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Historical perspective

Non-aqueous foams: Current understanding on the formation and stability mechanisms

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ABSTRACT

The most common types of liquid foams are aqueous ones, and correspond to gas bubbles dispersed in an aqueous liquid phase. Non-aqueous foams are also composed of gas bubbles, but dispersed in a non-aqueous solvent. In the literature, articles on such non-aqueous foams are scarce; however, the study of these foams has recently emerged, especially because of their potential use as low calories food products and of their increasing importance in various other industries (such as, for instance, the petroleum industry). Non-aqueous foams can be based on three different foam stabilizers categories: specialty surfactants, solid particles and crystalline particles. In this review, we only focus on recent advances explaining how solid and crystalline particles can lead to the formation of non-aqueous foams, and stabilize them. In fact, as discussed here, the foaming is both driven by the physical properties of the liquid phase and by the interactions between the foam stabilizer and this liquid phase. Therefore, for a given stabilizer, different foaming and stability behavior can be found when the solvent is varied. This is different from aqueous systems for which the foaming properties are only set by the foam stabilizer. We also highlight how these non-aqueous foams systems can easily become responsive to temperature changes or by the application of light.

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1. Introduction

A liquid foam is a two-phase media where a gas is dispersed into a continuous fluid. Aqueous foams are formed of gas bubbles dispersed into water (containing stabilizing agents). They are the most common

types of liquid foams. Aqueous foams are widely used in cosmetics, detergency, food, healthcare, fire-fighting and flotation of minerals [1,2]. Alternatively, if one tries to disperse a gas into a non-aqueous liquid (like an oil), one possibly gets what is called a non-aqueous foam. These systems are much less studied than the aqueous foams, despite the fact that they play important roles in various industries and processes, especially in relation with petroleum and manufacturing.

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Aqueous foams are thermodynamically unstable systems which tend to separate with time into their individual components: gas and water. Foam production and stabilization require the use of foaming and stabilizing components dispersed in the aqueous phase. Surfactants, polymers, proteins or particles can be used alone or mixed together, to provide both a good foamability and a subsequent long term stability [3,4]. Their role is to prolong the lifetime of the foam by slowing down the three main mechanisms of foam aging: drainage, coarsening and coalescence. One major challenge in foam science is indeed to control the foam lifetime (more precisely, to optimize this lifetime to any required application). Remarkable properties have emerged recently for aqueous foams including ultrastability. A recent review has been published on these ultrastable liquid aqueous foams [5]. In certain industrial processes, the stability of the foam needs to be tuned for specific performance requirements. For example, in the cleaning of radioactive vessels, a good foaming agent is applied to remove particles from the walls of the vessel, but then the foam needs to be destroyed to release a small volume of contaminated liquid. Thus, recent research progresses have resulted in the creation of responsive aqueous foams. Responsive foams refer to foams for which the stability can be switched between stable and unstable states with a change in environment (pH, ionic strength, etc.) or with external stimuli (light, temperature and magnetic field). The systems and the mechanisms which lead to responsive aqueous foams systems have been described recently in another review [6].

Contrary to aqueous foams, few studies have been devoted to foams made from oil. In the 1940's, Mc Bain and Perry reported that the surface tension of mineral oils, tetra-isobutylene and hydrogenated tetra-isobutylene, are slightly reduced from about 3 to 5 mN·m⁻¹ by adding lauryl sulfonic acid [7]. They showed that this surfactant had a less pronounced effect on the surface tension of benzene, xylene and heptane. In the 1980's, several studies have been published showing that foaming in several different types of crude oils was due to the presence of surface-active organic materials [8,9]. In the same time, Ross and co-workers detected some weak foaming in lubricating oils [2]. However, it is only twenty years after the publication of these papers that this topic really began to gain interest in the foam community. Foams from non-aqueous systems were the topic of a similar review from S.E. Friberg few years ago [10], but this topic has been intensively worked on further during the elapsed time, especially the last two years. The increasing need of low calories food products with new properties and textures in the food industry has induced a strong activity on this topic. The addition of gas bubbles to create low calories food products is indeed a relevant route to reduce the total fat content while providing a light and pleasant texture [11,12]. For example, it has been demonstrated that the characteristic chew mouth-feel and low fat content of chocolate including bubbles is of crucial importance for consumers [13]. Therefore, the key parameters controlling the foam formation and stability need to be understood, to develop such oil foams and low fat food products. For the lubricating oils industry, the air entrainment within the lubricating oils leading to non-aqueous foam formation causes problems such as oxidative and thermal oil degradation, impaired heat transfer, retarded oil supply and cavitation [14]. For this specific industry, it is important to understand the tendency of oil lubricating formulations to produce foam and how such foams can eventually be destroyed.

In a first step to describe and understand non-aqueous foams, all the information and concepts described in the literature for aqueous foam formation and stability are useful, but specific considerations must be taken into account by replacing water by non-aqueous solvents in the continuous phase. Indeed, water is unique since this low-viscosity liquid has a high surface tension due to extensive hydrogen bonding. In the case of non-aqueous solvents, the surface tension is relatively low. The main difference between non-aqueous and aqueous foaming systems comes from the ranges and variations of surface tension at the liquid-gas interface. In aqueous foams, surfactants strongly adsorb at the interface reducing the high water-air surface tension (≈ 72 mN·m⁻¹ at 25 °C) to lower values ranging from 20 to 40 mN·m⁻¹. For non-aqueous

foam systems, the typical non-aqueous liquids have already rather low surface tension between 15 and 30 mN·m⁻¹ making the adsorption of hydrocarbon based surfactants energetically unfavorable [10]. Moreover, the most common electrostatic stabilization of foam films by ionic surfactants, found in aqueous systems, is prevented in oil: this is mainly because ionic dissociation at the interfaces is unlikely, as a consequence of the very low dielectric constant of oil. Also, contrary to aqueous foams, the foaming properties are not only related to the foaming capacity and amphiphilicity of the foam stabilizer, and one has to take into account all the physical properties of the non-aqueous liquid phase (polarity, viscosity, density, conductivity, dielectric constant and Hansen solubility parameter values).

Despite these serious drawbacks, non-aqueous foams can still be produced, based on three different foam stabilizers categories: specialty surfactants, solid particles and crystalline particles [15]. As specialty surfactants, Polydimethylsiloxane (PDMS) based-surfactants and fluoroalkyl surfactants can be cited [10]. Fluoroalkyl surfactants can reduce the surface tension of liquids to low values (<20 mN·m⁻¹) due to their fluorocarbon moiety. The surface activity of PDMS based-surfactants is due to the presence of hydrophilic Si—O groups which are shielded by the lyophobic methyl groups, which orient and pack at the surface. Asphaltenes and resins are responsible for the formation of certain petroleum foams by protecting bubbles from coalescence [15]. This category of specialty surfactants and asphaltenes to produce non-aqueous foams has been recently reviewed [10,15]. We only focus in this review on the more recent advances in the non-aqueous foams field concerning the two other categories. We highlight how the presence of solid particles or crystals can lead to the formation of non-aqueous foams and stabilize them.

2. Non-aqueous foams stabilized by solid particles

Specific colloidal particles can adsorb at fluid-fluid interfaces leading to the stabilization of emulsions, aqueous foams or non-aqueous foams [16]. To obtain drops or bubbles completely stable against coalescence and coarsening, the particles need to be adsorbed irreversibly at the fluid-fluid interfaces. The adsorption of particles at fluid interfaces can provide a free energy gain by losing an area of bare interface. The adsorption of particles at an air/liquid surface depends on the wettability of the particles, which is quantified by the contact angle θ the particles make with the air/liquid interface (measured through the liquid phase, Fig. 1). The contact angle is given by the Young equation (Eq. (1)):

$$\cos\theta = \frac{\gamma_{\text{solid/air}} - \gamma_{\text{solid/liquid}}}{\gamma_{\text{liquid/air}}} \quad (1)$$

For a spherical particle, when $\theta = 0^\circ$, the particle is completely wetted by the liquid leading to oil dispersion of particles and no air incorporation, even after vigorous mixing (Fig. 1). When $\theta = 180^\circ$, the particle is completely non-wetted by the liquid. In these two cases, no particle adsorption occurs at the air/liquid surface. For intermediate θ values between 0° and 180° , particles are more wetted by one of the two phases: liquid or air. For $\theta < 90^\circ$, particles are more oleophilic than oleophobic, and stable oil foams should result after aeration of the mixture. For $\theta > 90^\circ$, particles are extremely oleophobic and the inverted case of oil-in-air droplets should be stabilized. Young's equation suggests that the particle contact angle could be changed by altering the respective interfacial tensions. In the framework of aqueous foams, there are two common approaches for changing the particle contact angle, thus tuning the particle wettability: chemical modification of the particle surface and surfactant adsorption to the particle surface [17].

