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 JOURNAL TITLE: International dairy journal
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 MUU CATALOG TITLE: INTERNATIONAL DAIRY JOURNAL / PUBLISHED IN ASSOCIATION WITH THE
 ARTICLE TITLE: ReviewColloidal aspects of ice cream?âââA review
 ARTICLE AUTHOR: H. Douglas Goff
 VOLUME: 7
 ISSUE: 6-7
 MONTH:
 YEAR: 1997
 PAGES: 363-373
 ISSN: 0958-6946
 OCLC #: 24603186
 CROSS REFERENCE ID: 133456
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Review

Colloidal Aspects of Ice Cream—A Review

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(Received 25 March 1997; accepted 4 July 1997)

ABSTRACT

Ice cream is a complex food colloid that consists of air bubbles, fat globules, ice crystals and an unfrozen serum phase. Ice crystals and air bubbles are usually in the range of 20–50 μm . The air bubbles are usually partially coated with fat globules and the fat globules are coated with a protein/emulsifier layer. The serum phase consists of the sugars and high molecular weight polysaccharides in a freeze-concentrated solution. Various steps in the manufacturing process, including pasteurization, homogenization, ageing, freezing, and hardening, contribute to the development of this structure. Proteins and emulsifiers compete for interfacial space during the homogenization of the fat and the creation of the mix emulsion. Following homogenization, the emulsion is further affected by changes occurring during the ageing step, viz., crystallization of the fat and rearrangement of the fat globule membrane to the lowest free energy state. This emulsion then undergoes both whipping and ice crystal formation during the dynamic freezing process, which contributes to the development of the four main structural components of the frozen product: a discontinuous foam, a network of partially coalesced fat surrounding the air bubbles, ice crystals, and a continuous, freeze-concentrated, unfrozen aqueous solution. © 1997 Elsevier Science Ltd. All rights reserved

Keywords: colloid; ice cream; emulsion; foam; freezing

INTRODUCTION

A colloid is defined (Dickinson and Stainsby, 1982) as a system of discrete particles of size from 1 nm to 1 μm in a continuous phase. Thus, homogenized dairy emulsions such as ice cream mix are generally colloids containing fat droplets, which are coated with a protein-emulsifier layer, as the dispersed phase. Ice cream is a complex food colloid in that the mix emulsion is subsequently foamed, creating a dispersed phase of air bubbles, and is frozen, forming another dispersed phase of ice crystals. Air bubbles and ice crystals are usually in the range of 20 to 50 μm (Caldwell *et al.*, 1992). The serum phase consists of the unadsorbed casein micelles in suspension in a freeze-concentrated solution of sugars, unadsorbed whey proteins, salts and high molecular mass polysaccharides. In addition, the partially-crystalline fat phase at refrigerated temperatures undergoes partial coalescence during the concomitant whipping and freezing process, resulting in a network of agglomerated fat, which partially surrounds the air bubbles and gives rise to a solid-like structure (Kalab, 1985; Goff and Jordan, 1989; Boode and Walstra, 1993). Various steps in the manufacturing process, including pasteurization, homogenization, ageing, freezing and hardening, contribute to the development of this structure. This paper will review the contribution of the ingredients and the processing

sequence to the development of both the ice cream mix emulsion and the final, partially-coalesced emulsion and foam structure in ice cream. While ice phase formation and stability is equally as important to ice cream structure as emulsion and foam formation and stability, this paper will only briefly describe the contribution of ice crystals, as ice crystallization in ice cream was recently reviewed by Hartel (1996).

THE ICE CREAM MANUFACTURING PROCESS

Ingredients

Ice cream mix formulations identify the content of milkfat, milk solids-not-fat (msnf), sweeteners, stabilizers, emulsifiers and water that are desired (Table 1). Dairy and other ingredients used to supply these components are chosen on the basis of availability, cost

Table 1. A Typical Compositional Range for the Components Used in Ice Cream Mix Formulations.

Component	Range (%)
Milkfat	10–16
Milk Solids-not-fat	9–12
Sucrose	9–12
Corn Syrup Solids	4–6
Stabilizers/Emulsifiers	0–0.5
Total Solids	36–45
Water	55–64

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and expected quality. Fat derived from milk ingredients is in common use in North America and many other parts of the world, while fat derived from non-dairy sources is more common in the United Kingdom and parts of Europe (Berger, 1990). The triglycerides in milkfat have a wide melting range, 40° to -40°C (Walstra and Jenness, 1984). Consequently, at refrigeration temperatures there is always a combination of liquid and crystalline fat within the globule. The resulting solid: liquid ratio at freezer barrel temperatures is important for ice cream structure formation, as crystalline fat is required for partial coalescence (van Boekel and Walstra, 1981a.; Boode *et al.*, 1991). Thus, non-dairy fat sources must also be chosen to provide suitable solid fat content.

The msnf contain the lactose, casein micelles, whey proteins, minerals (ash), vitamins, acids, enzymes, and gases of the milk or milk products from which they were derived. Proteins contribute much to the development of structure in ice cream, including emulsification, whipping, and water holding capacity (Halling, 1981; Phillips, 1981; Kinsella, 1984; Anderson *et al.*, 1987). Emulsification properties of proteins in the mix arise from their adsorption to fat globules at the time of homogenization (Goff *et al.*, 1989). Whipping properties of proteins in ice cream contribute to the formation of the initial air bubbles in the mix (Halling, 1981; Brooker, 1985). The water holding capacity of proteins leads to enhanced viscosity in the mix (Kinsella, 1984), which imparts a beneficial body to the ice cream, increases the meltdown time of ice cream and contributes to reduced iciness (Goff *et al.*, 1989).

Ice cream stabilizers are a group of ingredients (usually polysaccharides such as guar, locust bean gum, carboxymethyl cellulose, xanthan, etc.) commonly used in ice cream formulations. The primary purposes for using stabilizers in ice cream are to produce smoothness in body and texture, retard or reduce ice and lactose crystal growth during storage (or mask the effects of crystal growth), especially during periods of temperature fluctuation, known as heat shock, and to provide uniformity to the product and resistance to melting (Muhr and Blanshard, 1983). The mechanism of action of stabilizers in enhancing frozen stability is related primarily to their effect on the ice and unfrozen serum phases (Muhr and Blanshard, 1986; Muhr *et al.*, 1986). Stabilized ice cream has been observed by electron microscopy techniques to have smaller ice crystals than unstabilized ice cream both before and after storage at fluctuating temperatures (Caldwell *et al.*, 1992; Goff *et al.*, 1993). The control of iciness by stabilizers has been examined by several researchers (Harper and Shoemaker, 1983; Muhr and Blanshard, 1983.; Shirai *et al.*, 1985; Muhr *et al.*, 1986; Budiawan and Fennema, 1987a.; Buyong and Fennema, 1988; Goff *et al.*, 1993). While it was originally thought that stabilizers bind water, rendering it unfreezable and thereby exerting their stabilizing mechanism by reducing the quantity of ice present, recent research has failed to demonstrate this effect. The stabilizing effect of the polysaccharides presently appears to result from an alteration of the diffusion properties of water and solutes within the unfrozen phase following freeze-concentration (Levine and Slade, 1988a.; Sahagian and Goff, 1995).

