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Triglyceride nanocrystal aggregation into polycrystalline colloidal networks: Ultra-small angle X-ray scattering, models and computer simulation

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ABSTRACT

Triacylglycerols (TAGs) are the majority molecules present in edible fats and oils. Many of the functional characteristics of fat products depend on the colloidal fat crystal network present. Identifying the hierarchies of these colloidal networks and how they spontaneously self-assemble is important to understand their functionality and the oil binding capacity, and new insights into the nano- to meso-scale structure in these colloidal fat networks have been reported in recent years. Ultra small angle X-ray scattering (USAXS) is a technique new to the study of edible oil structures and, when combined with modelling and computer simulation, has enabled significant advances to be made in understanding the nano- to micro-scale crystalline structures of edible oils. In the four years since crystalline nanoplatelets (CNPs) were characterized, models have been made of these highly anisotropic nanoscale structures in which they were treated as the primary unit. In those models, CNPs were represented as close-packed rigid layers of spheres, so chosen because the van der Waals sphere–sphere interaction is known. The intent of the models was to predict the hierarchy of colloidal fat networks that would self-assemble from the components in edible oils. Initially, CNP aggregation was modelled under the assumption that all CNPs are present before aggregation begins and that their solubility in liquid oil is very low. The models successfully predicted the fractal dimensions subsequently measured using USAXS. This brief review reports on some of the latest models and simulations together with the results of USAXS experiments carried out on binary lipid systems, such as SSS in OOO, as well as certain complex systems that contain many different TAG molecules. The excellent agreement between the two approaches has established that USAXS is a powerful tool in the elucidation of the nano- to meso-length scales in fats and oils.

1. Introduction

Edible fats are a class of colloidal gels in which an oleogel crystal network is formed as the triacylglyceride (TAG) molecules crystallize from the melt. Crystalline nano-platelets (CNPs) [1–6] have been found to be the basic components of the complex macro-colloidal structure of these edible fats. These CNPs aggregate to form hierarchical structures where it is likely that low melting TAGs remain trapped in liquid state within the solid matrix. It is well known, that the macroscopic structure of the colloidal network can be changed by altering the processing conditions like undercooling temperature, cooling rates and shear [7–11]. It is of fundamental importance to understand what are the implications of having different CNP sizes and morphologies as well as to understand how these CNPs self-assemble via nucleation and growth, and which structures they form. In these colloidal systems of solid fat particles in oil, it is likely that the aggregation of CNPs into bigger aggregates is ultimately responsible for many of the macroscopic properties, such as oil binding capacity and viscoelasticity.

A novel technique to visualize nano-crystals was developed in 2010 by Acevedo and Marangoni [2]. CNPs were successfully imaged for fully hydrogenated canola oil in high oleic sunflower oil. Rigorous sample preparation [2] which included shearing the system at 30,000 rpm followed by the use of cryo-transmission electron microscopy (TEM) revealed the existence of highly anisotropic crystalline nanoplatelets (CNPs) composed of TAG bilayers. The CNPs observed for that system possess lateral dimensions of ~10^2–10^3 nm and thicknesses of ~20–80 nm. Those authors also showed that CNP sizes were affected by the ratio of high-melting to low-melting TAG species, as well as the degree of supersaturation, cooling rate and shear rate during the crystallization [1]. Following those first observations, other authors have shown the existence of the CNPs in lipid systems like: cocoa butter (CB) [12,4,3], fully hydrogenated soybean oil (FHSO) in soybean oil (SO) blends [13–15], FHCO in canola oil (CO) blends [16], tristearin (SSS) in triolein (OOO) [5] and cocoa butter substitutes [6]. The question as to whether

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the sample preparation for the cryo-TEM observation changed the size of the CNPs was answered by Peyronel et al. [5] when in-situ experiments were carried out using ultra small angle X-ray scattering (USAXS). These authors demonstrated that the SSS CNP sizes obtained using USAXS were essentially the same as the ones observed using the Acevedo and Marangoni visualization technique.

The USAXS technique is well suited to study opaque systems and an important advantage over other technique is that it requires little sample preparation. Thus shearing is not a requirement so that its effect can be studied separately. The absolute X-ray scattering intensity is reported as a function of the magnitude of the scattering wave vector, q, which is related to the length scale, L, of the system via $L = 2\pi/q$. This technique can cover length scales from ~100 nm to ~15 μm, well suited to study the nano- to meso-scale structures of edible fat colloidal networks. It is, however, important that the interpretation of the USAXS data be complemented with results from other experiments or by predictions from computer simulations.

The development of models which predicts or identify aggregating structures can be an important aspect to the interpretation of the data. Pink and collaborators [17,18] modelled lipid CNPs as a rigid aggregate of spheres chosen so that the rigid structures representing the CNPs mimicked those observed by Acevedo and Marangoni [2]. Spheres belonging to different CNPs interacted via van der Waals sphere–sphere interaction. It was assumed that the CNPs were essentially insoluble in liquid oils so that all model CNPs were present at the start of the simulation. Surfaces of the spheres comprising CNPs were modified as desired to represent the different scenarios that are believed to exist according to the TAGs present in the liquid–solid mixtures. These considerations are described in more details below. Predictions for the USAXS measurements were made and later confirmed by the experiments.