When the liquid phase is oil, particles must be partially oleophobic in order to exhibit contact angles between 0 and 180° . This means that one has to generate some repellency against oil on particle surfaces, to obtain an intermediate wettability. It turns out that particles coated by

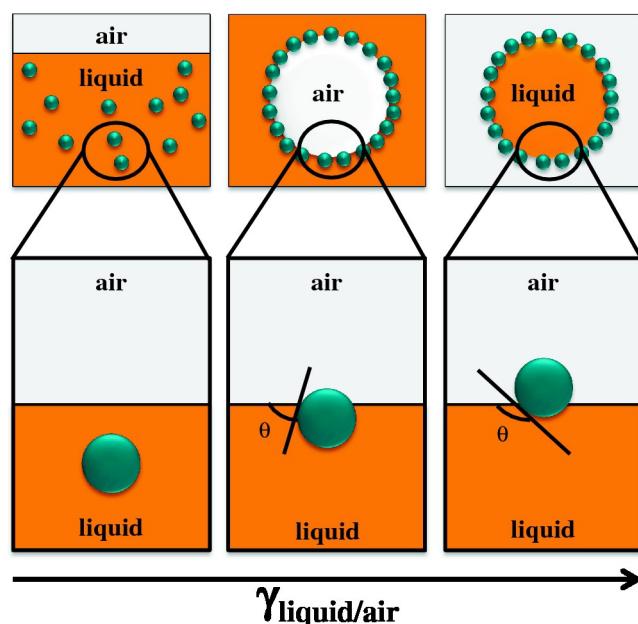


Fig. 1. Upper: oil dispersion (left), air-in-oil foam (center), and liquid-in-air powder (right). Lower: position of particle in mixtures of liquid and air as a function of contact angle and surface tension. Contact angle measured through the liquid phase increases from zero to medium to high values from left to right.

hydrocarbon-containing groups are fully wetted by many oils, while those coated by fluoro-groups are fully oleophobic to certain oils. This difference comes from the lower surface energy of fluorocarbons than hydrocarbons. Therefore the preparation of intermediate wettability and particle-stabilized oil foams, by chemical modification of the surface particles, is much more challenging than for aqueous foams [18]. However, in the framework of oil foams, one must keep in mind that the wettability of the particles can also be changed by the surface tension of the liquid phase, providing more degrees of freedom.

2.1. Surface tension of the non-aqueous liquid and contact angle

In the 1950's, Fox and Zisman worked on the wetting properties of smooth solid surfaces of polytetrafluoroethylene (PTFE) by various liquids [19]. They established a simple relation between the wetting angle θ and the surface tension $\gamma_{\text{liquid/air}}$ for the wetting of PTFE surfaces: $\cos(\theta)$ increases (θ decreases) more or less linearly with a decrease of $\gamma_{\text{liquid/air}}$. They defined the critical surface tension γ_{critical} such that liquids with $\gamma_{\text{liquid/air}} \leq \gamma_{\text{critical}}$ wet the solid completely, whereas those with $\gamma_{\text{liquid/air}} > \gamma_{\text{critical}}$ do not wet the solid. For PTFE, γ_{critical} is $18 \text{ mN} \cdot \text{m}^{-1}$ at 20°C . On smooth PTFE surfaces, $\theta = 0^\circ$ for pentane, 46° for hexadecane and 108° for water. The angle θ increases as the cohesive energy of the liquid increases, and due to interactions between molecules in the liquid shifting towards those including hydrogen bonds [20]. Thus, it was a first study showing that θ can be tuned by the nature of the liquid phase. From this concept, Binks and coworkers studied PTFE and OTFE particles with 30 oils of different structure in order to produce oil foams (Table 1) [20]. In the same way, Murakami and Bismarck studied OTFE particles with 9 liquids ranging from non-polar hydrocarbons to polar oils [18]. The size of the primary particles varies from 0.5 to around $10 \mu\text{m}$. Most of the time, these kind of particles are strongly agglomerated in air due to surface attractive forces leading to particle agglomerates ranging in size from tens to hundred micrometers.

There is an easy method to obtain qualitative information on the wetting behavior of the particles. To determine if the liquid wets the particles, the particles need to be placed on top of the liquid (in a glass bottle). As the particles are often in the form of a powder (containing

Table 1
Summary of works on non-aqueous foams obtained from solid particles.

Non-aqueous systems	Solid particle	References
30 liquids ranging from non-polar hydrocarbons and polar oils to glycerol	One kind of fluoroparticles (PTFE)	[20]
9 liquids ranging from non-polar hydrocarbons to polar oils	Trifluoromethyl-terminated oligomers of tetrafluoroethylene (OTFE) particles	[18]
26 liquids ranging from non-polar hydrocarbons and polar oils to glycerol	Four kinds of PTFE and one kind of OTFE particle	[21]
22 liquids ranging from non-polar hydrocarbons and polar oils to glycerol	Fumed silica particles coated to different extents with perfluoro-alkosilane	[24]
Ethylene glycol glycerine	Fumed silica particles coated to different extents with dichlorodimethylsilane	[27]
14 liquids including silicone, mineral vegetable, ester and UV-absorbing oils	Platelet sericite particles coated to different extents with perfluoroalkyl phosphate	[25]
6 liquids ranging from non-polar hydrocarbons to polar oils	TiO_2 particles coated to different extents with fluoroalkylsilane	[28]
24 liquids ranging from non-polar hydrocarbons to polar oils	Four kinds of fluorinated particles based on sericite and bentonite platelet clays and spherical zinc oxide	[26]

air), the bottle must be gently agitated to expel air before the solid gets in contact with the liquid. After such agitation, the wetting behavior depends if the particles get immersed or not in the liquid: the particle layer can either completely enters the liquid, can remain partially wetted, or stays non-wetted [21]. To obtain quantitative data on these systems, the main parameter to determine is the contact angle. The measurement of the contact angle of a small particle with a liquid surface is difficult. Most of the time it is better to prepare a flat substrate pellet composed of compressed particles to measure the contact angle [21]. Since the surface of the resulting pellet is not perfectly smooth, the value of θ depends on whether the liquid advances or recedes on the surface. To avoid any misinterpretation, both contact angles need to be measured and compared.

In the pioneering works, particles of OTFE or PTFE were shown to stabilize foams and mixtures of oils were used to tune the adsorption of the particles to the air-oil surface [18,20,21]. The oil foams can be produced by hand-shaking or by introducing air bubbles by mechanical mixing (blender, rotor-stator homogeniser, etc.). The important role of the oil surface tension to achieve particle adsorption in correlation with foam stability was highlighted. In the case of OTFE particles, a mixture between silicone oil and ethyl benzoate at different mole fractions of ethyl benzoate has been studied in order to modify the contact angle (Fig. 2a) [18]. The advancing contact angle and the wetting behaviour have been determined for the various mixtures between silicone oil and ethyl benzoate as described previously. All the systems have been aerated by hand-shaking to determine which ones could produce oil foams. It was found that a wetting transition between non-wetted and wetted state occurs around an advancing contact angle value of 46° . In parallel, from 32.8° to 49.6° , stable oil foams are observed. The maximal foam volume is reached around the wetting transition. This example illustrates the link between contact angle and the creation of foam (Fig. 2.b).

In the case of PTFE particles, a dispersion of particles in oil is obtained for oils of relatively low tension which wet the particles ($\gamma_{\text{liquid/air}} < 30 \text{ mN} \cdot \text{m}^{-1}$, such as squalane, benzene, etc.) [20]. Oil foams are obtained for liquids with intermediate tension ($45 \text{ mN} \cdot \text{m}^{-1} > \gamma_{\text{liquid/air}} > 30 \text{ mN} \cdot \text{m}^{-1}$) such as sunflower oil or eugenol. For polar liquids with higher tension like glycerol and water, the curvature of the interface is inverted and a powder-like material is formed containing droplets of water or glycerol coated by particles. This powder-like material is similar to dry oil or dry water

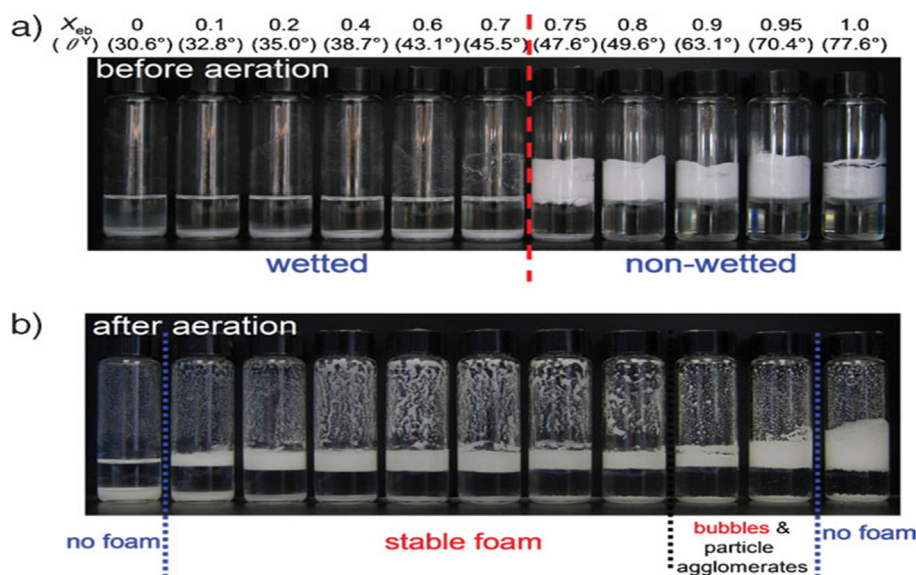


Fig. 2. Illustration of the wetting transition of OTFE particles at air–oil surfaces and effect of wetting states on foaming behavior of oils. a,b) Photographs of glass vials containing 0.20 g of OTFE particles and 3.0 mL of a mixture of silicone oil and ethyl benzoate at different mole fractions of ethyl benzoate (X_{eb} , given). θ^y values for the oil mixtures are also given. a) The vials just after gentle agitation (before aeration). At $X_{eb} \leq 0.7$ ($\theta^y < 46^\circ$), OTFE particles are wetted by oils and sediment to the bottom, whereas the particles are non-wetted by oils at $X_{eb} \geq 0.75$ ($\theta^y > 46^\circ$). b) The vials 4 months after aeration by hand shaking. No foams are made for pure oils, but particle stabilized non-aqueous foams are formed for the oil mixtures. Reproduced from [18] with permission from Wiley.

