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Coupling deterministic and random sequential approaches for structure and texture prediction of a dairy oil-in-water emulsion

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ABSTRACT

Dairy products made of concentrated milk protein powder and milk fat have been experimentally shown to behave like complex systems: The resulting textures depend on various factors, including concentration and type of proteins, nature of heat treatment and homogenisation process. The aim of this paper is to combine two models in order to predict the composition of the interface of a homogenised oil-in-water emulsion, and the resulting bridge structure between the fat droplets. This structure is then correlated to the texture of the emulsion.
Free unknown parameters of both models have been estimated from experimental data using an evolutionary optimisation algorithm. The resulting model fits the experimental data, and is coherent with the macroscopic texture measurements.
Industrial relevance: Sustainability is nowadays at the heart of industrial requirements. The development of mathematical approaches should facilitate common approaches to risk/benefit assessment and nutritional quality in food research and industry. These models will enhance knowledge on process–structure–property relationships from molecular to macroscopic level, and facilitate creation of in-silico simulators with functional and nutritional properties. The stochastic optimisation techniques (evolutionary algorithms) employed in these works allow the users to thoroughly explore the systems and optimise it. With regard to the complexity of the food systems and dynamics, the challenge of the mathematical approaches is to realise a complete dynamic description of food processing. In order to reach this objective, it is mandatory to use innovative strategies, exploiting the most recent advances in cognitive and complex system sciences.

1. Introduction

Surface-active molecules, such as proteins, polymers, ionic and non-ionic surfactants play a major role in the stabilisation of dispersed system such as oil in water emulsions (Dickinson, 2001). In food systems, proteins are an important class of emulsifiers: they are adsorbed on the oil droplet surface during homogenisation. Stabilisation is a consequence of the ability of the proteins to generate repulsive interactions (steric and electrostatic) between oil droplets (McClements, 2004).

The emulsifying properties of milk proteins are excellent and justify their wide use in food processing (Dickinson, 1999). Milk proteins are divided in two major categories: caseins (as casein micelles (CMs) or individual caseins) and native whey proteins (WPs).

During most of milk gel processing, the milk protein solution undergoes a heat treatment. Usually, a heat treatment denatures soluble proteins and aggregates of proteins appear, with a strong impact on the physicochemical properties of the final product. Above 70 °C, whey proteins are partly denatured and form aggregates (WPAs) while casein micelles are less sensitive to heat treatment but can form complexes with WPs (CMWPs). WPA and CMWP reactions occur in competition (Guyomarc'h, Law, & Dalgleish, 2003). All these phenomena lead to four potential types of proteins in the solution: (CMs), (WPs), (WPAs) and (CMWPs).

Several studies on milk gels (Dickinson, 2001; Dickinson, 2011; Gaygadzhiev, Hill, & Corredig, 2009; Knudsen, Ogendal, & Skibsted, 2008; Murray, 2002) showed the importance of the dynamics and competition between these types of particles taking place at a fluid–fluid interface of lipid droplets during the emulsion. Although studies describe the structuring of pure whey protein aggregates (WPAs) submitted to heat (Rabe, Verdes, & Seeger, 2011), nevertheless less is known about the behaviour of complex aggregates made of casein micelles and whey proteins (CMWPs) (Morand, Dekkari, Guyomarc'h, & Famelart, 2012). Moreover, the data and expertise collected on complex

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aggregates are generally difficult to integrate in existing models (Foucquier et al., 2012). Mixed solutions are not thermodynamically controlled processes of competitive adsorption, and cannot be predicted from any classical model like the Langmuir one (Dickinson, 1999; Rabe et al., 2011). In this context, stochastic approaches simulating the layer of adsorbed proteins at the nanoscopic level are relevant, but need important computing time if several types of particles are considered. The surface-active molecules, i.e. the CMWP aggregates, are in competition with the pure whey protein (WPA) aggregates at the oil in water interface and play a major role in the network created at a higher level. As highlighted by Dickinson (2011), the interpretation of surface composition in emulsion containing the full range of aggregated milk proteins is quite complex and certainly not yet fully understood. Modelling is an efficient strategy for understanding such systems.

Experiments have been previously performed, generating complex unexpected behaviour, for a same total concentration of proteins, when using different mass ratio of (CMs). A wide range of interfacial composition has been generated when changing this initial condition. The work presented in this paper starts from those observations.

We propose a computational approach to simulate the structure of a dairy emulsion, from a given composition and under some process conditions. The computational approach is validated on the available data set. The model uses a stochastic approach to generate at the nanoscopic scale a random spatial configuration of the physical elements of the emulsion. The purpose of the model is to predict the emergence of the macroscopic structure from the local organisation at the nanoscopic scale. This approach is strongly inspired by the Random Sequential Adsorption (RSA) model (Feder, 1980) and its derivatives (Nasir & McGuire, 1998), with the particularity that the interface is not represented as a plane, but as a 3D surface made of randomly distributed fat droplets in the space.

Additionally, our model is able to manage the competition of elements of different sizes, which is not considered in previous RSA models.