Emulsifiers have been used in ice cream mix manufacture for many years (Knightly, 1959). They are sometimes integrated with the stabilizers in proprietary blends but their function and action is very different from the stabilizers. They are used to: improve whipping quality of the mix; produce a drier ice cream to facilitate molding, fancy extrusion and sandwich manufacture; provide smoother body and texture in the finished product; and produce a product with good stand-up properties and melt resistance (Goff, 1988). Egg yolk was formerly in common use as an ice cream emulsifier. However, emulsifiers used in ice cream manufacture today are of two main types: the mono- and di-glycerides and the sorbitan esters. Mono- and di-glycerides are derived from the controlled reesterification of hydrolyzed fats or fatty acids of animal or vegetable (important for certain religious or ethnic considerations) origin with an excess of glycerine. The sorbitan esters differ from the mono-glycerides in that the sorbitan esters have fatty acids esterified to a sorbitol molecule whereas the mono-glycerides have fatty acids esterified to a glycerol molecule. To make the sorbitan esters water soluble, polyoxyethylene groups are attached to the sorbitol. Thus polysorbate 80, the most common of these sorbitan esters in use in ice cream manufacture, is actually polyoxyethylene sorbitan monooleate. Polysorbate 80 is a very active drying agent in ice cream and is used in many commercial stabilizer/emulsifier blends (Goff, 1988; Marshall and Arbuckle, 1996).

Manufacture

Ice cream processing operations can be divided into two distinct stages, mix manufacture and freezing operations (Fig. 1). Ice cream mix manufacture consists of several unit operations: combination and blending of ingredients, batch or continuous pasteurization, homogenization, cooling, and mix ageing. Ingredients are usually preblended prior to pasteurization, regardless of the type of pasteurization system used. Pasteurization is designed for the destruction of pathogenic bacteria. In addition, its role in colloid development is to melt the fat for proper homogenization (Marshall and Arbuckle, 1996).

Homogenization is responsible for formation of the fat emulsion by forcing hot mix through a small orifice under moderate pressures (e.g. 15.5 to 18.9 MPa (2000–3000 psi), depending on mix composition and valve construction). In milk at 3.5% fat, homogenization reduces average fat globule diameter from 3.3 to 0.4 μm , decreases maximum diameter from 10.0 to 2.0 μm , increases surface area from 0.08 to 0.75 $\text{m}^2 \text{mL}^{-1}$, and increases the number of globules from 0.015 to 12 μm^{-3} (Walstra and Jenness, 1984). The actual mechanism of fat disruption within the homogenizer is thought to result from turbulence, cavitation, and velocity gradients (energy density) within the valve body (Pandolfe, 1982). The 8–10 fold increase in surface area of the fat globules is responsible in part for formation of the fat globule membrane, comprised of adsorbing materials attempting to lower the interfacial free energy of fat globules (Oortwijn *et al.*, 1977; Oortwijn and Walstra, 1979). With single stage homogenizers, fat globules

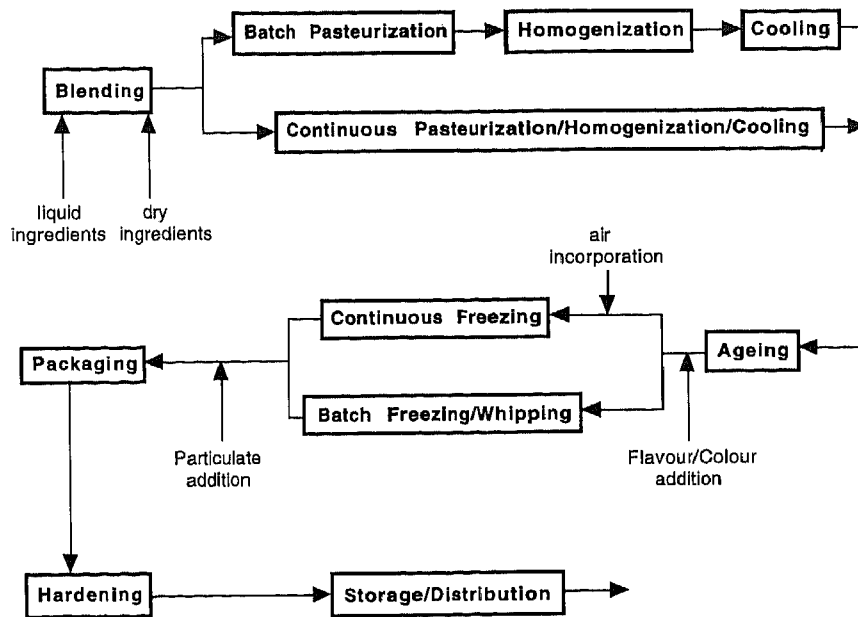


Fig. 1. A flow chart for the major unit operations involved in the manufacture of ice cream and the various ingredient inputs into the process.

tend to cluster as bare fat surfaces come together or adsorbed molecules are shared. Therefore, a second homogenizing valve is frequently placed immediately after the first with applied back pressures of 3.4 MPa (500 psi), allowing more time for surface adsorption to occur (Pandolfe, 1982). The net effects of homogenization are in the production of smaller, more uniform fat droplet size resulting in a greater stability of fat droplets during ageing, a better whipping ability and a smoother, more uniform final product. Homogenization also decreases the danger of churning the fat in the freezer and makes it possible to use products that could not otherwise be used, such as butter and frozen cream.

An ageing time of four hours or greater at 2–4°C is recommended following mix processing prior to freezing. This allows for hydration of milk proteins and stabilizers (some viscosity increase occurs during the ageing period), crystallization of the fat globules, and a membrane rearrangement, to produce a smoother texture and better quality product (Iversen and Pedersen, 1982). Non-aged mix exhibits a loose standup, is very wet at extrusion, and exhibits variable whipping abilities. The whipping qualities of the mix are usually improved with ageing.

Ice cream freezing also consists of two distinct stages: (1) passing mix through a swept-surface heat exchanger under high shear stress conditions to promote extensive ice crystal nucleation and air incorporation, and (2) freezing the packaged ice cream under conditions that continue to promote rapid freezing and small ice crystal sizes. The formation of the ice phase during this stage is also responsible for the creation of the unfrozen serum phase. As water freezes out of solution in pure form, the dissolved sugars, lactose, milk proteins, salts, and hydrocolloids are concentrated in a decreasing amount of water. Water and its dissolved components are referred to as the serum or matrix of the mix. Because the freezing point of the serum is a function of the concentration of dissolved solids, the

formation of more ice concentrates the serum and results in a decreasing freezing temperature for the remaining serum. Thus at temperatures several degrees below the initial freezing temperature, there is always an unfrozen phase present.

EMULSION FORMATION

Homogenization begins the process of fat structure formation. After preheating or pasteurization, the mix is at a temperature sufficient to have melted all the fat present, and the fat passes through one or two homogenizing valves, creating globules of 0.5 to 2.0 μm (Walstra and Oortwijn, 1982). Immediately following homogenization, the newly formed fat globule is practically devoid of any membranous material due to its tremendous increase in surface area and readily adsorbs amphiphilic molecules from solution (Darling and Butcher, 1978; Walstra and Oortwijn, 1982). The immediate environment supplies the surfactant molecules, which include caseins, casein micelles, undenatured or denatured whey proteins (depending on prior heat treatment), phospholipids, lipoprotein molecules, components of the original milkfat globule membrane, and any added chemical emulsifiers (Oortwijn and Walstra, 1979; Walstra, 1987; Berger, 1990). It is at this stage where manipulation of the membrane structure can occur, by homogenizing the fat in the presence of only the desired membrane components, as it has been shown in the past that different protein blends in ice cream mixes cause the emulsions to behave differently to subsequent partial coalescence (Goff *et al.*, 1989; Needs and Huitson, 1991). The action of the globular whey proteins needs to be differentiated from the action of micellar casein, which produces a much larger quantity of adsorbed material per surface area (Kinsella *et al.*, 1988).