[17], but it does not flow and the application of shear causes the rupture of the droplets and the release of liquid. The cosine of the contact angles (advancing and receding) increase linearly with a decrease of $\gamma_{liquid/air}$ confirming the relation established by Fox and Zisman (Fig. 3). Oil foams are obtained for $\cos(\theta)$ below 0.8 (i.e. θ above 40°).

Therefore, the wetting behavior of OTFE and PTFE particles significantly depends on the surface tension of the oils. The appropriate oil or oil mixtures need to be chosen in order to adjust the surface activity of such particles at the liquid–air surface to obtain oil foams. As already pointed out, in the case of particle-stabilized aqueous foams, it is the hydrophobicity of the particles themselves which is varied by either chemisorbed or physisorbed molecules and not the liquid phase [22,23].

2.2. Effect of particle surface chemistry on contact angle

The second approach studied in the literature to modify the contact angle was the modification of the particle surface chemistry in the same way than for aqueous foams.

The first study was done by Binks et al. on fluoro-coated fumed silica particles. They varied the extent of fluoro-modification to establish a link between contact angle and degree of fluorination [24]. Three degrees of fluorination have been studied: low amount of fluorine content (75% SiOH), intermediate (59% SiOH) and high content (50% SiOH). The surface energy of particles decreases upon increasing the degree of fluorination. By plotting $\cos \theta$ as a function of $\gamma_{liquid/air}$ for particles with different degrees of fluorination a nonlinear dependence can be observed in which $\cos \theta$ is more or less constant at high value over a range of values of $\gamma_{liquid/air}$ (Fig. 4). For all particles, a transition between wetted and non-wetted state occurs abruptly at a surface tension depending on the degree of fluorination. For particles with the lowest amount of fluorine (75% SiOH), the transition occurs at a surface tension around $65 \text{ mN} \cdot \text{m}^{-1}$. For particles with intermediate fluorine content (59% SiOH), this transition occurs at a lower surface tension around $33 \text{ mN} \cdot \text{m}^{-1}$. For particles with the highest fluorine content (50% SiOH), the transition occurs for surface tension around $28 \text{ mN} \cdot \text{m}^{-1}$. These particles are oleophobic to many oils and only oils of low surface tension ($< 28 \text{ mN} \cdot \text{m}^{-1}$) can lead to a complete wetting of those particles. Oil foams can be obtained both in systems of oils of high surface

tension ($> 32 \text{ mN} \cdot \text{m}^{-1}$) and particles of intermediate fluorine content (59% SiOH) and with oil of low surface tension ($< 28 \text{ mN} \cdot \text{m}^{-1}$) and particles of high fluorine content (50% SiOH). Oil foams can then be easily produced by choosing the appropriate fluorine content of the particles

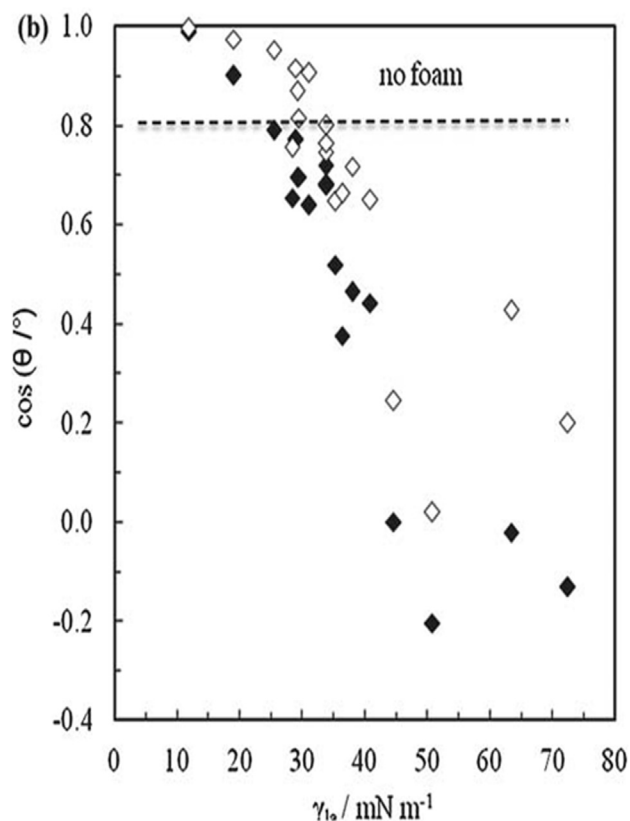


Fig. 3. Cosine of (◆) advancing and (◇) receding contact angle θ of liquid in air on a compressed powder tablet of Zonyl MP1100 particles as a function of the liquid surface tension. Reproduced from [21] by permission of the Royal Society of Chemistry.

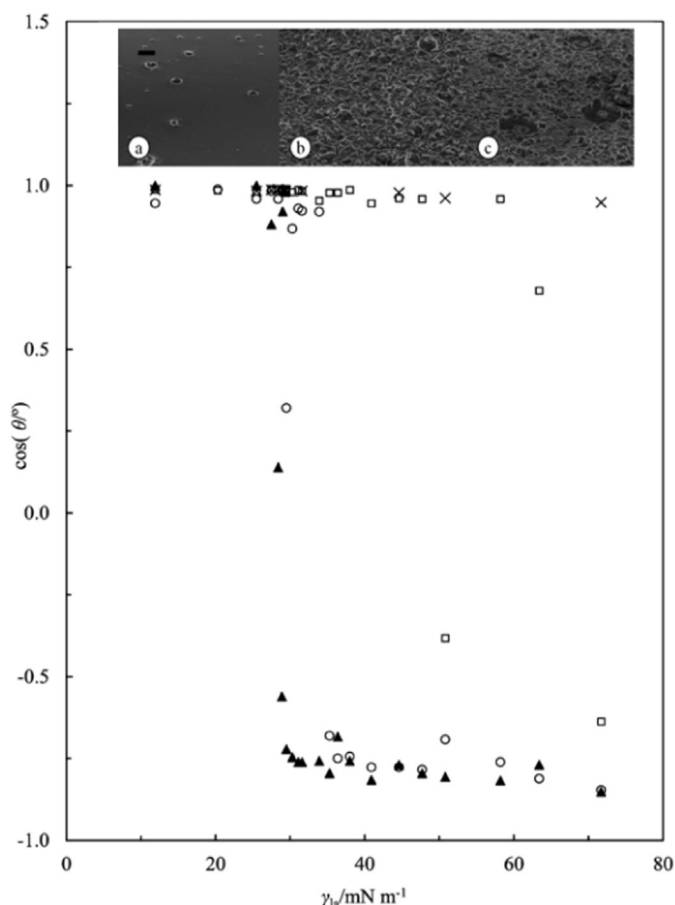


Fig. 4. Cosine of advancing contact angle (measured through the liquid) of 0.1 cm³ of various liquids in air on glass slides spin coated with 100% SiOH silica (x), 75% SiOH fluorosilica (□), 59% SiOH fluorosilica (○) and 50% SiOH fluorosilica (▲) particles as a function of the surface tension of the liquid at 20 °C. Inset: SEM images of particle coated slides for (a) 75% SiOH, (b) 59% SiOH and (c) 50% SiOH fluorosilica particles; scale bar = 200 μm. Reproduced from [24] by permission of the Royal Society of Chemistry.

and the oil in order to obtain contact angle suitable for oil foam production. The same conclusions have been obtained for other kinds of fluorinated particles [25,26], for silica particles coated to different extents with dichlorodimethylsilane instead of perfluoro-alkoxysilane and for TiO₂-based particles coated to different extents with fluoroalkylsilane (Table 1) [25,27].

The formation of oil foams thus depends on both the surface tension of the oil and the surface energy of the particles which control their degree of wetting. The surface energy of the particle can be tuned by modifying the particles surface chemistry.

2.3. Characteristics of non-aqueous foams obtained from solid particles

In non-aqueous foams stabilized by solid particles, non-spherical bubbles are observed (Fig. 5). The presence of non-spherical bubbles is consistent with a dense, rigid layer of jammed particles preventing relaxation to a spherical shape. Bubbles surface are also textured as a result of packing of irregularly shaped particles. The presence of an irreversibly adsorbed layer of particles at the bubble surfaces acts as a physical barrier against coalescence and coarsening [21]. The resulting foams are ultrastable since the foam volume remains constant during months. In some cases, the oil phase drains and the bubbles slowly cream upwards. Although their volume fraction increases, they remain stable to coarsening and coalescence due to the particles layer. This behavior is similar to particle-stabilized aqueous foams in which the close-packed particle layer also acts as a physical barrier to these destabilization mechanisms. However, some oil foams are not such stable and the foam collapse slowly during days. The collapse of these foams comes from the progressive wetting of the particles by the oil which desorb from bubble surfaces [26].

