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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 micrometer emulsions.
Dear Professor Phillips,

Festschrift fur Professor Eric Dickinson

I am pleased to submit my revised version of my manuscript.

Best wishes,

Malcolm Povey

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Crystal nucleation in food colloids

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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 micrometer emulsions.

Keywords: Crystal, nanoparticle, colloid, emulsion, ultrasound, sound speed
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 crystallisation 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 (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, Komasa, & Davey, 1997; Hirai, Okamoto, & Komasa, 1998) and is one example of materials processing based on emulsions (Bibette, 1991; Davey, Garside, Hilton, Mcewan, & Morrison, 1995, 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, and Kloek, 1995).

2.2 Classical nucleation theory

A number of authors have cast doubt on the applicability of classical nucleation theory (CNT), for example (Sanz, Valeriani, Frenkel, & Dijkstra, 2007; Prestipino, Laio, & Tosatti, 2012; Kashchiev, 2008; Cabriolu, Kashchiev, & Auer, 2012). 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, Borissova, Hammond, & Roberts, 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, 1948) “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, Hollomon, & Turnbull, 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 (\(\varphi\)) 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:

\[
\frac{d\varphi}{dt} = k(1 - \varphi)
\]  

(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 $v_d$.

$$k_v = Jv_d$$  \hspace{1cm} (2)

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

$$k_s = Ja_d$$  \hspace{1cm} (3)

Solving the differential Equation 1 gives

$$\varphi = 1 - e^{-kt}$$  \hspace{1cm} (4)

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

$$\varphi = 1 - \int_0^\infty \varphi_d^0 e^{-kt} \delta d$$  \hspace{1cm} (5)

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

Whether homogeneous volume nucleation or nucleation catalyzed by the homogeneous droplet boundary, the isothermal crystallization rate can be modelled by one nucleation rate independent of particle diameter if it is assumed that the droplet composition and the composition of the droplet surface do not change.

The Gibbs energy change $\Delta G_{\text{nucleus}}$ for formation of a nucleus is the result of a balance between a positive energy term $\Delta G_s$ due to surface tension and a negative volume term $\Delta G_v$ due to enthalpy of fusion. The nucleus is assumed to be either a sphere in which case nucleation is isotropic or a cube with a surface energy $\gamma_i$ on the $i^{th}$ face. The surface area of
each face is $A_i$. $V$ is the volume of the nucleus and $\Delta G_{\varphi}$ is the change in Gibbs energy per unit volume arising from the phase transition.

$$\Delta G_{\text{nucleus}} = \Delta G_s + \Delta G_v = \sum_i A_i \gamma_i + V \Delta G_{\varphi}$$  \hspace{1cm} (6)

For a spherical nucleus this becomes

$$\Delta G_{\text{nucleus}} = 4\pi \gamma^2 + \frac{4}{3} \pi R^3 \Delta G_{\varphi}$$  \hspace{1cm} (7)

Surface energies for triacylglycerols in water have been measured by (Lucassenreynders & Kuijpers, 1992) and in their Figure 4 values tend to 30 mN/m at zero surfactant concentration to around 1 mN/m for concentrations above 1% w/w of an unsaturated monoacylglcerol (Dimodan LS, Danisco), for the sunflower oil-water interface. Volume energies can be estimated from the latent heat of fusion (Charbonnet & Singleton, 1947) who quote around 40 cal/gm (167 J/kg) for the alpha form of pure triacylglycerols. The calculations in Figure 1 have been carried out for trilaurin using a value of 30 mN/m for the surface tension and 167 J/kg for the enthalpy change on crystallization into the alpha form.
Figure 1 Plot of surface and volume energy as a function of particle radius for a trilaurin droplet, together with the number of molecules per droplet and the energy of formation of the nucleus. The surface tension in this plot is 30 mN/m and the enthalpy change of the trilaurin into the alpha form is taken as 167 J/kg.

It may be noted from Figure 1 first of all that initially the surface term (increasing energy) grows more quickly than the volume term (decreasing energy) and that this forms an energy barrier to the formation of a stable nucleus. For trilaurin a nucleus needs to exceed around 120-nm in order for it to grow and this corresponds to nearly 10 million molecules, a highly unlikely event.