The membrane formed at the time of homogenization continues to develop subsequent to

homogenization and rearrangement (including protein sloughing) occurs until the lowest possible surface free energy state is reached (Walstra and Jenness, 1984; Berger, 1990; Barfod *et al.*, 1991). The transit time through a homogenization valve is in the order of 10^{-5} to 10^{-6} s (Pandolfe, 1982). Protein adsorption occurs quickly, but unfolding and rearrangement at the interface may take minutes or even hours to be complete (Chen and Dickinson, 1993). In the absence of chemical emulsifiers, Gelin *et al.* (1994) reported that a fat globule membrane in homogenized ice cream mix was comprised of both caseins and whey proteins, with a greater portion of the total quantity of whey proteins in solution adsorbing to the surface than caseins. Considerable experimentation on competitive adsorption of milk proteins in simple emulsions and rearrangement of membranes post-formation has been reported in the literature (Dickinson *et al.*, 1988; Aynié *et al.*, 1992; Dickinson and Gelin, 1992; Chen and Dickinson, 1993; Fang and Dalgleish, 1993a; Hunt and Dalgleish, 1994).

Dickinson *et al.* (1988) showed from exchange experiments that β -casein rapidly displaced α_{s1} -casein from an emulsion droplet surface, but the reverse was true to a much lesser extent. Dickinson and Gelin (1992) reported that α_s -casein addition to a β -lactoglobulin-stabilized emulsion did not lead to any displacement of the globular protein from the interface. They also concluded that the adsorption of β -lactoglobulin at the interface was strongly dependent upon the species present during emulsion formation; if β -lactoglobulin was the emulsifying species, then its adsorption was highly irreversible. van Dam *et al.* (1995) showed a large increase in the surface coverage with the adsorption of casein micelles compared to caseinates, and the subsequent increased stability of the fat globules with adsorbed casein micelles when subjected to shear, indicating the importance of steric stabilization of the fat globule by the physical thickness associated with adsorbed micelles. Thus, when milkfat is homogenized in the presence of various milk proteins, adsorption results in a membrane that is somewhat stable to rearrangement by other proteins, and also provides sufficient emulsion stability to subsequent coalescence (Melsen and Walstra, 1989).

The added emulsifiers, however, contribute to the formation of a much different membrane. Their action is related to their effect on the surface of the fat globule. The emulsifier has been shown to have no effect on the size distribution of the globules in the mix, as determined by TEM micrographs (Goff *et al.*, 1987). Emulsifiers are not needed in an ice cream mix to stabilize the fat emulsion, due to an excess of protein and other amphiphilic molecules in solution (Govin and Leeder, 1971; Goff and Jordan, 1989). If surfactants such as polysorbate 80 or mono- and diglycerides are present prior to homogenization, they have the ability to lower the interfacial tension between the fat and the water phases lower than the proteins (Chen *et al.*, 1993). It has been reported that the adsorption of milk proteins to fat globules lowered the interfacial tension of the fat/serum interface from $8.26 \text{ dyne cm}^{-1}$ to 5.5 dyne cm^{-1} (Goff and Jordan,

1989). However, the addition of a surfactant (polysorbate 80) to the system lowered the interfacial tension further than was accomplished by the proteins alone, to $2.24 \text{ dyne cm}^{-1}$ in the presence of the milk protein (Goff and Jordan, 1989). Thus, the emulsifiers become preferentially adsorbed to the surface of the fat (Darling, 1982; Walstra and Jenness, 1984; Goff and Jordan, 1989; Barfod *et al.*, 1991; Gelin *et al.*, 1996).

It is likely that some quantity of protein is excluded from the membrane during homogenization, but also that emulsifiers cause subsequent protein desorption after homogenization, during the ageing step. Numerous studies on model emulsion systems have reported on the competitive adsorption between proteins and small-molecule surfactants during and after emulsion formation (Courthaudon and Dickinson, 1991; Courthaudon *et al.*, 1991; Fang and Dalgleish, 1993b; Euston *et al.*, 1995), with the main conclusion being that protein displacement occurs both during and after emulsion formation. It is known from practice that polysorbate 80 can be added subsequent to homogenization, causing proteins to desorb within minutes (Goff and Jordan, 1989). It has been reported that the quantity of adsorbed material in the absence of an emulsifier is approximately 16% of the total protein in the ice cream mix, and this decreases to $<8\%$ in the presence of the polysorbate 80, causing the actual membrane to become weaker to subsequent destabilization (Goff and Jordan, 1989). The extent of protein displacement from the membrane, and hence the extent of dryness achieved, is a function of the emulsifier concentration (Tomas *et al.*, 1994) and type of emulsifier used (Goff and Jordan, 1989).

On the fat surface, the fatty acid component of the emulsifier is likely in close contact with, perhaps even dissolved into, the bulk fat. The polar component resides at the surface. Protein molecules, particularly the casein micelles, are adsorbed mostly on the aqueous side of the membrane, with orientation of the hydrophobic regions at the interface. Protein molecules are considerably larger than the emulsifier molecules, especially the polar component, such that a membrane developed in the presence of emulsifier is very thin (Fig. 2), i.e. much lower quantity of adsorbed material per surface area, compared to a proteinaceous membrane in the absence of emulsifier (Fig. 3), which is more heavily dominated by casein micelles. Thus, the fat globules with adsorbed emulsifier membranes become much less stable to shear-induced partial coalescence. However, Dickinson *et al.* (1993) point out that subsequent instability to shear is not induced by the protein displacement *per se*, but by some change in the adsorbed layer properties caused by the replacement of a pure protein monolayer by a mixed protein/surfactant monolayer. Surface rheology no doubt plays an important role.

It is clear from the above discussion that the immediate membrane formed upon homogenization is a function of the micro-environment at the time of its creation, and that the recombined membrane of the fat globule in the aged mix is not fully developed until well into the ageing process (Berger, 1990). The appropriate ratio of solid:liquid fat must also be attained during ageing (Fig. 4), a function of temperature and the

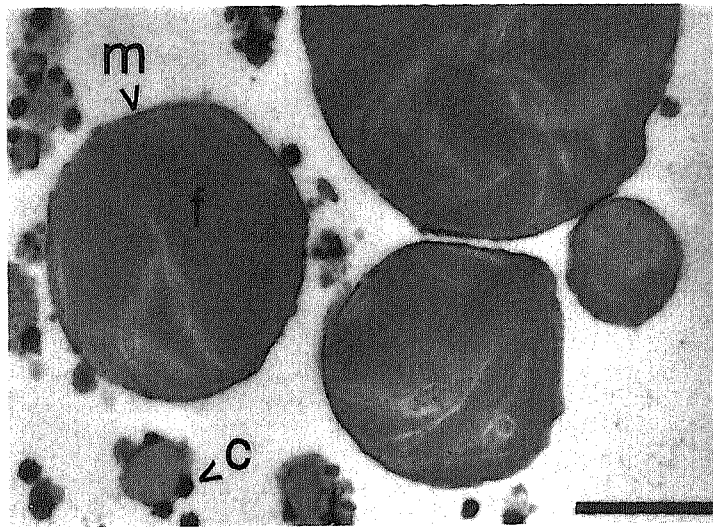


Fig. 2. Transmission electron micrograph of fat globules (f) from homogenized ice cream mix with 0.08% polysorbate 80 added. Membranes (m) are formed from a combination of original milk fat globule membrane fragments from homogenization, and adsorbed emulsifiers and other amphiphilic molecules from solution. Casein micelles (c) can also be seen, with the arrow pointing to a few adsorbed to the surface of the smaller fat globules (from Goff *et al.*, 1987). Bar = 1 μm .