In terms of foamability, the concentration of particles is obviously an important parameter. In the case of PTFE particles, Binks et al. have shown that the foamability increases progressively with particles concentration since a larger area of air-oil surface can be covered and stabilized [21]. Moreover, the foamability has been shown to not only depend on the particles concentration but also on the initial aggregation state in the case of fluoro-coated fumed silica particles [24]. If the aggregates are broken into smaller aggregates by ultrasound to disperse them inside the liquid before foam production, no more oil foams can be produced and viscous dispersions are obtained. This phenomenon comes from the formation of a three-dimensional network of particles in the liquid oil due to the formation of siloxane bond between free silanol groups on adjacent aggregates. However, when the particles powder and liquid are hand-shaked to produce oil foams, the aggregates are bigger and attach directly to the air bubbles before entering to the continuous phase preventing the formation of siloxane bond between aggregates. The viscosity of oil is another important parameter modifying the foamability. During foam formation, the oil viscosity can act to retard oil drainage from oil films between bubbles and reduce the frequency of coalescence between bubbles that are not or only partially coated by particles [18]. However, when the oil is very viscous and the method to produce foam is a low energy method such as hand-shaking, the oil viscosity may also prevent bubble formation. All these results highlight that the production of oil foams stabilized by particles is sensitive to the gas incorporation process.

An interesting process to obtain oil foam is to induce a catastrophic phase inversion from dry oil powders similarly to catastrophic phase inversion occurring in aqueous systems for dry water [25,26]. This catastrophic phase inversion is driven by the oil/particle ratio. When the oil content increases at a fixed mass of particles, the size of oil droplets or their number can increase and the amount of non-adsorbed particles

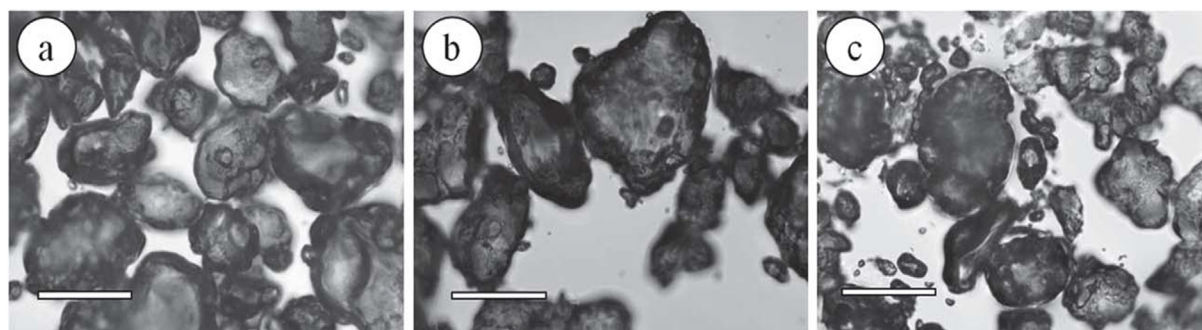


Fig. 5. Optical microscopy images of foams stabilized by 0.5 wt% of fluorosilica particles (59% SiOH) in three solvents. (a) a-Hexylcinnamaldehyde, (b) eugenol and (c) benzyl acetate. Scale bar = 100 μm. Reproduced from [25] by permission of the Royal Society of Chemistry.

decreases. Above the critical oil/particle ratio (COPR), the amount of particles to stabilize the total area of oil droplet surfaces is not sufficient: the dry powder is metastable and upon gentle shaking it converts to oil foam. The COPR depends on both the particle and the surface tension of oil (Fig. 6). For example, COPR increases with an increase in the degree of fluorination on clay platelet particles [24].

3. Non-aqueous foams stabilized by crystalline particles

In the 1970's, Sanders et al. demonstrated that certain types of hydrocarbon surfactant with specific functional groups (i.e. alcohols, glycols, soaps, acids, amines) in mineral oil could lead to non-aqueous foam formation [2,29]. For example, mineral oil foams can be stabilized by ethoxylated stearyl alcohol or polyethylene based surfactants. It was one of the first papers highlighting that the solubility of the surfactant in the oil phase seems to be the critical parameter to produce oil foams. In the 1980's, Friberg et al. reinforced this hypothesis by studying xylene foams stabilized by triethanolammonium oleate surfactant [2]. No foam was produced when the surfactant formed an isotropic liquid phase, but foams were produced in the region where the surfactant became insoluble and formed crystalline particles. In the same years, Ross and coworkers demonstrated the importance of the solubility phase limit of the added foam stabilizer to produce oil foams from lubricating oils [2]. They showed that foamability and foam stability dramatically increased close to the condition where the foam stabilizer becomes insoluble. This condition is likely to maximize the tendency of the foam stabilizer to adsorb at the oil-air surface and therefore promote the foam formation. The same conclusion was obtained for poly(decene) oil with low molar mass and polymeric surfactants [14]. Based on this concept, oil foams have been designed recently from various crystalline particles (Table 2). Two factors are important in terms of solubility: the solvent properties (oil) and the molecular structure of the foam stabilizer.

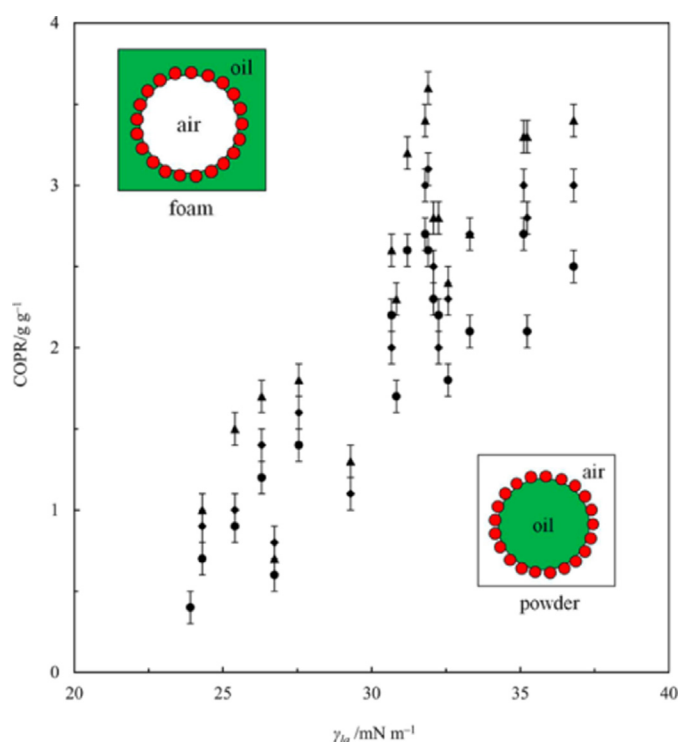


Fig. 6. Variation of COPR with γ_{la} of the oils for PFX-10 ZnO (TP) (●), PF-10 Eight Pearl 300S-Al (▲), and PF-10 FSE-Al (◆). Inset: schematic illustration of dry oil powder below COPR and air-in-oil foam above COPR. For simplicity, the particles, oil droplets, and air bubbles are spherical. Reprinted with permission from [26]. Copyright 2015 American Chemical Society.

3.1. Formation of crystalline particles: the importance of solubility boundary

The solubility of a chemical substance depends on the physical and chemical properties of both the solute and solvent, of the balance of intermolecular forces between solvent and solute molecules, as well as on temperature and pressure. A chemical substance that has high solubility will lead to strong solute-solvent interactions, hence promoting dissolution. Conversely, chemical substance that has a low solubility has weak solute-solvent interactions (as solute-solute interactions are favored, self-aggregation is obtained). For an ideal solution, the variation of solubility as a function of the temperature is given by Eq. (2):

$$\ln x = \frac{\Delta_{fus}H}{R} \left(\frac{1}{T_f} - \frac{1}{T} \right) \quad (2)$$

where x is the mole fraction of solute in the saturated solution at absolute temperature T , R is the gas constant, $\Delta_{fus}H$ is the enthalpy of fusion and T_f is the temperature of fusion.

Binks et al. used this equation to calculate the concentration dependence of the myristic acid solubility temperature in high oleic sunflower oil, to better understand the foaming properties of this system (Fig. 7) [11].

The solubility of a substance in a given solvent is measured by the saturation concentration, which corresponds to the concentration at which the addition of more solute does not increase the molecular concentration in solution, while the excess of solute begins to self-assemble. First, the compound such as myristic acid must be dissolved in the solvent (for example high oleic sunflower oil) by heating the mixture. Upon a fast enough cooling, the solution becomes supersaturated. Accompanying the supersaturation is the crystals formation, occurring by nucleation and growth. Above certain concentration of crystals, the critical gelation concentration can be reached leading to the formation of a gel, called 'organogel' (and 'oleogel' is the solvent is an oil). The crystalline particles melt upon heating above the solubility boundary leading to a gel-sol transition. For example, for the myristic acid in high oleic sunflower oil system, by cooling the molecular solution below the solubility boundary the formation of plate-like crystals occurs [11]. To produce oil foams from these systems, the appropriate concentration of myristic acid needs to be well chosen. Above the solubility boundary,

Table 2
Summary of works on non-aqueous foams obtained from crystalline particles.

