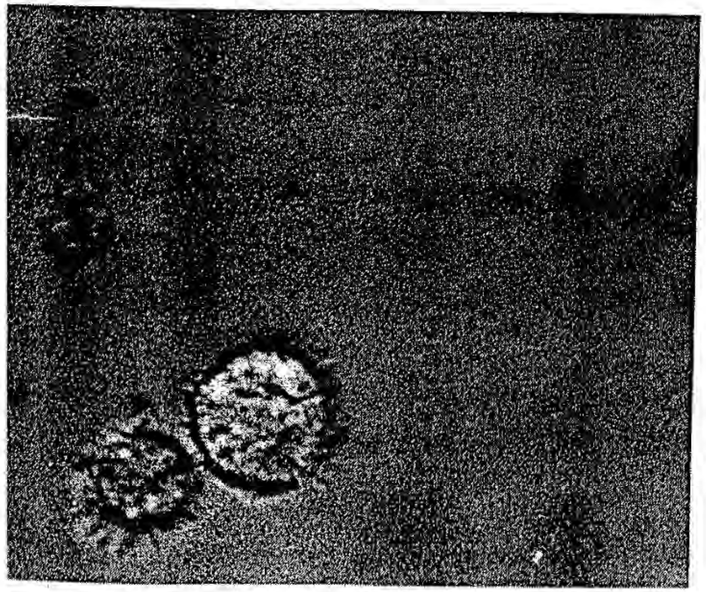
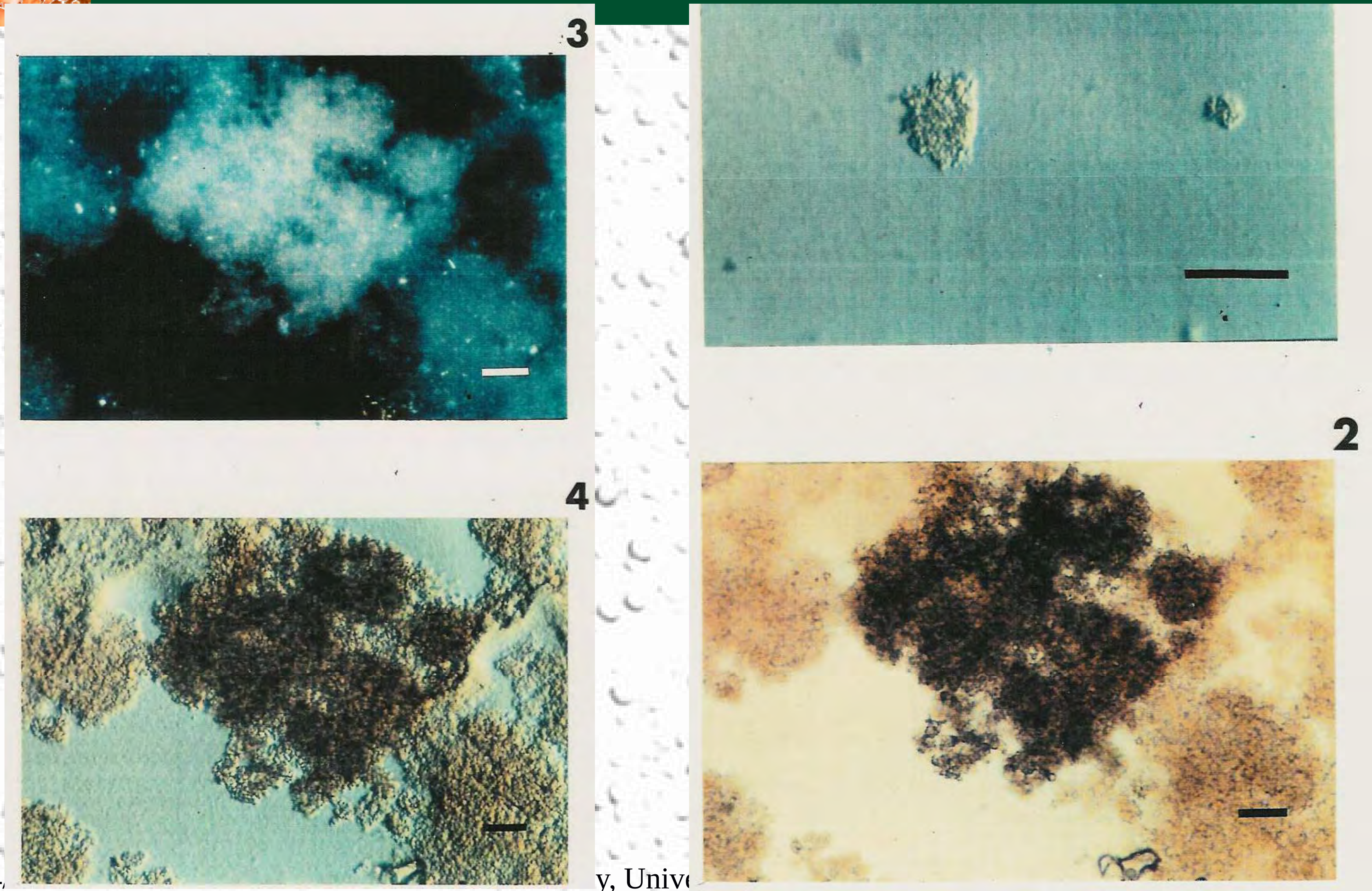