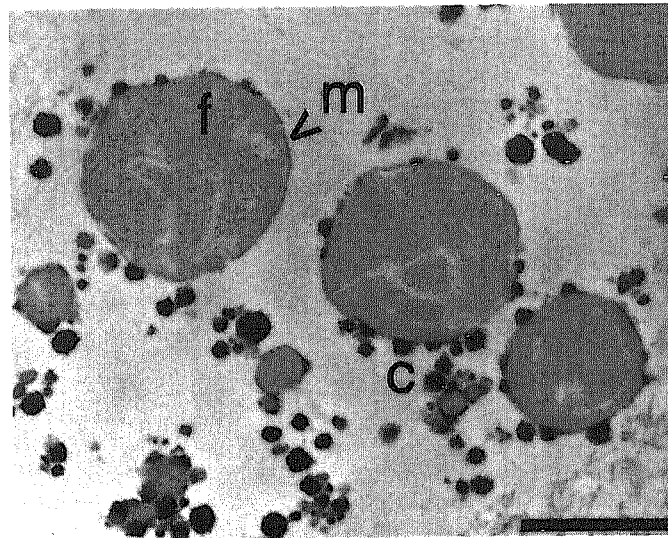


Fig. 3. Transmission electron micrograph of fat globules (f) from homogenized ice cream mix with no emulsifier present. Membranes (m) are formed from original milk fat globule membrane fragments from homogenization and from the adsorption of serum proteins. Numerous, darkly-stained casein micelles (c) are seen adsorbed on the surface (from Goff *et al.*, 1987). Bar = 1 μm .

triglyceride composition of the fat used, as a partially crystalline emulsion is needed for partial coalescence in the whipping and freezing step (Barfod and Krog, 1987; Boode and Walstra, 1993; Boode *et al.*, 1993). van Boekel and Walstra (1981a), showed the importance of crystalline fat for partial coalescence by demonstrating an increase in partial coalescence of orders of magnitude when crystals were present. This was attributed to the ability of crystals to distort the surface of the fat globule and these distortions, then, pierce the film between two colliding globules and wet the interface to allow sufficient liquid fat to cement the colliding globules together (Darling, 1982). The displacement of proteins by emulsifiers during this stage likely causes fat crystals distorting the globule surface to be more exposed and more subject to collision during subsequent shear.

FOAMING AND EMULSION DESTABILIZATION

The next stage of structure development occurs during the concomitant whipping and freezing step. Air is incorporated either through a lengthy whipping process (batch freezers) or drawn into the mix by vacuum or injected under pressure (continuous freezers) (Berger, 1990). Air being incorporated into the mix at this time (especially if pre-whipping devices are being used) is thought to be first surrounded by a proteinaceous membrane (Brooker *et al.*, 1986). In addition to air incorporation, the whipping process applies a considerable shear stress to the mix, and that shear rate increases as ice crystals form during freezing, likely due to a combination of the addition of particles (ice crystals) and to freeze-concentration of the fat and aqueous phase (Goff and Jordan, 1989). The continued

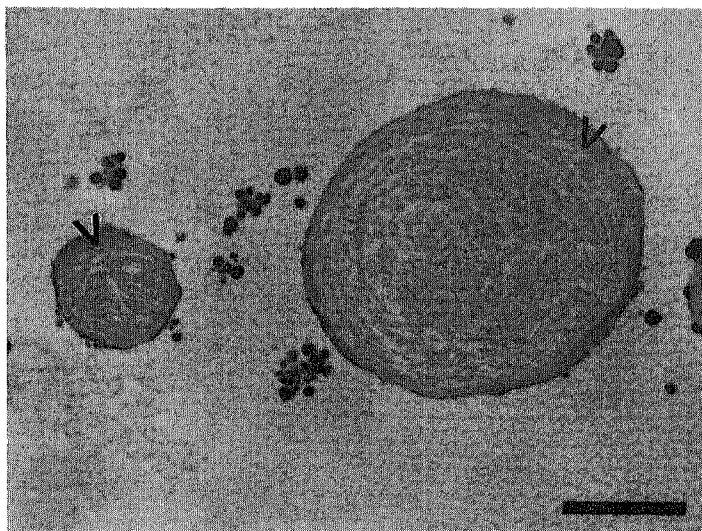


Fig. 4. Transmission electron micrograph of fat globules from homogenized ice cream mix showing the extent of fat crystallization (arrows) occurring after ageing 24 h. at 4°C. Fat crystals, being more saturated, do not react with the fixative (osmium tetroxide) and with the metal salt stains and thus appear light in colour on the background of gray stained unsaturated non-crystalline fat (from Goff *et al.*, 1987). Bar = 1 μ m.

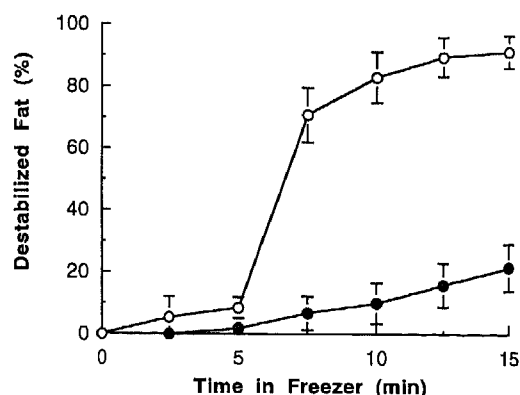


Fig. 5. Fat destabilization as a function of presence of emulsifier in ice cream mix and time of whipping in a batch freezer. Ice crystallization began at about 4–5 minutes. ● = no emulsifier; ○ = 0.08% polysorbate 80 added. Error bars are 95% confidence limits (from Goff *et al.*, 1987).

whipping process and applied shear stress cause the emulsion to undergo partial coalescence or fat destabilization (Figs 5 and 6), during which clumps and clusters of the fat globules form and build an internal fat structure or network into the frozen product by entrapping air within the coalesced fat (Walstra, 1987). This coalescing fat interacts with the proteins at the air bubble membrane (Fig. 7), in a very analogous manner to the whipping of heavy cream (Schmidt and van Hooydonk, 1980; Darling, 1982; Brooker *et al.*, 1986; Noda and Shiinoki, 1986; Berger, 1990; Stanley *et al.*, 1996).

Partial coalescence occurs in the absence of air through mechanisms such as calcium bridging (Agboola and Dalgleish, 1995), but the presence of air during shear stress will increase partial coalescence considerably (Walstra, 1987). Likewise, the applied shear stress also increases partial coalescence considerably compared to the sparging of air (Williams and Dickinson, 1995). In ice cream, a combination of air, applied shear stress (from the dashers and scraper

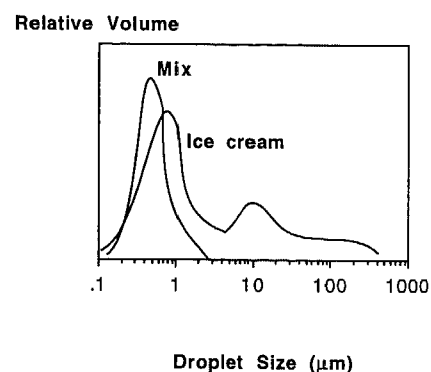


Fig. 6. Fat globule size distribution in ice cream mix with 0.05% polysorbate 80 and melted ice cream after continuous freezing, from light scattering determinations (Malvern Mastersizer X).

blades), and ice formation all contribute to partial coalescence (Fig. 8). During partial coalescence in ice cream, infrastructure formation is less likely than in whipped cream due to the lower fat content, however, it must also be borne in mind that the air bubbles, fat globules, and aqueous phase are being freeze-concentrated at the same time. The fat globule clusters formed during the process of partial coalescence are thus responsible for surrounding and stabilizing the air cells and creating a semi-continuous network or matrix of fat throughout the product resulting in the beneficial properties of dryness upon extrusion during the manufacturing stages (aids in novelty molding, for example), a smooth-eating texture in the frozen dessert, and resistance to meltdown or good stand-up properties (necessary for soft serve operations) (Lin and Leeder, 1974; Buchheim *et al.*, 1985; Berger, 1990).