Non-aqueous systems	Crystals particle	References
Liquid paraffin, squalane and squalene	Monoglycerol fatty acid ester (glycerol α -monooctanoate, glycerol α -monodecanoate and glycerol α -monododecanoate)	[30]
Liquid paraffin, squalane, squalene and glycerol tris (ethylhexanoic) ester	Diglycerol fatty acid ester (diglycerol monolaurate and diglycerol monomyristate)	[31]
Olive oil	Diglycerol fatty acid ester (diglycerol monolaurate)	[32]
Olive oil	Diglycerol fatty acid ester (diglycerol monomyristate)	[33]
Rapeseed oil	Lamemul®K200K (mixture of mono and diglycerides)	[34]
Sunflower oil	Fatty alcohols (1-tetradecanol, 1-hexadecanol and 1-octadecanol)	[35]
9 vegetable oils (High oleic sunflower oil, rapeseed oil, coconut oil, soybean oil, corn oil, olive oil, peanut oil, cottonseed oil and sesame oil)	Myristic acid	[11]
Salad oil (mixture of soybean and rapeseed oil)	Fully hydrogenated rapeseed oil rich in behenic acid	[12]
Rapeseed oil	Sucrose ester and sunflower lecithin	[36]

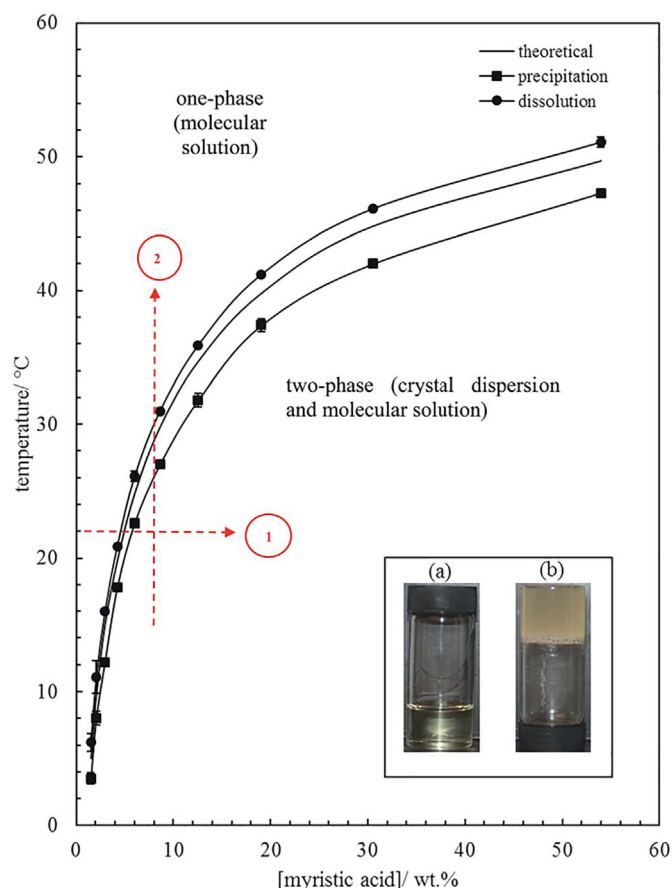


Fig. 7. Variation of the myristic acid solubility in high oleic sunflower oil with temperature, with points obtained from cooling at $0.1\text{ °C}\cdot\text{min}^{-1}$ (squares) and heating at $0.1\text{ °C}\cdot\text{min}^{-1}$ (circles). The full line without points is calculated using Eq. (2). Inset: photographs of (a) oil solution, upright at 40 °C , and (b) oil gel, inverted at 22 °C , for 10 wt\% myristic acid. Reproduced from [11] by permission of the Royal Society of Chemistry.

no foams can be produced from the molecular solution, while below this threshold foams can be obtained. The determination of the solubility boundary is the main parameter to determine for these systems before studying the foaming properties. The Differential Scanning Calorimetry (DSC) is a useful technique to determine both the temperature at which the crystals begin to melt and the temperature at which this melting process is over [35]. The solubility limit can be approximated in these systems as the temperature at which the melting is finished.

3.2. Formation of non-aqueous foams from crystalline particles

The foamability and foam stability depend on the size, shape and concentration of the crystals; these parameters are linked to both the properties of solvent and the molecular structure of the foam stabilizer. Crystalline particles from various systems have been used to obtain non-aqueous foams: mono or diglycerol fatty ester [30–33,37], mixture of mono and diglycerides [34], fatty alcohol [35], fatty acid [11] or sucrose ester and sunflower lecithin [36] (Table 2). Myristic acid and fatty alcohols crystallize into two-dimensional plate-like crystals [11, 35]. Triacylglycerols form three-dimensional spherulitic crystals [12]. The size and polymorphs (α , β and β') of triacylglycerol are linked to the crystallization process.

Non-aqueous foams stabilized by crystals particles have been obtained by two different foaming techniques. The first one used by Shrestha and coworkers in all their studies is the foaming through phase transition [30–33]. They used liquid petroleum gas (LPG), which is easily available and commonly used for hair care cosmetics or shaving

foams. LPG can be liquefying under pressure at ambient temperature. In their studies, LPG was partially soluble in the chosen hydrocarbon oil. LPG is dissolved under high pressure and then released to create the bubbles in the oil phase. In this foaming device, the solution containing oil and crystals is poured in an air-tight bottle fitted with a nozzle and then the LPG is added into this solution. The LPG content is around 20 wt\% in total. Before foaming, the mixture is shaken and the gas is released through the nozzle. For some systems at high concentration, the solubility boundary is above 25 °C , so crystals particles are present inside the bottle at high amount leading to the formation of a gel network, which is difficult to release through the nozzle. Thus, to avoid the formation of gel, it is important to adjust the temperature closer to the solubility boundary before foaming with this technique.

The second foaming technique is the highly popular foaming device based on air entrainment and systematic bubble-breakup under shear: the kitchen blender. In this foaming technique, air is entrained at the free surface of the blended liquid, which creates large bubbles, which are then broken under the continuous shearing action of the blender [38]. A gradual increase of the gas fraction and a decrease of the average bubble size are observed over time. At the macroscopic scale, the oil foam becomes white and solid-like. This process happens until an equilibrium state is reached and the gas fraction and the bubble size cannot be changed anymore by the beating device. The characteristic gas fraction and bubble size of a foaming solution depend both on the rheological properties of the liquid and the beating speed [38]. The reader can keep in mind: the higher the viscosity of the foaming liquid, the smaller the bubble sizes and the lower the gas fraction which can be obtained. Various kitchen mixers have been used to produce oil foams with whisk of different size and at different beating speed. The main difference between all these studies is the temperature at which the foam is produced. Foams can be produced directly at room temperature from the crystalline particles dispersion [11,34] or during the crystallization process induced by decreasing the temperature below the solubility boundary during shearing [35].

Whatever the foaming process, foam formation is only possible when crystals are present in solution that is to say below the solubility boundary. In these oil foams obtained from crystalline particles, most of the bubbles are non-spherical and possess textured surfaces (Fig. 8a). Each foam bubble is covered by adsorbed crystalline particles which prevent the relaxation of the bubble to a spherical shape. This non-spherical bubble shape is similar to the one previously described in the case of oil foams stabilized by solid particles. The crystals can be clearly observed on the bubbles surface by using microscopy techniques. As previously described for solid particles, if crystalline particles are wetted completely by the oil phase, the contact angle measured through the oil phase is 0° . Binks et al. have measured the contact angle through the high oleic sunflower oil by using discs of compressed myristic acid powder [11]. The contact angle is around 40° and consistent with the adsorption of myristic acid crystals to the air bubble surfaces in oil (Fig. 1).

Mishima and coworkers have recently used synchrotron radiation microbeam X-ray diffraction to study salad oil foams stabilized by triacylglycerols crystals (fully hydrogenated rapeseed oil rich in behenic acid) [12]. They demonstrated that the lamellar planes of the crystals near the air-oil surface are arranged almost parallel to the surface. It means that the lamellar planes composed of methyl end groups are facing the air phase, whereas the lateral planes composed of glycerol groups are connected to each other through the crystals adsorbed at the air-oil surface. The same hypothesis can be done for fatty acid and fatty alcohol plate-like crystals. It is supposed that the faces expose methyl groups which are in contact with air, whereas the edges expose mainly methylene and carboxylic or hydroxyl groups interacting with each other through these groups within the air-oil surface [11]. This elegant hypothesis still needs to be more precisely confirmed.

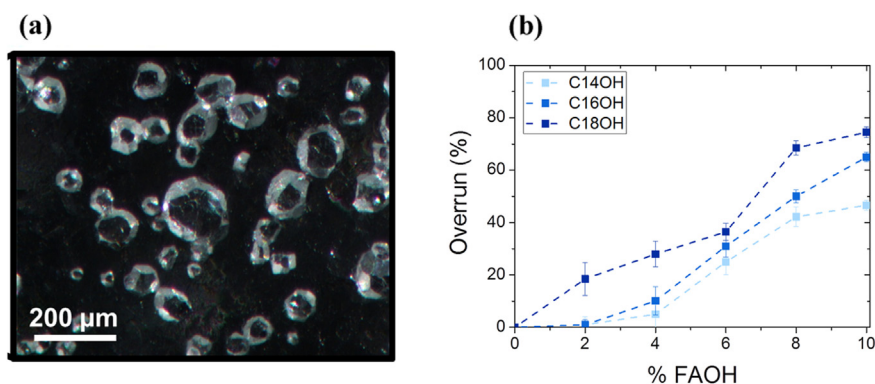


Fig. 8. (a) Micrographs of foams taken 1 min after foam formation from an oleogel containing 10 wt% 1-octadecanol in sunflower oil under polarized light. Foam bubbles are stabilized by the fatty alcohol particles, which adsorb to the bubble surface, leading to the formation of non-spherical bubbles with textured surfaces. (b) Foam overrun for samples produced from sunflower oil and containing 1-tetradecanol (C14OH), 1-hexadecanol (C16OH) and 1-octadecanol (C18OH) as a function of FAOH concentration. Reprinted with permission from [35]. Copyright 2015 American Chemical Society.