Fig. 8. Triglyceride blend B globules in 14 mM SDS solution at 4°C. Note the crystals protruding from the o/w interface (magnification, × 3000).



lend B globules in 14 mM SDS solution at 4 °C. Note the crystals protruding I

Coalescence of fat crystals



Partial coalescence

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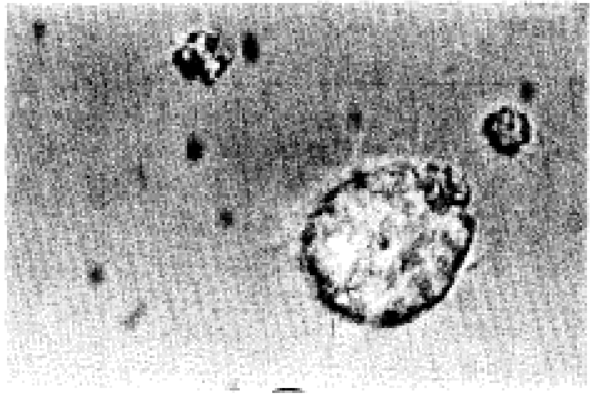
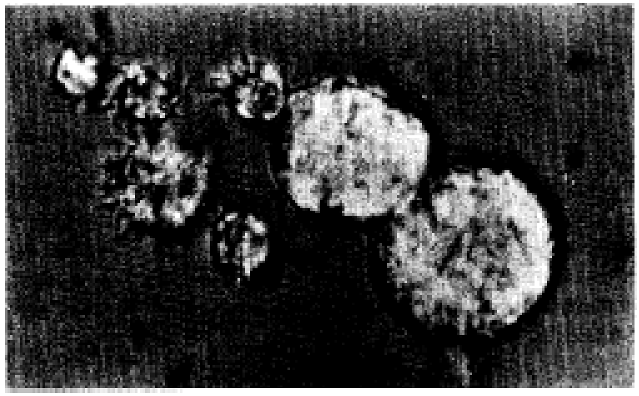
Table I
Influence of the type of fat and the solid fat fraction ϕ_s on the yield stress of the bulk fat σ_y, on the presence of a fat network in an emulsion globule (diameter < 10 μm) and on the minimum pressure P_o needed to squeeze oil out of the globule

Fat type	ϕ_s	σ_y (Pa)	Fat network in an emulsion globule	P_o (Pa)
Milk fat	0.092	0	No	0
	0.120	46	No	0
	0.146	71	No	0
	0.180	$\gg 642$	Yes	$< 5 \times 10^2$
Blend A	0.102	65	No	0
	0.135	470	No	0
	0.162	$\gg 642$	Yes	3×10^4
	0.203	$\gg 642$	Yes	6×10^4
Blend B	0.091	0	No	0
	0.193	2.5	No	0
	0.285	47	No	0
	0.836	$\gg 642$	Yes	$\gg 10^5$



(a)



(b)

Fig. 5. Crystallization habit of blend B globules in a 0.4% SDS solution (a) or a 1% caseinate solution (b) as recorded by polarized light microscopy (magnification × 4000).

References and Recommended Reading

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Links

Molecular Expressions - Microscopy Site

Snow Crystal Growth