It has been recognized for a long time that fat destabilization is enhanced by some of the emulsifiers in common use (Kloser and Keeney, 1959; Knightly, 1959). When the emulsion is subjected to the tremendous shear forces in the barrel freezer, the thin membrane created by the addition of surfactant is not

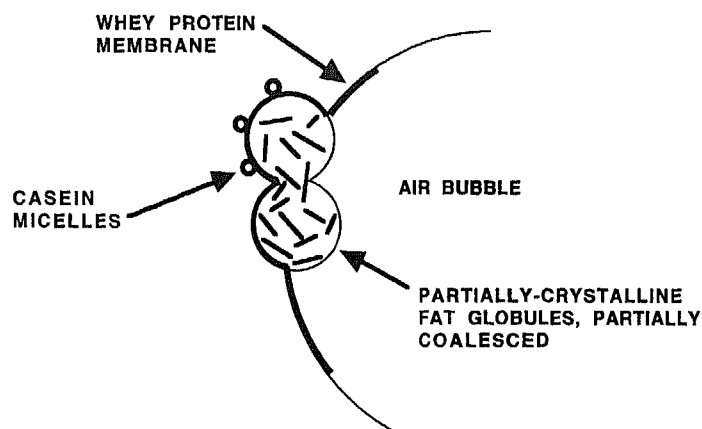


Fig. 7. A schematic illustration of the adsorption of partially-coalesced fat globules and their associated protein membranes to the surface of an air bubble interface.

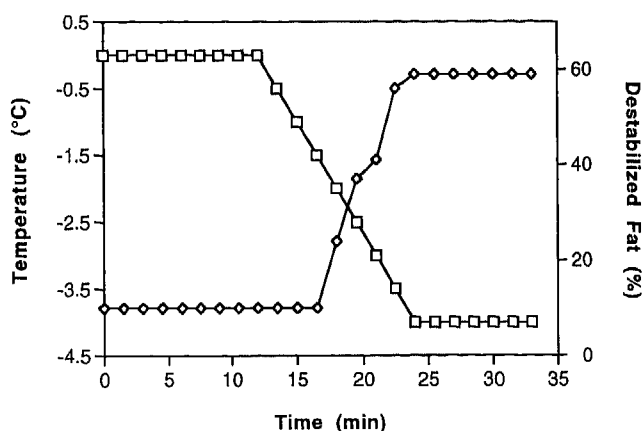


Fig. 8. Fat destabilization (\diamond) and temperature (\square) as a function of time in a continuous freezer. The freezer was operated with constant pump speed and back pressure, with the refrigeration turned on at time = 12 min.

sufficient to prevent the fat globules from coalescing during collision, thus setting up the internal fat matrix (Fig. 5). Figures 9–12 demonstrate the importance of emulsifiers to structure formation at this stage. In Figs 9 and 10 in the absence of emulsifier, globular fat can be seen and fat structure formation is less evident. However, in Figs 11 and 12, the process of partial coalescence has led to a distinct structural layer at the air-water interface in the ice cream, and the extent of partial coalescence is evident. If an ice cream mix is subjected to excessive shearing action or contains too much emulsifier, the formation of objectionable butter particles can occur as the emulsion is churned beyond the optimum level.

It should be possible to predict the destabilizing power of an emulsifier in the barrel freezer by knowing the adsorbed interfacial load and integrity of the membrane, assuming that either protein load or membrane integrity correlate with emulsion stability and partial coalescence (Goff and Jordan, 1989; Dalgleish *et al.*, 1995). This is a logical assumption, given the difference between surface adsorption behavior between proteins (large molecules, mostly on the aqueous side with hydrophobic rearrangement toward the interior) and small-molecule surfactants (fatty acids dissolved or in close contact with the fat surface, very small polar component on the aqueous side). Fat destabilization might be related indirectly to

the interfacial tension between the fat and water phases in the presence of the emulsifier, which may be the primary factor dictating the extent of protein coverage that will result. Polysorbate 80, having a small molecular weight and producing the lowest interfacial tension, displaces more protein, resulting in a very thin membrane, and thus produces the maximum amount of fat destabilization (Goff *et al.*, 1987). Alternatively, membrane integrity, as determined by a parameter such as interfacial viscosity (either shear modulus or dilational modulus), may be a better predictor of destabilizing power than either interfacial tension or quantity of adsorbed membrane per surface area (Dickinson *et al.*, 1993).

Changes to the fat emulsion have been studied recently by Gelin *et al.* (1994). They have demonstrated through light scattering measurements of fat globule size distribution and aggregation that the freezing step is responsible for considerable fat aggregation, but that this aggregation is reversible through dissociation with sodium dodecyl sulfate (SDS). It was obvious from their study that the homogenization step accounted for a large amount of adsorbed protein, and that casein was preferentially adsorbed over the whey protein. The ageing and freezing-hardening-thawing steps each accounted for subsequent protein desorption, again mostly of the caseins. The emulsifier used in the mixes of Gelin *et al.* (1994) contained saturated mono- and

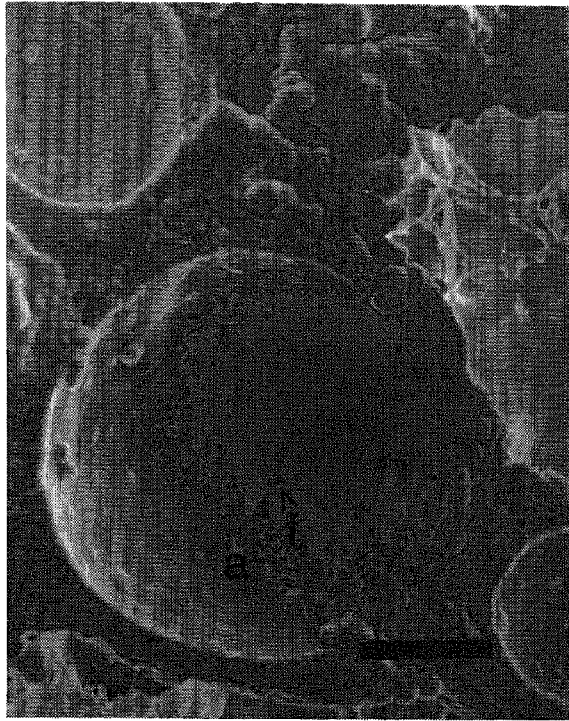


Fig. 9. Cryo-scanning electron micrograph of the structure of air bubbles (a) in ice cream after batch freezing of mix with no emulsifier present. Note the small number of fat globules (f) adsorbed to the air surface. Bar = 5 μm .