The paper is organised as follows. After a description of the experimental data used to optimise and validate the model (Section 2), the model is developed in Section 3. Results are presented in Section 4: after a sensitivity analysis, the parameters of the model are fitted using an evolutionary optimisation approach (CMA-ES) (Hansen & Ostermeier, 2001). Discussion, conclusions and future work are finally developed in Sections 5 and 6.

2. Experimental data

Various emulsions were generated with a range of controlled interfacial compositions (weight ratio of casein micelles (CMs) to whey proteins (WPs) from 80:20 to 12:88). Two sets of experiments were made:

- To build the model, a first database was collected from experiments conducted at the pilot plant of INRA BIA (Institut National de Recherche Agronomique, Biopolymères–Interactions–Assemblages, Nantes, France) (Surel et al., in review).
- To validate the model, a second database was collected from experiments conducted in the laboratory of IFR (Institute of Food Research, Norwich, England) (Rouland, 2011).

Both sets of experiments were made with the same preheat treatment and protein solutions, but with different experimental devices and volumes. The protein phases of both experimental data sets were made of the same powders, with the same ionic strength, pH and ion composition.

The two emulsion processes were based on the same principle: a continuous phase made of milk proteins dissolved in permeate. These milk proteins were a mixture of caseins (Promilk 852B, IDI company, France with 5% moisture, 1.5% fat, 85.5% nitrogenous matter/dry matter, 8.5% mineral matter, 4% lactose, 81% nitrogenous matter (on powder), 92% casein micelle, 2.6% Ca, 1.5% P, 0.3% K, 0.1% Na and 0.1% of Mg) and native whey proteins (BiPro, DAVISCO company, Minnesota with 5% max of moisture, 95% min of protein, dry basis, 1% max fat, 3% max ash, 1% max lactose, a pH between 6.7 and 7.5) with milk permeate powder (Armor protéines, France with a pH of 6.0 min, 3% max moisture, 3% min proteins, 1% max fat, 82% lactose, 8% ashes). The continuous phase was prepared the day before use, was stored at 4 °C and then was heated at 80 °C. The dispersed phase of the emulsion is made of saturated lipid: anhydrous milk fat (AMF) heated at 60 °C to become liquid. These two phases were then homogenised in order to get an emulsion.

The processes are different for the homogenisation and volume of resulting emulsion. For Database 1, the blending was made using a rotor stator (Polytron, Heidolph Silent Crusher M), in a low pressure homogeniser (Stansted Fluid Power, Stansted, UK) at 50 bar, whereas experiments in Database 2 were made with a blender (BL450 series, KENWOOD) with a shearing cycle (30 second low speed, 30 second rest, then 2 × 30 second high speed) and in a manual homogeniser (EmulsiFlex-B3, AVESTIN) using 6 passes at 20 × 200 psi.

In Database 1, the emulsion mass was 70 g (49 g of continuous phase and 21 g of dispersed phase) and in Database 2, the emulsion mass was 260 g (182 g of continuous phase and 78 g of dispersed phase).

In order to evaluate the impact of initial conditions on the structure and texture of the emulsion, experiments were carried out with various initial conditions (Table 1). The following initial conditions were kept the same for every experiment:

- For Database 1, the pre-heat treatment temperature of milk proteins was 80 °C, the denaturation level, i.e. the proportion of denatured WPs in the solution, was around 0.6 and the mass of lipid was 21 g, for a total emulsion volume of 70 mL.
- For Database 2, the pre-heat treatment temperature of milk proteins was 80 °C and the mass of lipid was 78 g, for a total emulsion volume of 260 mL.

The following measurements were collected for characterising the emulsions at a micro/nanoscale.

- *Diameter and size distribution of lipid droplets.* Laser light scattering was used to measure the diameter of the lipid droplets in the emulsion and to evaluate the size distribution. In Database 1, measurements were made using a Saturn DigiSizer 5200 (Micromeritics, Norcross, USA). These measurements allowed the calculation of the initial free lipid surface S_0. In Database 2, measurements were made using an LS 13320 Laser Diffraction Particle Size Analyser (Beckman

Table 1
Initial conditions and measurement results for Databases 1 and 2.

w_{cm_0} (%)	$d_{3,2}$ (μm)	$d_{4,3}$ (μm)	c_{prot} ($g \cdot L^{-1}$)	$w_{cm_{ads}}$ (%)	Γ ($mg \cdot m^{-2}$)
Database 1					
13	0.5	0.8	48.4	9	7.1
19	0.45	0.7	48.8	13	4.4
21	0.5	0.8	48.9	22	3.9
26	0.4	0.7	48.9	41	3.4
32	0.45	1.1	49.4	68	5.7
49	0.57	0.9	49.7	61	7.2
80	0.8	1.0	50.4	83	6.1
Database 2					
13	0.76	1.19	48.3	0	7.79
31	0.94	1.55	47.5	4	5.48
49	0.94	1.60	49.7	54	8.04
80	0.86	1.43	50.4	80	7.22

$d_{3,2}$: surface area mean diameter of fat droplets.
$d_{4,3}$: volume mean diameter.
w_{cm_0}: initial percentage of caseins in the solution.
$w_{cm_{ads}}$: percentage of adsorbed caseins.
c_{prot}: protein concentration in water phase.
Γ: interfacial concentration.