However, if the surface energy may be reduced then the situation is transformed. For example, in anticipation of the colloid section (Section 2.4) of this discussion, if the surface energy term is greatly reduced to 1 mN/m which may be achieved through the addition of 1% w/w of an unsaturated mono-acylgllycerol (Dimodan LS, Danisco), for a sunflower oil-water interface (Lucassenreynders, et al., 1992); only a few hundred molecules are needed to achieve the point where growth is favourable (Figure 2). In this figure the energy is calculated in units of $k_B T$ and it can be seen that energies of only a few $k_B T$ are sufficient for...
crystal nucleation which then becomes a much more likely event. This becomes even clearer in Figure 3 where the energy per molecule added to the nucleus is shown to have a value below 1 \( k_B T \) indicating that nucleation is highly probable. This suggests that, contrary to the views of some authors, for example (Sear, 2007), there are circumstances where homogeneous nucleation may become highly likely and this will be examined in the next section (Section 2.4).

Figure 2 Plot of surface and volume energy in units of \( k_B T \) as a function of particle radius for a trilaurin droplet, together with the number of molecules per droplet and the energy of formation of the nucleus. The surface tension in this plot is 1 mN/m and the enthalpy change of the trilaurin into the alpha form is taken as 167 J/kg.
Figure 3 Plot of surface and volume energy in units of $k_B T$ as a function of particle radius for a trilaurin droplet, together with the estimated attachment energy per molecule in units of $k_B T$. The surface tension in this plot is 1 mN/m and the enthalpy change of the trilaurin into the alpha form is taken as 167 J/kg.

Differentiation of Equation 7 with respect to $r$ and equating to zero gives a critical size $r^*$ for a cubic nucleus and for a sphere of:

$$r_{cube}^* = \frac{-4\bar{\gamma}}{\Delta G_{\gamma}};$$

$$r_{sphere}^* = \frac{-2\gamma}{\Delta G_{\gamma}};$$

$$\bar{\gamma} = (\gamma_{ab} \gamma_{ac} \gamma_{bc})^{\frac{1}{3}}$$

where ab, ac and bc refer to the different nucleus faces.

Here it is assumed that the cubic nucleus adopts an orthogonal co-ordinate system described by the axes a, b and c and $\bar{\gamma}$ is the corresponding average Gibbs surface energy.
The activation Gibbs energy for the formation of a spherical nucleus can be expressed as a function of supersaturation. Substitute \( r^* \) and \( \Delta G = \Delta \mu / \overline{V} \) into Equation 7, where \( \overline{V} \) is the molar volume in a crystal lattice and \( \Delta \mu \) the chemical potential difference between the supersaturated and the saturated solution or melt.

\[
\Delta G_{\text{nucleus}}^* = \frac{16\pi \overline{V}^2 r^3 N_0^2}{3\Delta \mu_i^2}
\]

where

\[
\Delta \mu_{\text{solution}} = RT \ln(\beta)
\]

\[
\Delta \mu_{\text{melt,i}} = \Delta H_i \frac{T_{\text{m,i}} - T}{T_{\text{m,i}}}
\]

Here \( \beta \) is the supersaturation ratio which is the ratio between the solubilities of the crystallizing component at saturated and unsaturated conditions; \( R \) is the gas constant; \( T \) the crystallization temperature; \( N \), Avogadro's number; \( \overline{V}^* \) the molecular volume of a crystal; \( T_{\text{m,i}} \) the melting temperature of polymorph \( i \) and \( \Delta H_i \), the enthalpy of fusion of polymorph \( i \).

The nucleation rate for crystallization, \( J \), is given by the following semi-phenomenological equation for the case of homogeneous nucleation. It is based on the product of the collision frequency in a system of \( N \) crystallizable molecules, together with a kinetic barrier factor that delays crystallization and the entropy loss associated with the formation of a nucleus:

\[
J = N \frac{k_B T}{h} \exp \left( -\frac{\alpha \Delta S_i}{R} \right) \exp \left( -\frac{\Delta G_{\text{nucleus}}^*}{k_B T} \right)
\]
where \( \exp(-\alpha \Delta S/R) \) is the probability that a fraction \( \alpha \) of the molecule is in the right conformation to crystallize and the loss of entropy \( \Delta S \) on incorporation of material in a nucleus is given by:

\[
\Delta S_i = \frac{\Delta H_i}{T_{m,i}}
\]

Here \( k_B \) is Boltzman’s constant; \( R \) is the gas constant; \( T \) the crystallization temperature in \(^\circ\)K; \( T_{m,i} \) the melting temperature of polymorph \( i \). \( \Delta G^*_\text{nucleus} \), activation Gibbs energy for the formation of a spherical nucleus and \( \Delta H_i \), the enthalpy of fusion of polymorph \( i \).