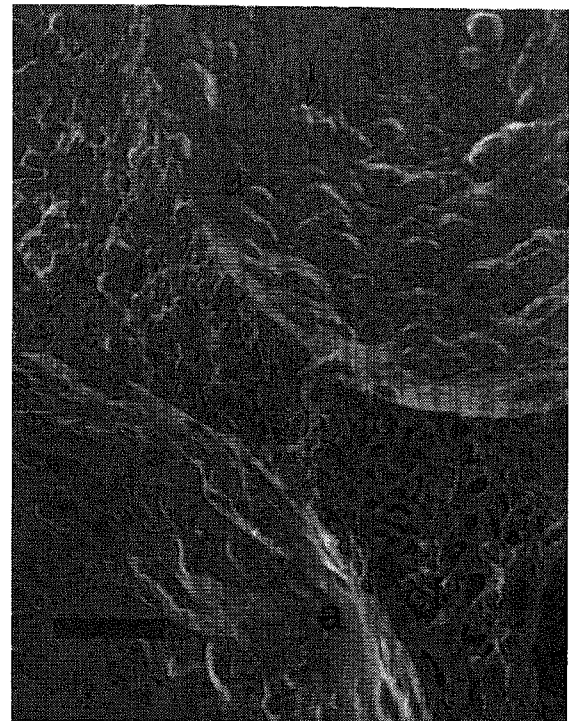


Fig. 11. Cryo-scanning electron micrograph of the structure of air bubbles (a) in ice cream after batch freezing of mix with 0.08% polysorbate 80 added. Note the more extensive adsorption of fat globules (f) to the air interface and the extent of coalescence of fat (cf) at the air periphery and extending into the serum phase. Bar = 5 μm .

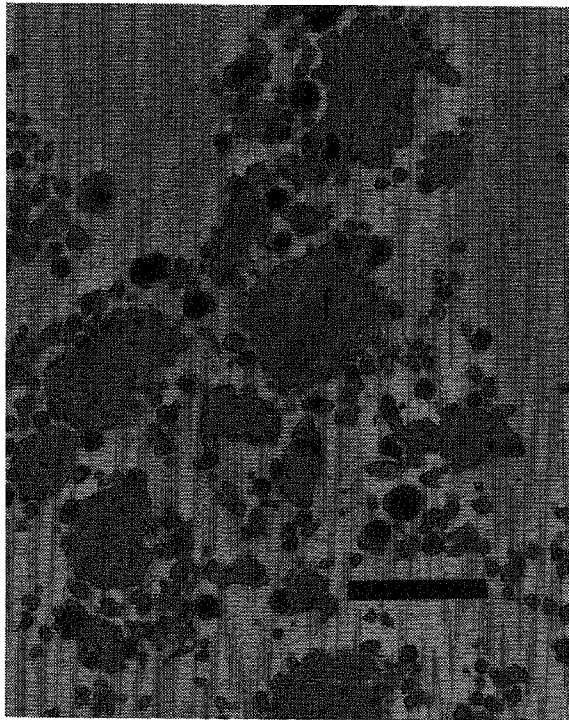


Fig. 10. Transmission electron micrograph of fat (f) from melted ice cream after batch freezing of mix with no emulsifier present. The fat globules show numerous irregularities, but remain distinct. Bar = 1 μm .

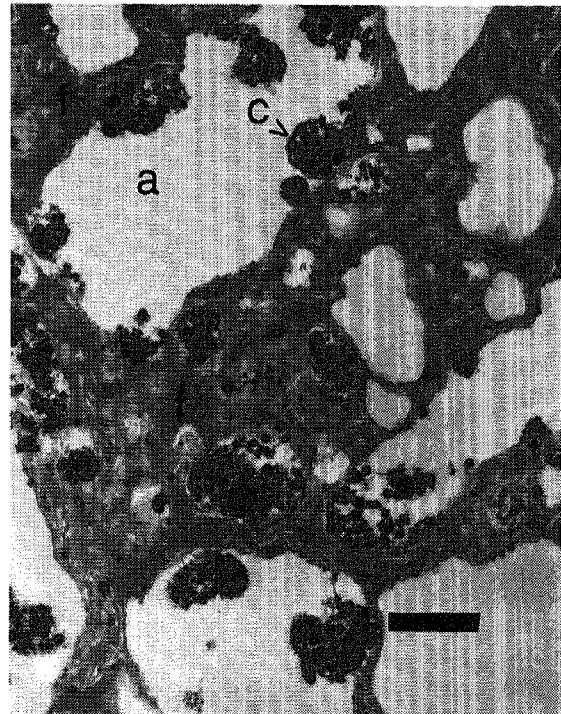


Fig. 12. Transmission electron micrograph of fat from melted ice cream after batch freezing of mix with 0.08% polysorbate 80 added. The fat (f) has formed a continuous mass surrounding the spaces which formerly held the air bubbles (a). The casein micelles (c) have been concentrated into isolated areas. Bar = 1 μm .

di-glycerides but no polysorbate 80, which if present, based on the results of Goff and Jordan (1989), may have led to greater amounts of protein desorption during the ageing period. The reversibility

demonstrated by SDS may be due to the migration of fat crystals from the partially coalesced cluster into the serum phase in the presence of this detergent. This has been demonstrated in the early stages of partial coalescence, but longer times lead to sintering of the fat crystals in the clusters, causing them to become more stable (Boode and Walstra, 1993; Boode *et al.*, 1993).

Kokubo *et al.* (1994) have also demonstrated, in a study of the relationship between draw temperature and overrun of ice cream and resulting de-emulsified fat, that increased fat de-emulsification as a result of decreased draw temperature or increased overrun caused changes in the fat particle size distribution. Particles $\leq 1.2 \mu\text{m}$ decreased while particles $3\text{--}4 \mu\text{m}$ and $8\text{--}15 \mu\text{m}$ increased in frequency with increased fat de-emulsification, as a result of fat globule clustering. The sequential process of partial coalescence during ice cream freezing has also been examined (Goff and Jordan, 1989). The incorporation of air alone, or the shearing action alone, independent of freezing, are not sufficient to cause the same degree of fat destabilization as when ice crystallization occurs concomitantly. The freezing process causes an increase in concentration of the mix components, such as proteins and mineral salts, in the unfrozen water phase. It is believed that the ice crystals contribute to the shearing action on the fat globules, due to their physical shape, and that the concentration of components also leads to enhanced destabilization. However, to create the desired fat destabilization, whipping and freezing must occur simultaneously.

CONCLUSIONS

Ice cream texture, perhaps one of its most important attributes, is a result of its structure as contributed by the various phases present: ice crystals, air bubbles, partially-coalesced fat globules, and the continuous serum phase of dissolved and suspended solutes and macromolecules. Structure formation in ice cream is extremely complex, resulting from several stages of manufacture, especially during homogenization, ageing, and whipping/freezing. Colloidal aspects play an important role in this structure formation: interactions between proteins and emulsifiers at the fat interface, fat-fat partial coalescence, and interactions between proteins and partially-coalesced fat at the air interface. An understanding of these colloidal aspects allows for the appropriate directions and interpretations when dealing with numerous industrial situations, e.g. manufacturing and textural defects, ingredient assessment, research and product development. Research into colloidal aspects of ice cream and model systems applicable thereto, is on-going, and future results will continue to improve our understanding of this unique system.

ACKNOWLEDGEMENT

Appreciation is expressed to the Natural Sciences and Engineering Research Council of Canada and the Ontario Ministry of Agriculture, Food and Rural Affairs for their financial support of ongoing research,

and to Sandy Smith, Godefroy Aubery, and Andres Flores for contributions to this work.

