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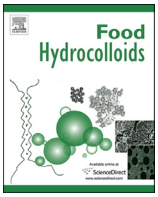

Crystal nucleation in food colloids

Malcolm J.W. Povey*

School of Food Science and Nutrition, University of Leeds, Leeds LS2 9JT, UK

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ABSTRACT

Crystal nucleation in food colloids is considered in the light of recent developments in classical nucleation theory (CNT); it is shown that CNT remains a sound basis upon which to understand nucleation in colloids and in particular nucleation in lipids such as triacylglycerols. Computation of the energy barrier to nucleation for a studied triacylglycerol system (Cocoa butter oil-in-water emulsion) indicates that whilst homogeneous nucleation is unlikely at higher surface energies the addition of surfactant, lowering the interfacial energy may have a dramatic impact on surface nucleation rates. Data is included supporting this contention. The impact of reducing the size of colloidal particles to the point where the interfacial region occupies a significant proportion of the total volume of the dispersed phase is discussed and it is suggested that in these circumstances undercooling may fall significantly in comparison with the undercooling measured in micrometre emulsions.

1. Introduction

It was Eric Dickinson who showed me that it was possible to carry out scientifically rigorous and repeatable measurements on systems which gave insight into the behaviour and structure of food. I had begun my scientific career in Food Science by studying ultrasound propagation in whole eggs with a view to developing a practical method for the automated testing of eggs. I was immediately confronted with the problem that no two eggs were the same acoustically and there began my transformation from physicist to physicist and food scientist. Eric's method was a form of reductionism in which a food system like milk was modelled by producing a much simpler but reproducible system such as n-alkane oil in water emulsion. At the time he was criticised for studying these model systems on the basis that they were not real foods and were usually comprised of materials you would not dream of eating. Looking back now of course, it is possible to see that this method helped establish the science of food colloids as a scientific discipline, a discipline which has underpinned a whole variety of innovations in practical food production involving foods as diverse as cream liqueurs through fatty spreads to dairy products.

From my point of view as a physicist, collaboration with a chemical physicist such as Eric gave me access to a laboratory containing a wide variety of colloid characterisation techniques which allowed me to test my new ultrasound techniques using well characterised and reproducible systems. We collaborated in the development of techniques for the study of colloid stability and also crystallization in emulsions, part of the subject of this paper.

2. Nucleation theory

2.1. Introduction

In this work we consider crystal nucleation and growth in the dispersed phase of a colloidal system. By a colloidal system is meant any substance dispersed through another with particle diameters between 2 nm and 2000 nm, although the suspending phase considered will always be water. Micro emulsions are excluded from this discussion in order to keep it short. There is no discussion here of the impact of van der Waals forces although it is common knowledge that these dominate the interactions between small colloidal particles and are responsible for the well-known phenomenon of nano-particle aggregation.

We adopt the approach that there are three phases in crystallization: induction, nucleation and growth. Firstly we consider the relevance of classical nucleation theory and briefly explain what it is, then consider its application to bulk fluids and finally to colloidal fluids. This work will not consider the growth phase in any detail, primarily because nucleation is the rate limiting step for crystallization in colloids.

Crystallization in emulsions is an increasingly important area both technically and scientifically. Agrochemicals, pharmaceuticals

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* Tel.: +44 1133432963; Fax: +44 1133432982.
E-mail address: m.j.w.povey@leeds.ac.uk.

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(Espitalier, Biscans, Authelin, & Laguerie, 1997), ceramic manufacture, food, cosmetics (Wang & Lee, 1997), speciality chemicals, photographic emulsions are examples of processes were emulsion crystallization is employed or in development. In ceramics manufacture emulsion crystallization offers more uniform stoichiometry, smaller ceramic particle size and a superior fired ceramic (Hirai, Hariguchi, Komasawa, & Davey, 1997; Hirai, Okamoto, & Komasawa, 1998) and is one example of materials processing based on emulsions (Bibette, 1991; Davey, Garside, Hilton, Mcewan, & Morrison, 1995; Davey, Garside, Hilton, McEwan, & Morrison, 1996; Davey, Hilton, & Garside, 1997; Davey, Hilton et al., 1996; Dinsmore, Crocker, & Yodh, 1998; Espitalier et al., 1997; Pileni, 1997). In foods, emulsion crystallization was discovered accidentally as part of the butter churning process (Fredrick et al., 2011; Walstra & Vanberesteyn, 1975). In the case of margarine manufacture (Haighton, 1976) nucleation is initiated in the dispersed oil phase of an oil-in-water emulsion, the emulsion is inverted under shear during the crystallization process so that crystallization completes when the oil forms the continuous phase. The result is a kinetically stable water-in-oil emulsion, which would otherwise be a kinetically stable oil-in-water emulsion. This has the interesting property of inverting back to a water continuous emulsion when the crystal network melts in the mouth. In ice cream, the role of crystallization in stabilizing and structuring the product is even more complex (Goff, 1997a, 1997b). In foods, fat crystals formed from a colloidal oil dispersion play an important role in structuring emulsions (Garti, Aserin, Tiunova, & Binyamin, 1999; Garti, Binyamin, & Aserin, 1998; Walstra, Van Vliet, & Kloek, 1995).