3.3. Foaming efficiency of crystalline particles systems

By comparing results described in the literature, we observe that the maximal gas volume fraction is around 55% whatever the nature of the crystals and the concentration. This value is close to the random close packing fraction of monodisperse spheres (64%) above which randomly distributed spheres are compressed against each other due to packing constraints. These observations show that air bubbles stabilized by crystalline particles, when forced to be in close contact at high volume fractions, likely coalesce or are expelled from the foam. We can point out the difference with aqueous foams for which the maximal air fraction can be higher than 99%. This relatively low value of the maximal air fraction is a specific feature of these non-aqueous foams based on crystalline particles.

In all the studies, it has been shown that the foamability of the system increases until reaching the maximum overrun by increasing the concentration of the component which crystallizes. The foam overrun is defined by Eq. (3):

$$\text{Overrun (\%)} = \left[\frac{V_t - V_0}{V_0} \right] * 100 \quad (3)$$

with V_t the volume of foam after a time t and V_0 the initial volume of oil.

The increase of the concentration of the component which crystallizes has two effects. It leads to an increase of both the boundary solubility temperature and of particles concentration below the boundary solubility. For example, at 20 °C below the solubility boundary in 1-octadecanol fatty alcohol in sunflower oil system, the overrun increases from 20% at 2 wt% to 75% for 10 wt% (Fig. 8b) [35,39]. Below the solubility boundary, the foamability increases by increasing the crystalline particles amount in the system since a larger area of air-oil surface can be stabilized. The same conclusions have been obtained for various systems. The reader needs also to keep in mind that the increase the crystalline particles concentration in such systems can lead to the formation of an oleogel, which is highly viscoelastic since large amounts of liquid oil are immobilized by the presence of crystalline particles. The rheological properties of the oleogel have therefore a great importance on the foam formation, but this specific point still needs to be studied.

For a fixed concentration, the temperature at which the foam is formed is another crucial parameter in the foamability of these systems. For example, in the case of 8 wt% myristic acid dispersed in high oleic sunflower oil, the foam volume decreases by increasing the temperature from 20 to 35 °C (Fig. 9) [11]. At 20 °C and for 8 wt% myristic acid, the system is below the solubility boundary leading to the presence of crystalline particles, which stabilize the

air bubbles to reach an air fraction of 50% (Fig. 7). Above 25 °C, the solubility boundary is crossed and the crystalline particles amount decreases due to progressive crystals melting. At 30 °C, the gas volume fraction is around 20%. From 35 °C, above the solubility boundary, no crystalline particles are present in the system to stabilize the air bubbles; it is only a molecular solution. As expected, no foam can be produced. This foamability decrease is linked directly to the solubility boundary of the system.

From the current state-of-art, the two main parameters tuning the foaming efficiency (or foamability) in these systems linked to the solubility limit are: the concentration of crystalline particles and the temperature at which the foam is produced. Foamability can be tuned either by modifying the particles concentration at a fixed temperature or producing the foam at different temperatures at a fixed particles concentration. Mishima et al. have recently produced oil foams based on fully hydrogenated rapeseed oil rich in behenic acid (triacylglycerol) in salad oil [12]. They modified the crystallization and tempering process in order to change the size and polymorphs of triacylglycerols crystals. They have shown that the overrun is modified by the tempering process, highlighting the influence of crystals size and morphology. Nevertheless, more studies are still needed to better understand how the crystal shape and size modify the foamability.

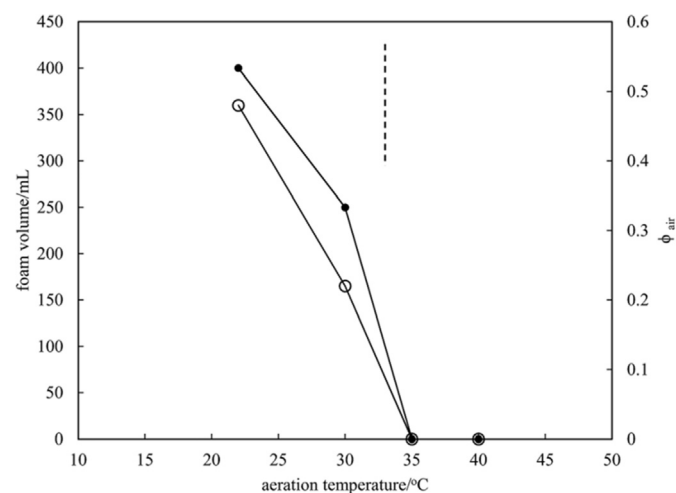


Fig. 9. Variation of foam volume produced (filled points) and volume fraction of air in foam (unfilled points) versus aeration temperature for 8 wt% myristic acid in high oleic sunflower oil. Mixtures originate from the crystalline dispersion to the left of the dashed line and from the molecular solution to the right of it. Reproduced from [11] by permission of the Royal Society of Chemistry.

3.4. Foam stability based on crystalline particles systems

The oil foam evolution in time depends on the same three main mechanisms of foam destabilization as for aqueous foams: drainage, coarsening and coalescence. In these oil foam systems, the interfaces are covered by a dense layer of irreversibly adsorbed crystals around the bubbles that considerably reduces gas permeability and coalescence. Moreover, the fraction of non-adsorbed crystals, which increases with crystals concentration, serve to strengthen the gel network in the continuous oil phase. When the excess of crystalline particles in the continuous oil phase forms a network, an oleogel is created which prevents buoyancy-driven creaming of air bubbles within the foam [11]. The oil drainage is directly linked to the rheological properties of the continuous phase, which depend on the crystals network. The ultrastable oil foams are indeed in a gelled state since no flow is observed when the foam is turned upside down (Fig. 10). Foams behave like a strong gel as shown by rheological measurements [35]. They sustain their own weight without any apparent deformation. These non-aqueous foams are resistant to the three instability mechanisms due to the combination of solid crystals at air bubbles surfaces and gelling of the continuous oil phase. These ultrastable characteristic has been emphasized by Brun and coworkers who studied the shear resistance of oil foams by processing them in a Couette cell, at a shear rate of 1000 s^{-1} [34]. The foams are not destabilized by the applied shear, the air fraction remains the same and the bubble size is decreased by a factor two.

For the oil foams stabilized by crystalline particles, the literature shows that there is a link between foam stability and crystalline particles concentration at a fixed temperature: the higher the crystalline particles concentration, the higher the foam stability. For example, in the case of foams generated in diglycerol mono-myristate/olive oil at $25\text{ }^{\circ}\text{C}$, with 1 wt% of surfactant the foam is stable 1 h, but with 10 wt%

for months [33]. In the same way, foams obtained by myristic acid dispersed in high oleic sunflower oil have different stabilities as a function of the myristic acid concentration [11]. The foams stability has been followed at $22\text{ }^{\circ}\text{C}$ during months. After one day, for low myristic acid concentration ($<6\text{ wt}\%$), around 30% of the initial oil volume drains. For high myristic acid concentration ($>8\text{ wt}\%$), no oil drainage occurs and no signs of bubble coalescence or disproportionation is observed. The bubble size distribution remains constant. Some of the foams are stable during months without any sign of destabilization. These non-aqueous foams are ultrastable against drainage, coalescence and coarsening. This increase of foam stability by increasing the myristic acid concentration at a fixed temperature is again linked to the solubility boundary. For low myristic acid concentration ($<6\text{ wt}\%$), the solubility boundary is almost reached at $22\text{ }^{\circ}\text{C}$, temperature at which the foam is produced and kept. The foaming systems do not contain a large amount of crystalline particles to stabilize the foam, since a large amount of the crystals have melted to form the molecular solution. For high myristic acid concentration ($>8\text{ wt}\%$), the solubility boundary is much higher than $22\text{ }^{\circ}\text{C}$. A large quantity of crystals is therefore present to stabilize the foam.

Another example to illustrate the effect of the boundary solubility temperature on foam stability is to study the foam stability as a function of the temperature: far below the boundary solubility and close to it. The system containing 10 wt% of 1-tetradecanol in sunflower oil has a boundary solubility between 13.1 and $26.6\text{ }^{\circ}\text{C}$, which corresponds to the beginning and the end of crystals melting process determined by DSC (Fig. 11) [35]. For a foam produced from this system, at $10\text{ }^{\circ}\text{C}$ below the boundary solubility (no crystals melting), the foam is ultrastable, whereas at $20\text{ }^{\circ}\text{C}$ close to the solubility boundary, drainage occurs. Some of the crystals already melted and the crystals amount is not sufficient to avoid drainage. The foam is less stable.