REFERENCES

- Agboola, S. O. and Dalgleish, D. G. (1995) Calcium-induced destabilization of oil-in-water emulsions stabilized by caseinate or by β -lactoglobulin. *Journal of Food Science* **60**, 389–394.
- Anderson, M., Brooker, B. E. and Needs, E. C. (1987) The role of proteins in the stabilization/destabilization of dairy foams. In *Food Emulsions and Foams*. ed. E. Dickinson, pp. 100–109. Royal Society of Chemistry, London, England.
- Aynié, S., Le Meste, M., Colas, B. and Lorient, D. (1992) Interactions between lipids and milk proteins in emulsion. *Journal of Food Science*, **57**, 883–886, 891.
- Barfod, N. M. and Krog, N. (1987) Destabilization and fat crystallization of whippable emulsions (toppings) studied by pulsed NMR. *Journal of the American Oil Chemists Society* **64**, 112–119.
- Barfod, N. M., Krog, N., Larsen, G. and Buchheim, W. (1991) Effect of emulsifiers on protein-fat interaction in ice cream mix during aging I. Quantitative analyses. *Fat Science and Technology* **93**, 24–29.
- Berger, K. G. (1990) Ice cream. In *Food Emulsions*, 2nd edn., eds. K. Larsson and S. Friberg, pp. 367–444. Marcel Dekker Inc., New York.
- Boode, K., Bisperink, C. and Walstra, P. (1991) Destabilization of O/W emulsions containing fat crystals by temperature cycling. *Colloids Surfaces* **61**, 55–74.
- Boode, K. and Walstra, P. (1993) Partial coalescence in oil-in-water emulsions. 1. Nature of the aggregation. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **81**, 121–137.
- Boode, K., Walstra, P. and deGroot-Mostert, A. E. A. (1993) Partial coalescence in oil-in-water emulsions. 2. Influence of the properties of the fat. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **81**, 139–151.
- Brooker, B. E. (1985) Observations on the air serum interface of milk foams. *Food Microstructure* **4**, 289–296.
- Brooker, B. E., Anderson, M. and Andrews, A. T. (1986) The development of structure in whipped cream. *Food Microstructure* **5**, 277–285.
- Buchheim, W., Barfod, N. M. and Krog, N. (1985) Relation between microstructure, destabilization phenomena and rheological properties of whippable emulsions. *Food Microstructure* **4**, 221–232.
- Budiaman, E. R. and Fennema, O. (1987) Linear rate of water crystallization as influenced by temperature of hydrocolloid suspensions. *Journal of Dairy Science* **70**, 534–546.
- Budiaman, E. R. and Fennema, O. (1987) Linear rate of water crystallization as influenced by viscosity of hydrocolloid suspensions. *Journal of Dairy Science* **70**, 547–554.
- Buyong, N. and Fennema, O. (1988) Amount and size of ice crystals in frozen samples as influenced by hydrocolloids. *Journal of Dairy Science* **71**, 2630–2639.
- Caldwell, K. B., Goff, H. D. and Stanley, D. W. (1992) A low-temperature scanning electron microscopy study of ice cream. I. Techniques and general microstructure. *Food Structure* **11**, 1–9.
- Chen, J. and Dickinson, E. (1993) Time-dependent competitive adsorption of milk proteins and surfactants in oil in water emulsions. *Journal of the Science of Food and Agriculture* **62**, 283–289.
- Chen, J., Dickinson, E. and Iveson, G. (1993) Interfacial interactions, competitive adsorption and emulsion stability. *Food Structure* **12**, 135–146.