### 2.3.2 Impact of thermal diffusion

Thermal diffusion is often neglected when considering crystal nucleation and growth. It is worth noting that very large enthalpy changes occur during the transformation from a liquid oil to a solid (Charbonnet, et al., 1947; Wesdorp, 1990). This is a significant factor during nucleation since the energy released during the transformation from solid to liquid heats the surrounding liquid, reducing the supercooling and the probability of growth. The likelihood that this will occur can be estimated from the thermal wave length (\( 2\pi \mu \) where \( \mu \)=thermal diffusion length, \( \mu = \sqrt{2\alpha/\omega} \), \( \alpha \)=thermal diffusivity, \( \omega \) is radial frequency). If for the sake of argument we require that a nucleus must persist in order to grow for at least 50 ns (R. P. Sear, 2007) \( (\omega = 2\pi f = \frac{2\pi}{50 \times 10^{-9}} = 12.6 \times 10^6) \) then the thermal diffusion length will be approximately 300 nm (thermal diffusivity of water is \( 0.143 \times 10^{-6} \) m\(^2\) s\(^{-1}\) at 25 C). It would be reasonable to assume therefore that no other nucleus could begin to form within this distance of an existing nucleation event.
Table 1: Entropy and enthalpy of fusion for some triacylglycerols and n-alkanes (Wesdorp, 1990). MMM – trimyristin, PPP – tripalmitin; StStSt – tristearin.

<table>
<thead>
<tr>
<th>TAG-name</th>
<th>$\Delta H_f$</th>
<th>$\Delta S_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\alpha$</td>
<td>$\beta'$</td>
</tr>
<tr>
<td>MMM</td>
<td>84</td>
<td>107</td>
</tr>
<tr>
<td>PPP</td>
<td>98</td>
<td>132</td>
</tr>
<tr>
<td>StStSt</td>
<td>113</td>
<td>156</td>
</tr>
<tr>
<td>n-C19</td>
<td>45</td>
<td>60</td>
</tr>
<tr>
<td>n-C21</td>
<td>48</td>
<td>63</td>
</tr>
</tbody>
</table>

Table 2: Melting temperature and enthalpies of fusion of pure triacylglycerols in polymorph i, together with the composition of fully hydrogenated palm oil (Wesdorp, 1990).

<table>
<thead>
<tr>
<th>TAG</th>
<th>Percentage</th>
<th>$T_{m,\alpha}$</th>
<th>$\Delta H_{f,\alpha}$</th>
<th>$T_{m,\beta'}$</th>
<th>$\Delta H_{f,\beta'}$</th>
<th>$T_{m,\beta}$</th>
<th>$\Delta H_{f,\beta}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPP</td>
<td>4.0</td>
<td>44.7</td>
<td>95.8</td>
<td>55.7</td>
<td>126.5</td>
<td>65.9</td>
<td>171.3</td>
</tr>
<tr>
<td>PStP</td>
<td>26.1</td>
<td>47.2</td>
<td>112.2</td>
<td>67.7</td>
<td>165.5</td>
<td>65.3</td>
<td>173.6</td>
</tr>
<tr>
<td>PStSt</td>
<td>39.0</td>
<td>50.1</td>
<td>106.0</td>
<td>61.8</td>
<td>-</td>
<td>64.4</td>
<td>172.9</td>
</tr>
<tr>
<td>StStSt</td>
<td>14.5</td>
<td>54.7</td>
<td>108.5</td>
<td>64.3</td>
<td>156.5</td>
<td>72.5</td>
<td>194.2</td>
</tr>
<tr>
<td>PPSt</td>
<td>6.0</td>
<td>46.4</td>
<td>100.0</td>
<td>58.7</td>
<td>124.0</td>
<td>62.6</td>
<td>166.3</td>
</tr>
<tr>
<td>StPSt</td>
<td>2.2</td>
<td>50.7</td>
<td>103.0</td>
<td>-</td>
<td>-</td>
<td>68.0</td>
<td>170.3</td>
</tr>
</tbody>
</table>
2.3.3 Heterogeneous nucleation

In the case of heterogeneous nucleation the process cannot be modelled by a single nucleation rate, as the number of impurities in each droplet will vary with diameter. Initially, the droplets containing the greatest number of catalytic impurities will crystallize. The maximum nucleation rate can probably be related to the nucleation of bulk fats. As solidification continues, smaller droplets will crystallize because they contain fewer impurities. At the end of the crystallization process, the volume fraction of solidified droplets will reach a plateau value $\Phi_m$ because some droplets do not contain impurities and thus will not nucleate heterogeneously. If it is assumed that the catalytic impurities are distributed randomly, the maximal achievable volume fraction of solid droplets can be related to the number of impurities per volume by

$$\Phi_m = 1 - e^{-v_d N_{imp}} \quad (9)$$

where $N_{imp}$ is the number density of catalytic impurities (strongly dependent on temperature).