2.2. Classical nucleation theory

A number of authors have cast doubt on the applicability of classical nucleation theory (CNT), for example (Cabriolu, Kashchiev, & Auer, 2012; Kashchiev, 2008; Prestipino, Laio, & Tosatti, 2012; Sanz, Valeriani, Frenkel, & Dijkstra, 2007). However, it has been our experience that it explains very well nucleation in colloidal systems and recent work (Lechner, Dellago, & Bolhuis, 2011, Kashchiev, Borissova, Hammond, & Roberts, 2010) has placed classical nucleation theory (albeit in a modified form) on a firm theoretical footing in both colloidal and bulk fluids. In particular, the underpinning idea that there is a critical nucleus size at which crystal growth may begin and that size is determined through an energy balance between surface (proportional to diameter squared) and volume terms (proportional to diameter cubed) has been vindicated. This idea is not challenged by some critics of CNT (Prestipino et al., 2012) and interestingly their modifications to the surface energy term account for the relatively large thermal surface fluctuations which occur in nano-scale particles (of which see Section 2.3 below).

2.3. Nucleation in bulk fluids

2.3.1. Homogeneous nucleation

Detailed accounts of crystallization in bulk materials can be found in (Kashchiev, 2000; Kashchiev et al., 2010; Kashchiev & van Rosmalen, 2003; McClements, 2012).

We adopt a model (Ozilgen, Simoneau, German, Mccarthy, & Reid, 1993; Sear, 2007; Volmer, 1939) whereby the initial stage of crystallization involves nucleation. In crystal nucleation ordered domains are formed from the melt. In energy terms these domains possess a reduced energy and entropy throughout their volume but an increased energy by virtue of the creation of an interface between the ordered domain and the disordered liquid. Thus a critical size is inherent in the energy balance which underlies their formation. Below this critical size the surface energy expenditure required to create the domain boundary exceeds the volume energy gain arising from condensation of the liquid into the ordered material constituting the nucleus. The volume energy gain will relate to the undercooling or supercooling relative to the bulk melting point of the ordered material. Hence the critical size of the crystal nucleus will reduce as the undercooling increases. If only pure material exists and extraneous surface and material is absent, then the formation of an ordered domain capable of growth will be a purely stochastic process, involving the diffusion of the liquid molecules, their encounter in a specific, lower entropy conformation and the critical size of the nucleus. This is *homogeneous* nucleation.

According to (Fisher, Hollomon, & Turnbull, 1949) "Particles of a new phase that exceed the critical size required for continuous growth are commonly called nuclei. Particles of subcritical size will be called embryos in order to differentiate them from nuclei. Turnbull has discussed the way in which the sizes of embryos change by statistical fluctuations. Nuclei do not leap into existence with a single fluctuation; rather, they arise from embryos that change their sizes continuously at finite rates by losing or gaining atoms *one at a time* from the surrounding matrix. An important consequence of this idea is that the transient concentration of embryos of every size can differ greatly from the equilibrium or steady state concentration whenever insufficient time has been allowed for steady-state conditions to be realized."

More recent versions of CNT allow more than one atom or molecule to join and leave the nucleus at a time (e.g. Prestipino et al., 2012). The phase prior to nucleation where embryos in an undercooled system come into existence and then disappear is related to the induction period referred to above but is not considered further in this discussion.

Turnbull and co-workers (Fisher et al., 1949; Turnbull, 1950a, 1950b, 1950c, 1952; Turnbull & Cormia, 1961; Turnbull & Fisher, 1949; Turnbull & Vonnegut, 1952) provide comprehensive details on the crystallization kinetics of liquid metals and alkane liquids. Nucleation rates in emulsified fats can be determined by measuring the volume fraction of solid fat (φ) as a function of time (t). The crystallization rate will be proportional to the volume fraction of droplets that contain no crystals ($1-\varphi$) and therefore decreases with time:

$$\frac{d\varphi}{dt} = k(1-\varphi) \tag{1}$$

The reaction rate constant k can be expressed as a function of J, the nucleation rate. For homogeneous volume nucleation, the rate constant k_v is proportional to the droplet volume v_d,

$$k_v = Jv_d \tag{2}$$

If homogeneous nucleation proceeds at the droplet surface, the rate constant k_s is proportional to the droplet surface a_d,

$$k_s = Ja_d \tag{3}$$

Solving the differential Equation (1) gives

$$\varphi = 1 - e^{-kt} \tag{4}$$

Taking into account the droplet size distribution, Equation (4) has to be summed over all the droplet sizes:

$$\varphi = 1 - \int_0^\infty \varphi_d^0 e^{-kt} \delta d \tag{5}$$

where φ_d^0 is the differential volume fraction of droplets with sizes between d and $d + \delta d$.