Moreover, studies have shown that foam stability increases with monoglycerides chain length at a fixed concentration of monoglycerides and at fixed temperature. Foam stability at $25\text{ }^{\circ}\text{C}$ was on the order of minutes for systems stabilized by glycerol monocaprylin (11 carbons) and hours for systems stabilized by glycerol monocaprin (13 carbons) [30]. For glycerol monocaprylin, the solubility boundary was almost reached at $25\text{ }^{\circ}\text{C}$, whereas for glycerol monocaprin the solubility boundary was much higher than $25\text{ }^{\circ}\text{C}$. The amount of crystalline particles to stabilize the foam at $25\text{ }^{\circ}\text{C}$ is higher for glycerol monocaprin than monocaprylin leading to higher foam stability. The same conclusions have been obtained for oil foam stabilized by fatty alcohol crystals: the higher the fatty alcohol chain length, the higher the foam stability at a fixed temperature. As a conclusion, it turns out that the foam stability can be tuned from stable to unstable either by modifying the particles concentration at a fixed temperature or changing the foam temperature at a fixed particles concentration.

3.5. Towards responsive non-aqueous foams

Since the crystals form from the molecular solutions on cooling below the solubility boundary and melt upon heating above the solubility boundary, the oil foams stabilized by crystalline particles can then be considered as responsive and reversible to temperature changes [11, 35]. When ultrastable non-aqueous foams are stored at temperatures for which crystals melt, they completely collapse due to a combination of oil drainage and bubbles coalescence. No foam remains and only a clear molecular solution is present. Both the particles at the bubble surface as well as those located in the continuous oil phase melt leading to the rapid disappearance of air bubbles. As the melting of crystals particles is reversible, the foam stability can be easily alternated between high and low by tuning the temperature above or below the solubility boundary through multiple temperature cycles. For example, the Fig. 12 shows an oil foam produced from 10 wt% of 1-octadecanol in sunflower oil [35]. The temperature at which the crystals completely melt is $48.3\text{ }^{\circ}\text{C}$ and they form at $31.7\text{ }^{\circ}\text{C}$ as determined by DSC experiments.



Fig. 10. Photographs of foams taken 30 min after foam generation at $20\text{ }^{\circ}\text{C}$ below the solubility boundary of the system. Foam did not flow when the vial is inverted. Reprinted with permission from [35]. Copyright 2015 American Chemical Society.

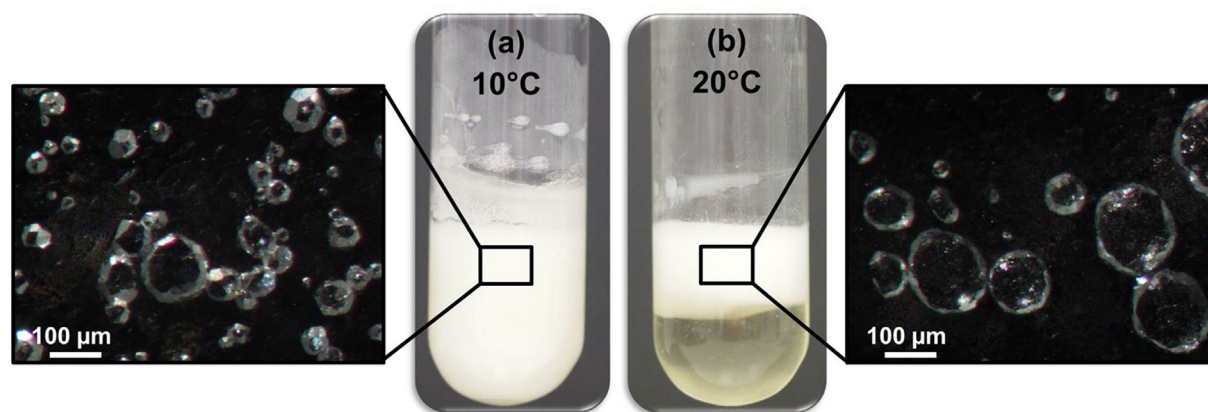


Fig. 11. Photographs of foams taken after two days at (a) 10 °C and (b) 20 °C from foams made using 10 wt% 1-tetradecanol in sunflower oil. The corresponding micrographs of the foams show that the particle layer at the interface was less dense in the sample stored at 20 °C than at 10 °C. In the system stored at 20 °C, the bubbles are also larger and appear more spherical. This shows that in the presence of fat crystals, the bubbles in the foam are arrested in a nonequilibrium shape. On the contrary, in a system containing the same concentration of fatty alcohol but with less lipid crystals due to partial melting, the bubbles are able to relax into a spherical shape. Reprinted with permission from [35]. Copyright 2015 American Chemical Society.

At 20 °C, the foam is stable since the temperature is below the solubility boundary. However, when temperature is increased to 50 °C (above the solubility boundary), the crystals begin to melt and the continuous phase between the bubbles shifted from a gel to a liquid state, leading to an onset in foam destabilization. By cooling the foam back to 20 °C, the destabilization process is halted and the foam becomes stable again due to the re-crystallization process both in the continuous phase and around the bubbles. By again increasing the temperature to 50 °C, foam destabilization mechanisms are reactivated and the foam completely collapses in few minutes. Same results have been obtained for other oil foam systems [11,34]. Moreover, an approach used for aqueous photo-thermo-responsive foams have been extended to develop non-aqueous photo-responsive foams [40]. The concept is based on the use of internal heat sources incorporated into the foam matrix to generate the heat. Carbon black particles have been used since they can absorb UV light and dissipate the adsorbed energy as heat. The advantage of using light as a stimulus instead of heating the foam externally is that light avoid the physical contact with the sample and can be directed at a precise location of interest with high resolution. The carbon black particles are entrapped inside the continuous oily phase. Without UV, the oil foams are ultrastable, but under UV illumination, the foam destabilization process begins and bubbles disappear [35]. Under UV illumination, the carbon black particles absorb the light and act as photothermal heat generators leading to a foam temperature increase above the solubility boundary. The crystals melt inside the foam leading to foam destabilization. By removing the UV light, the foam destabilization process is stopped. These non-aqueous foams based on crystalline particles can be responsive similarly to aqueous foams.

4. Perspectives and conclusion

Many examples of non-aqueous foams stabilized by solid and crystalline particles were reported recently in the literature. In non-aqueous foams, the physical properties of the non-aqueous liquid phase play an important role on their stability and formation, whatever the foam stabilizer used: solid or crystalline particles. The non-aqueous liquids can be crude oils, lubricants, vegetable oils, etc. All these liquids have different physical-properties such as: polarity, viscosity, density, conductivity, dielectric constant and Hansen solubility parameter values. For solid particles, the solvent modifies the contact angle and for soluble oil component which can crystallize, it modifies its solubility and drives the formation of crystalline particles.

To obtain oil foams from solid particles, they need to exhibit a suitable wettability in order to be adsorbed irreversibly at the oil-air interface. The wettability of the particles can be tuned by the surface tension of the non-aqueous liquid phase or by chemical modification of the particles surface. Then, the presence of an adsorbed layer of particles at the bubble surfaces acts as physical barrier against coalescence and coarsening, leading to ultrastable foams. However, the link between particles size and foamability is not so clear. The particles studied are aggregated and the size of the aggregates is modified as a function of the foaming process. Some factors such as the size, shape, concentration of the particles still need to be studied more deeply in order to perfectly control the foaming properties of these systems.

For crystalline particles in non-aqueous system, the main parameter governing their foaming properties is the solubility limit. Below the solubility limit, crystals are present and coat air bubbles reducing coarsening and coalescence. At high concentration, the non-adsorbed crystals

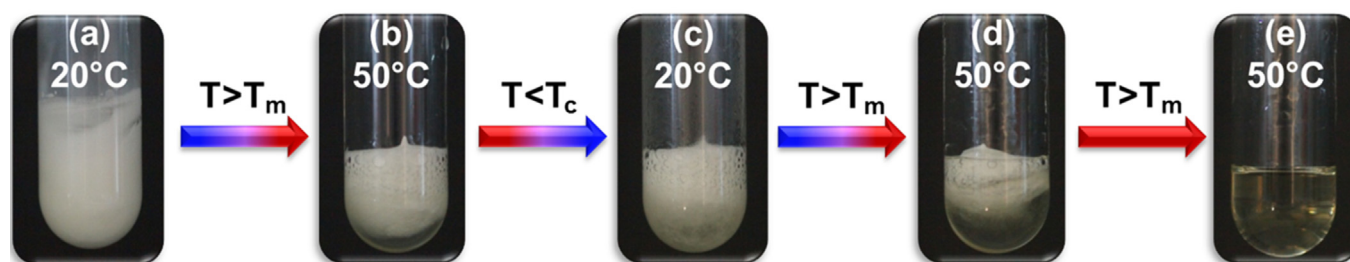


Fig. 12. Photographs showing the stabilization/destabilization phenomena with temperature for a foam produced from oleogel containing 10 wt% 1-octadecanol in sunflower oil. (a) Stable foam at 20 °C. (b) At 50 °C, foam destabilization started occurring in <1 min. (c) By decreasing the temperature back to 20 °C, the foam became stable again. (d) Upon increasing the temperature to 50 °C for a second time, the onset of foam destabilization could again be observed in <1 min. (e) After 2 min at 50 °C, the foam was completely destroyed. Reprinted with permission from [35]. Copyright 2015 American Chemical Society.

form an oleogel in the continuous oil phase reducing the oil drainage. Therefore, ultrastable non-aqueous foams which do not drain, coalesce or coarsen can be easily obtained from these systems below the solubility limit when enough crystals are present. The foaming properties may be tuned either by modifying the particles concentration at a fixed temperature or producing the foam at different temperatures at a fixed particles concentration. The foam stability can be easily tuned by temperature changes since the crystals stabilizing the foams are temperature-sensitive.