Combining Equations 1 and 9 with observations by Walstra and van Berestyn (Walstra, et al., 1975) the volume fraction of droplets containing crystals during heterogeneous nucleation as a function of time can be expressed as

$$\Phi = \Phi_m \frac{J_0 v_d t}{1 + J_0 v_d t} \quad (10)$$

where $J_0$ is the maximum nucleation rate. Fitting crystallization curves of emulsified triglycerides to a heterogeneous nucleation model requires the fit parameters $J_0$ and $N_{imp}$, while homogeneous nucleation requires only the nucleation rate as a fit parameter (Kloek, 1998). To take particle size distributions into account, (Wu, Sirota, Sinha, Ocko, & Deutsch, 2006).
273 1993). Equation 10 has to be summed over all the droplet sizes as in (Turnbull, et al., 1961).
274 Similarly, when surface fits are to be expressed, $v_d$ becomes $a_d$.
275
2.3.4 Secondary nucleation
276 Once the first nucleus has formed and a crystal has begun to grow, other types of nucleation may come into play. Of course primary nucleation may occur independently in many different places throughout the volume of liquid. However, the growing crystal may itself nucleate new centres of crystal growth by a variety of processes (Herhold, Ertas, Levine, & King, 1999; Walstra, 1998; Walstra, Van Vliet and Kloek, 1995; Walstra, et al., 1975). In the case of emulsions for example, solid droplets can nucleate crystallization in liquid droplets through collision (Dickinson, Kruizenga, Povey, & Vandermolen, 1993; Dickinson, McClements 1995; McClements, 2012; McClements, Dickinson, et al., 1993; McClements, Dickinson, & Povey, 1990; McClements & Dungan, 1993, 1997; McClements, Dungan, German, & Kinsella, 1992, 1993a, 1993b; McClements, Dungan, German, Simoneau, & Kinsella, 1993; McClements, Han, & Dungan, 1994; Ostwald, 1897).

2.4 Nucleation in dispersed fluids
288 In this Section we will assume that once nucleation occurs within an emulsion droplet its growth embracing the whole droplet is effectively instantaneous. This is a convenient simplification that glosses over the details of the crystallization process, particularly within larger droplets.
293 In bulk liquids guest molecules and foreign surface may catalyse crystal nucleation. This process is called heterogeneous nucleation. Once such a liquid is subdivided into very many particles, subdivision of the bulk liquid into a large number of smaller ones also partitions...
those nuclei that may catalyse heterogeneous nucleation amongst the droplets (Gibout, Jamil, Kousksou, Zéraouli, & Castaing-Lasvignottes, 2007). As a result the number of catalytic impurities per droplet may vary, depending on particle size, between many per droplet to approximately zero. This is generally observed as a greatly increased supercooling, also called undercooling (Figure 4).
Figure 4 Velocity of sound and density plotted against temperature for a 20 vol. % n-hexadecane oil-in-water emulsions containing 2 wt % Tween 20. Closed circles, velocity on cooling; open circles, velocity on heating; closed squares, density on cooling; open squares, density on heating. Average volume-surface diameter of 800 nm. taken from (E. Dickinson, et al., 1993)
In Figure 4 the bulk melting point of n-hexadecane is around 18.2 °C. However, the emulsion droplets do not freeze until the temperature reaches 3.5 °C. When the emulsion is heated it does not melt at its freezing temperature; instead it melts close to the melting point of the bulk liquid. When the number of catalytic impurities is less than one per droplet, the kinetics will initially be proportional to the volume of each drop and hence to the cube of droplet diameter.

The dramatic impact on crystallization rate due to reduction in emulsion droplet size is illustrated in Figure 5 where nucleation in droplets sized around 100-nm is almost completely absent. This plot of solids fraction against particle diameter is based on the knowledge of the number of crystal nuclei per unit volume in the sodium caseinate-stabilized Cocoa Butter (CB) emulsions. Thus, below a certain droplet size the probability of one of these droplets containing a catalytic impurity (i.e., CB seed crystal) able to initiate nucleation is negligibly small. Figure 5 also illustrates the temperature sensitivity of CB seed crystals. For example, at a 1-µm oil droplet size the calculated solids fraction at 15.5 and 15.8°C (based on the number of catalytic impurities determined per unit volume, $N_{imp}$, values of $2.86 \times 10^{16}$ m$^{-3}$ and $2.74 \times 10^{16}$ m$^{-3}$, respectively) is around 0.02, whereas at 14.2°C ($N_{imp} = 2.33 \times 10^{17}$ m$^{-3}$) this value approaches 0.14.