This article begins with an outline of the models, their computer simulation and the predictions arising. A brief description of the system used to collect and analyze the data is presented which is followed by an account of the experimental USAXS results obtained for different lipid systems.

2. Models, theory and computer simulation

Here we are primarily concerned with describing modelling aggregation of structures which have been formed from triacylglycerol (TAG) molecules. The spatial scales range from tens of nanometers to hundreds of microns. However, molecular scale studies will be described when relevant. Here we briefly touch on the variety of techniques related to modelling aggregation. Aggregation is a wide-ranging field and involves the formation of clusters in a colloidal suspension. During this process, particles dispersed in the liquid phase stick to each other and spontaneously form particle clusters, flocs, or aggregates. The process can be driven by external controlled means such as, for example, enzymatic activity as in the case of rennet-driven aggregation of casein micelles, or via the addition of polymers to induce flocculation. The process can also be driven by the van der Waals attraction between the components of the colloidal suspension such as particles in aerosols or solid structures in oils. These processes have been modelled in essentially two ways: (i) analytically via the Smoluchovsky equation, the Langevin equation and analogous dynamical equations and (ii) models which rely upon computer simulation to elucidate the dynamics and/or static structures. Of importance to applications to solid structures in edible oils, especially at high solid concentration, is tortuosity. A number of definitions of tortuosity in 2-dimensions have been given which involve local or average curvatures, or defined in terms of an effective diffusion coefficient. In what follows, we focus our attention upon modelling the hierarchy of solid networks which come about via solid aggregation in edible oils.

At low solid fat content, the starting point is the existence of highly-anisotropic crystalline nanoplatelets (CNPs) first characterized by Acevedo and Marangoni [2] and the question to be addressed is: to what aggregation structures do such CNPs give rise? The models assume that a majority of solid has condensed as the sample is cooled from a sufficiently high temperature to about room temperature leaving either a 1-component liquid oil or one that contains minority components. One consideration will be whether there is essentially only one solid component or whether the minority components condense together with the majority solid component, and how the majority and minority components are structurally related. Another question is whether crystal morphology plays a role in aggregation. For a given system, different solid morphologies are effectively determined by the cooling rates which give rise to the solids. If these procedures all result in essentially similar, highly-anisotropic 2-dimensional CNPs as reported by Acevedo and Marangoni, then the only physical difference between CNPs which possess different morphologies would be the slightly different van der Waals interactions due to the small differences in mass density. Mass fractal aggregates can be defined by the relationship between the mass, $M(R_g)$ and the radius of gyration, R_g, $M(R_g) = KR_g^D$. The small differences in the van der Waals interaction might affect the prefactor, K, but not the fractal dimension, D, and so would have no effect upon the structure of aggregates. Since the models described here start with an assumption of highly-anisotropic CNP existence, then they ignore questions of crystal morphology.

We shall restrict ourselves to CNPs which have very low solubilities at the temperature of the liquid oils in which they are immersed. This important restriction is reflected in the assumption that all CNPs have been formed before significant aggregation begins and that, once they are formed, the CNPs are unchanging structures. CNPs have been modelled using coarse grained models [19,20]. In order to help understand and guide scattering experiments geared towards structural characterization [21,22] of these systems, static structure functions, $S(q)$, for the different structures that emerged from simulations, were computed as functions of wave vector magnitude q and used to predict the results of small and ultra-small angle X-ray scattering (SAXS and USAXS).

2.1. Component oil. Tristearin solids in triolein liquid oil

When an oil comprising a mix of liquid tristearin (SSS) and triolein (OOO) is cooled to room temperature, SSS condenses into solids. These are irregularly-shaped highly-anisotropic crystalline structures 100–1000 nm on a side and 50–200 nm thick. To model such structures we have to be able to calculate the van der Waals interaction between two such rigid objects an arbitrary distance apart with arbitrary relative orientation. This was achieved by representing a CNP, as shown in Fig. 1A, as a rigid array of monodisperse spheres, each of radius R. Such model CNPs are described by a set of integers, {l, m, n} where the first two specify the number of spheres in the rows of the hexagonal lattice and the third integer gives the number of layers of such lattices. Fig. 1A shows a {10, 6, 1} model CNP. The advantage of this model is that one knows the analytical form of the van der Waals sphere–sphere interaction [23] and, if one makes the assumption that the total interaction between two such model CNPs is the sum of all pairwise sphere–sphere interactions with one sphere in each model CNP, then one can trivially calculate the CNP–CNP interaction for arbitrary separation and relative orientation. This is illustrated in Fig. 1C where the interaction, $V_d(R, r)$, is shown. Fig. 1F shows the form of the interaction.

We write the interaction between two identical homogeneous spheres, each of radius R, a centre-to-centre distance, r, apart as

$$V(r) = V_d(R, r) \quad r > 2(R + \Delta) \tag{1}$$

$$V(r) = V_B \quad r \leq 2(R + \Delta) \tag{2}$$

where Δ is the thickness of a region into which another sphere, belonging to a different CNP, cannot penetrate, and $V_B < 0$ is a binding energy. The distance, 2Δ, is approximately the nearest distance to which a pair