- Courthaudon, J.-L. and Dickinson, E. (1991) Competitive adsorption of lecithin and β -casein in oil in water emulsions. *Journal of Agricultural and Food Chemistry* **39**, 1365–1368.
- Courthaudon, J.-L., Dickinson, E. and Dalgleish, D. G. (1991) Competitive adsorption of β -casein and nonionic surfactants in oil in water emulsions. *Journal of Colloid and Interface Science* **145**, 390–395.
- Dalgleish, D. G., Srinivasan, M. and Singh, H. (1995) Surface properties of oil-in-water emulsion droplets containing casein and Tween 60. *Journal of Agricultural and Food Chemistry* **43**, 2351–2355.
- Darling, D. F. (1982) Recent advances in the destabilization of dairy emulsions. *Journal of Dairy Research* **49**, 695–712.
- Darling, D. F. and Butcher, D. W. (1978) Milkfat globule membrane in homogenized cream. *Journal of Dairy Research* **45**, 197–208.
- Dickinson, E. and Gelin, J.-L. (1992) Influence of emulsifier on competitive adsorption of α_s -casein and β -lactoglobulin in oil-in-water emulsions. *Colloids and Surfaces* **63**, 329–335.
- Dickinson, E., Rolfe, S. E. and Dalgleish, D. G. (1988) Competitive adsorption of α_{s1} -casein and β -casein in oil-in-water emulsions. *Food Hydrocolloids* **2**, 397–405.
- Dickinson, E. and Stainsby, G. (1982) *Colloids in Food*. Applied Science Publ., New York, NY.
- Dickinson, E., Owusu, R. K. and Williams, A. (1993) Orthokinetic destabilization of a protein-stabilized emulsion by a water-soluble surfactant. *Journal of the Chemical Society, Faraday Transactions* **89**, 865–866.
- Euston, S. E., Singh, H., Munro, P. A. and Dalgleish, D. G. (1995) Competitive adsorption between sodium caseinate and oil-soluble and water-soluble surfactants in oil-in-water emulsions. *Journal of Food Science* **60**, 1151–1156.
- Fang, Y. and Dalgleish, D. G. (1993) Dimensions of the adsorbed layers in oil-in-water emulsions stabilized by caseins. *Journal of Colloid and Interface Science* **156**, 329–334.
- Fang, Y. and Dalgleish, D. G. (1993) Casein adsorption on the surfaces of oil-in-water emulsions modified by lecithin. *Colloids and Surfaces B* **1**, 357–364.
- Gelin, J.-L., Poyen, L., Courthaudon, J.-L., Le Meste, M. and Lorient, D. (1994) Structural changes in oil-in-water emulsions during the manufacture of ice cream. *Food Hydrocolloids* **8**, 299–308.
- Gelin, J.-L., Poyen, L., Rizzotti, R., Le Meste, M., Courthaudon, J.-L. and Lorient, D. (1996) Interactions between food components in ice cream. Part 1: unfrozen emulsions. *Food Hydrocolloids* **10**, 385–393.
- Goff, H. D. (1988) Emulsifiers in ice cream: How do they work? *Modern Dairy* **673**, 15–16.
- Goff, H. D., Caldwell, K. B., Stanley, D. W. and Maurice, T. J. (1993) The influence of polysaccharides on the glass transition in frozen sucrose solutions and ice cream. *Journal of Dairy Science* **76**, 1268–1277.
- Goff, H. D. and Jordan, W. K. (1989) Action of emulsifiers in promoting fat destabilization during the manufacture of ice cream. *Journal of Dairy Science* **72**, 18–29.
- Goff, H. D., Kinsella, J. E. and Jordan, W. K. (1989) Influence of various milk protein isolates on ice cream emulsion stability. *Journal of Dairy Science* **72**, 385–397.
- Goff, H. D., Liboff, M., Jordan, W. K. and Kinsella, J. E. (1987) The effects of polysorbate 80 on the fat emulsion in ice cream mix: evidence from transmission electron microscopy studies. *Food Microstructure* **6**, 193–198.
- Govin, R. and Leeder, J. G. (1971) Action of emulsifiers in ice cream utilizing the HLB concept. *Journal of Food Science* **36**, 718–722.
- Halling, P. J. (1981) Protein stabilized foams and emulsions. *CRC Critical Reviews in Food Science and Nutrition* **15**, 155–203.
- Harper, E. K. and Shoemaker, C. F. (1983) Effect of locust bean gum and selected sweetening agents on ice recrystallization rates. *Journal of Food Science*, **48**, 1801–1803, 1806.
- Hartel, R. W. (1996) Ice crystallization during the manufacture of ice cream. *Trends in Food Science and Technology* **7**, 315–321.
- Hunt, J. A. and Dalgleish, D. G. (1994) Adsorption behaviour of whey protein isolate and caseinate in soya oil-in-water emulsions. *Food Hydrocolloids* **8**, 175–187.
- Iversen, E. K. and Pedersen, K. S. (1982) Ageing of ice cream, Grinsted Technical Paper TP 33-1e.
- Kalab, M. (1985) Microstructure of dairy foods. 2. Milk products based on fat. *Journal of Dairy Science* **68**, 3234–3248.
- Kinsella, J. E. (1984) Milk proteins: physicochemical and functional properties. *CRC Critical Reviews in Food Science and Nutrition* **21**, 197–262.
- Kinsella, J. E., Whitehead, D. M., Brady, J. and Bringe, N. A. (1988) Milk proteins: possible relationships of structure and function. In *Developments in Dairy Chemistry. 4. Functional Milk Proteins*, ed. P. F. Fox, pp. 55–95. Applied Science Publishers, London.
- Kloser, J. J. and Keeney, P. G. (1959) A study of some variables that affect fat stability and dryness in ice cream. *Ice Cream Trade Journal*, **55** (5), 26–32, 86–88, 92, 121.
- Knightly, W. H. (1959) The role of the liquid emulsifier in relation to recent research on ice cream emulsification. *Ice Cream Trade Journal*, **55** (6), 24–28, 76, 90, 119–120.
- Kokubo, S., Sakurai, K., Hattori, M. and Tomita, M. (1994) Effect of drawing temperature at a freezer and overrun on de-emulsified fat of ice cream. *Journal of the Japanese Society of Food Science and Technology*, **41**, 347. (as referenced in *Dairy Science Abstracts*, 1995, **57**, 3397).
- Levine, H. and Slade, L. (1988a) Cryostabilization technology: thermoanalytical evaluation of food ingredients and systems. In *Thermal Analysis of Foods*, ed. C.Y. Ma and V.R. Harwalker, pp. 221–305. Elsevier Applied Science, London.
- Levine, H. and Slade, L. (1988) Principles of cryo-stabilization technology from structure/property relationships of carbohydrate/water systems. A Review. *Cryo-Letters* **9**, 21–63.
- Lin, P. M. and Leeder, J. G. (1974) Mechanism of emulsifier action in an ice cream system. *Journal of Food Science* **39**, 108–111.
- Marshall, R. T. and Arbuckle, W. S. (1996) *Ice Cream*, 5th edn. Chapman and Hall, New York, NY.
- Melsen, J. P. and Walstra, P. (1989) Stability of recombined milk fat globules. *Netherlands Milk and Dairy Journal* **43**, 63–78.
- Muhr, A. H. and Blanshard, J. M. V. (1983) The effect of polysaccharide stabilizers on ice crystal formation. In *Gums and stabilisers for the food industry. 2. Applications of hydrocolloids*, ed. G.O. Phillips, D.J. Wedlock, and P.A. Williams, pp. 321–331. Pergamon Press, New York.
- Muhr, A. H. and Blanshard, J. M. V. (1986) Effect of polysaccharide stabilizers on the rate of growth of ice. *Journal of Food Technology* **21**, 683–710.
- Muhr, A. H., Blanshard, J. M. V. and Sheard, S. J. (1986) Effects of polysaccharide stabilizers on the nucleation of ice. *Journal of Food Technology* **21**, 587–603.
- Needs, H. C. and Huitson, A. (1991) The contribution of milk serum proteins to the development of whipped cream structure. *Food Structure* **10**, 353–360.
- Noda, M. and Shiinoki, Y. (1986) Microstructure and rheological behaviour of whipping cream. *Journal of Texture Studies* **17**, 189–204.
- Oortwijn, H., Walstra, P. and Mulder, H. (1977) The membranes of recombined fat globules. 1. Electron microscopy. *Netherlands Milk and Dairy Journal* **31**, 134–147.
- Oortwijn, H. and Walstra, P. (1979) The membranes of recombined fat globules. 2. Composition. *Netherlands Milk and Dairy Journal* **33**, 134–154.

- Pandolfe, W. D. (1982) Development of the New Gaulin Micro-Gap Homogenizing Valve. *Journal of Dairy Science* **65**, 2035–2044.
- Phillips, M. C. (1981) Protein conformation at liquid interfaces and its role in stabilizing emulsions and foams. *Food Technology* **35**, 50–57.
- Sahagian, M. E. and Goff, H. D. (1995) Thermal, mechanical and molecular relaxation properties of stabilized sucrose solutions at sub-zero temperatures. *Food Research International* **28**, 1–8.
- Schmidt, D. G. and van Hooydonk, A. C. M. (1980) A scanning electron microscopical investigation of the whipping of cream. *Scanning Electron Microscopy III*, 653–658.
- Shirai, Y., Nakanishi, K., Matsuno, R. and Kamikubo, T. (1985) Effects of polymers on secondary nucleation of ice crystals. *Journal of Food Science* **50**, 401–406.
- Stanley, D. W., Goff, H. D. and Smith, A. S. (1996) Texture-structure relationships in foamed dairy emulsions. *Food Research Internat.* **29**, 1–13.
- Tomas, A., Courthadon, J. L., Paquet, D. and Lorient, D. (1994) Effect of surfactant on some physico-chemical properties of dairy oil-in-water emulsions. *Food Hydrocolloids* **8**, 543–553.
- van Boekel, M. A. J. S. and Walstra, P. (1981) Effect of couette flow on stability of oil-in-water emulsions. *Colloids and Surfaces* **3**, 99–107.
- van Boekel, M. A. J. S. and Walstra, P. (1981) Stability of oil-in-water emulsions with crystals in the disperse phase. *Colloids and Surfaces* **3**, 109–118.
- van Dam, B., Watts, K., Campbell, I. and Lips, A. (1995) On the stability of milk protein-stabilized concentrated oil-in-water food emulsions. In *Food Macromolecules and Colloids*, eds. E. Dickinson and D. Lorient, pp. 215–222. Royal Society of Chemistry, London, England.
- Walstra, P. (1987) Overview of emulsion and foam stability. In *Food Emulsions and Foams*, ed. E. Dickinson, pp. 242–257. Royal Society of Chemistry, London, England.
- Walstra, P. and Jenness, R. (1984) *Dairy Chemistry and Physics*. John Wiley and Sons, New York.
- Walstra, P. and Oortwijn, H. (1982) The membranes of recombined fat globules. 3. Mode of formation. *Netherlands Milk and Dairy Journal* **36**, 103–113.
- Williams, A. and Dickinson, E. (1995) Shear-induced instability of oil-in-water emulsions. In *Food Macromolecules and Colloids*, eds. E. Dickinson and D. Lorient, pp. 252–255. Royal Society of Chemistry, London, England.