Many open questions remain on the foaming properties of these systems:

- 1/ What are the links between the foaming and rheological properties of the crystalline particles dispersions?
- 2/ What are the effects of the size, shape and polymorphic state of crystalline particles on the foam stability?
- 3/ Is it possible to form non-aqueous foams from all the organogel or oleogel systems described in the literature?
- 4/ How to achieve higher gas fraction? Can bubbles be compacted?
- 5/ What are the links between the rheological properties of the initial dispersions or oleogels and those of the produced foams?
- 6/ What are the rheological properties of these interfaces stabilized by adsorbed particles? And how this interfacial rheology can modify the foam properties?

Lastly, it is important to point out that a further understanding of the non-aqueous foams could be obtained by making connections with the stabilization mechanisms of Ramsden-Pickering emulsions. These systems are somehow similar, and the abundant literature about Ramsden-Pickering emulsion could be helpful and inspiring to answer the open questions on the foaming properties [41–46].

References

- [1] Cantat I, Cohen-Addad S, Elias F, Graner F, Höhler R, Pitois O, et al. *Foams: structure and dynamics*. OUP Oxford; 2013.
- [2] Pugh RJ. *Bubble and foam chemistry*. Cambridge University Press; 2016.
- [3] Golemanov K, Denkov N, Tcholakova S, Vethamuthu M, Lips A. Surfactant mixtures for control of bubble surface mobility in foam studies. *Langmuir* 2008;24:9956–61.
- [4] Fameau A-L, Salonen A. Effect of particles and aggregated structures on the foam stability and aging. *Comptes Rendus Physique* 2014;15:748–60.
- [5] Rio E, Drenckhan W, Salonen A, Langevin D. Unusually stable liquid foams. *Adv Colloid Interf Sci* 2014;205:74–86.
- [6] Fameau AL, Carl A, Saint-Jalmes A, Von Klitzing R. Responsive aqueous foams. *ChemPhysChem* 2015;16:66–75.
- [7] McBain M, Perry L. Type III surface tension curves with minimum in dilute solution in pure hydrocarbons. *J Am Chem Soc* 1940;62:989–91.
- [8] Callaghan I, Gould C, Hamilton R, Neustadter E. The relationship between the dilatational rheology and crude oil foam stability. I. Preliminary studies. *Colloids Surf* 1983;8:17–28.
- [9] Callaghan I, McKechnie A, Ray J, Wainwright J. Identification of crude oil components responsible for foaming. *Soc Pet Eng J* 1985;25:171–5.
- [10] Friberg SE. Foams from non-aqueous systems. *Curr Opin Colloid Interface Sci* 2010;15:359–64.
- [11] Binks BP, Garvey EJ, Vieira J. Whipped oil stabilised by surfactant crystals. *Chem Sci* 2016;7:2621–32.
- [12] Mishima S, Suzuki A, Sato K, Ueno S. Formation and microstructures of whipped oils composed of vegetable oils and high-melting fat crystals. *J Am Oil Chem Soc* 2016;93:1453–66.
- [13] Haedelt J, Beckett S, Niranjana K. Bubble-included chocolate: relating structure with sensory response. *J Food Sci* 2007;72 (E138–E42).
- [14] Binks B, Davies C, Fletcher P, Sharp E. Non-aqueous foams in lubricating oil systems. *Colloids Surf A Physicochem Eng Asp* 2010;360:198–204.
- [15] Blázquez C, Emond E, Schneider S, Dalmazzone C, Bergeron V. Non-aqueous and crude oil foams. *Oil Gas Sci Technol* 2014;69:467–79.
- [16] Binks BP. Particles as surfactants—similarities and differences. *Curr Opin Colloid Interface Sci* 2002;7:21–41.
- [17] Binks BP, Murakami R. Phase inversion of particle-stabilized materials from foams to dry water. *Nat Mater* 2006;5:865–9.
- [18] Murakami R, Bismarck A. Particle-stabilized materials: dry oils and (polymerized) non-aqueous foams. *Adv Funct Mater* 2010;20:732–7.
- [19] Fox H, Zisman W, et al. *J Colloid Sci* 1950;5:514–31.
- [20] Binks BP, Rocher A. Stabilisation of liquid–air surfaces by particles of low surface energy. *Phys Chem Chem Phys* 2010;12:9169–71.
- [21] Binks BP, Rocher A, Kirkland M. Oil foams stabilised solely by particles. *Soft Matter* 2011;7:1800–8.
- [22] Binks BP, Horozov TS. Aqueous foams stabilized solely by silica nanoparticles. *Angew Chem* 2005;117:3788–91.
- [23] Gonzenbach UT, Studart AR, Tervoort E, Gauckler LJ. Ultrastable particle-stabilized foams. *Angew Chem Int Ed* 2006;45:3526–30.
- [24] Binks BP, Tyowua AT. Influence of the degree of fluorination on the behaviour of silica particles at air–oil surfaces. *Soft Matter* 2013;9:834–45.
- [25] Binks BP, Sekine T, Tyowua AT. Dry oil powders and oil foams stabilised by fluorinated clay platelet particles. *Soft Matter* 2014;10:578–89.
- [26] Binks BP, Johnston SK, Sekine T, Tyowua AT. Particles at oil–air surfaces: powdered oil, liquid oil marbles, and oil foam. *ACS Appl Mater Interfaces* 2015;7:14328–37.
- [27] Dyab AK, Al-Haque HN. Particle-stabilised non-aqueous systems. *RSC Adv* 2013;3:13101–5.
- [28] Lai Y, Zhou H, Zhang Z, Tang Y, Ho JWC, Huang J, et al. Multifunctional TiO₂-based particles: the effect of fluorination degree and liquid surface tension on wetting behavior. *Part Part Syst Charact* 2015;32:355–63.
- [29] Sanders PA. Stabilization of aerosol emulsions and foams. *J Soc Cosmet Chem* 1970;21:377–91.
- [30] Shrestha LK, Aramaki K, Kato H, Takase Y, Kunieda H. Foaming properties of monoglycerol fatty acid esters in nonpolar oil systems. *Langmuir* 2006;22:8337–45.
- [31] Kunieda H, Shrestha LK, Acharya DP, Kato H, Takase Y, Gutiérrez JM. Super-stable nonaqueous foams in diglycerol fatty acid esters—non polar oil systems. *J Dispers Sci Technol* 2007;28:133–42.
- [32] Shrestha LK, Shrestha RG, Sharma SC, Aramaki K. Stabilization of nonaqueous foam with lamellar liquid crystal particles in diglycerol monolaurate/olive oil system. *J Colloid Interface Sci* 2008;328:172–9.
- [33] Shrestha RG, Shrestha LK, Solans C, Gonzalez C, Aramaki K. Nonaqueous foam with outstanding stability in diglycerol monomyristate/olive oil system. *Colloids Surf A Physicochem Eng Asp* 2010;353:157–65.
- [34] Brun M, Delamplé M, Harte E, Lecomte S, Leal-Calderon F. Stabilization of air bubbles in oil by surfactant crystals: a route to produce air-in-oil foams and air-in-oil-in-water emulsions. *Food Res Int* 2015;67:366–75.
- [35] Fameau A-L, Lam S, Arnould A, Cd Gaillard, Velev OD, Saint-Jalmes A. Smart non-aqueous foams from lipid-based oleogel. *Langmuir* 2015;31:13501–10.
- [36] Karp K. *Fabrication and characterization of arrested non-aqueous foam*. Lodz University of Technology; 2016.
- [37] Shrestha LK, Shrestha RG, Solans C, Aramaki K. Effect of water on foaming properties of diglycerol fatty acid ester-oil systems. *Langmuir* 2007;23:6918–26.
- [38] Drenckhan W, Saint-Jalmes A. The science of foaming. *Adv Colloid Interf Sci* 2015;222:228–59.
- [39] Marangoni AG. Organogels: an alternative edible oil-structuring method. *J Am Oil Chem Soc* 2012;89:749–80.
- [40] Fameau A-L, Lam S, Velev OD. Multi-stimuli responsive foams combining particles and self-assembling fatty acids. *Chem Sci* 2013;4:3874–81.
- [41] Schmitt V, Destribats M, Backov R. Colloidal particles as liquid dispersion stabilizer: pickering emulsions and materials thereof. *C R Phys* 2014;15:761–74.
- [42] Dickinson E. Food emulsions and foams: stabilization by particles. *Curr Opin Colloid Interface Sci* 2010;15:40–9.
- [43] Aveyard R, Binks BP, Clint JH. Emulsions stabilised solely by colloidal particles. *Adv Colloid Interf Sci* 2003;100:503–46.
- [44] Rousseau D. Trends in structuring edible emulsions with Pickering fat crystals. *Curr Opin Colloid Interface Sci* 2013;18:283–91.
- [45] Chevalier Y, Bolzinger M-A. Emulsions stabilized with solid nanoparticles: pickering emulsions. *Colloids Surf A Physicochem Eng Asp* 2013;439:23–34.
- [46] Lam S, Velikov KP, Velev OD. Pickering stabilization of foams and emulsions with particles of biological origin. *Curr Opin Colloid Interface Sci* 2014;19:490–500.