It can be concluded therefore that at 15.5 and 15.8°C very few active seed nuclei would likely be found in emulsion droplets of less than 1 µm diameter. In the case of CB seed crystals, the proportion of seed crystals is itself temperature dependent.
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Figure 5 Cocoa butter solids content plotted as a function of particle diameter crystallized at 14.2 °C (open squares), 15.0 °C (open diamonds), 15.5 °C (open triangles) and 15.8 °C (open circles). (S. Hindle, et al., 2000)

A big impact on crystal nucleation in emulsions arises as a result of the creation of an enormous interfacial surface area. In the example of Table 3, 1 litre of 20% v/v trilaurin oil-in-water emulsion contains 1.2 m² of surface area when the drops have a diameter of 1-mm and this increases to 1.2 x 10⁵ m² when the diameter falls to 10-nm. Under these circumstances nucleation at the interface between the crystallizable, dispersed material and the non-crystallizable continuous phase becomes more probable. For example surfactant molecules such as Tween 20 contain a hydrophobic tail of lauric acid. If the droplets comprise trilaurin, then the surfactant may catalyse crystal growth from the surface (Smith, Cebula, & Povey, 1994; Smith & Povey, 1997; Smith, 1995). Thus the probability of nucleation will be related to the surface interfacial area and hence to the square of droplet diameter. The impact of reducing surface energy has already been examined in Section 2.3
where it is shown that nucleation may become a certainty if the surface energy is lowered sufficiently. In order to obtain a monolayer coverage of Tween 20 (estimated head-group size of 1.3-nm, for a 1227 gm mol wt and a density of 1100 kg m\(^{-3}\) assuming the head group is spherical and tightly packed in a monolayer at the surface of a spherical droplet) in a 20% v/v trilaurin oil-in-water emulsion around 0.16% v/v Tween 20 is required for a 1-µm emulsions, 1.6% for a 0.1-µm emulsion and 16% for a 10-nm emulsion. Not only is the total volume of potential nucleator material increasing as particle size decreases but the volume occupied by the lauric acid moiety which forms the hydrophobic tail of Tween 20 within the trilaurin is also increasing (Figure 6).

![Diagram](image)

**Figure 6** Proportion of total volume of a trilaurin droplet occupied by a surface layer 6–nm deep. This choice of surface layer depth is based on the assumption that the lauric acid moiety of Tween 20 organises a trilaurin layer one unit cell deep.

In such cases (Kaneko, et al., 1999; Katsuragi, Kaneko, & Sato, 2001), we would expect the likelihood of nucleation to increase as particle size decreases, contrary to what is observed for the sodium caseinate stabilized CB emulsions (Figure 5).
Another consequence of the dissolution of the methylene chain into the oil is that the melting point of any solid phase formed is depressed since the surface layer is actually a solution of the methylene chains in the oil (Povey, Hindle, Aarflot, & Hoiland, 2006).

Droplets with sizes smaller than a few µm in water undergo Brownian diffusion. As a result, collisions between droplets that have crystallized with ones that have not may catalyse crystallization (Hindle, Povey, & Smith, 2000). Alternatively the growth of needle crystals out of a droplet and the collision of this crystalline material with other droplets and subsequent nucleation may lead to a process called partial coalescence in which the crystallized droplets are connected together through needle crystals reaching through the aqueous phase (Boode, Bisperink, & Walstra, 1991; Boode & Walstra, 1993a, 1993b; Boode, Walstra, & Degrootmostert, 1993; Brooker, Krog, Dickinson, & Boode, 1993; Hindle, et al., 2000). This is a secondary nucleation process since it cannot occur until primary nucleation, either homogeneous or heterogeneous, has occurred somewhere in the system. This type of crystal growth through an emulsion will be critically dependent on the surface energy of the triple contact (Figure 7). For example, if $\theta$ is small the oil phase (liquid in Figure 7) will
spread into the water and feed the growth of the crystal; on the other hand if $\theta >> 90^\circ$, the liquid oil will not spread into the water at the water/crystal interface and crystal growth will be confined to the oil phase. The contact angle will be affected by surfactant which will therefore influence the crystal morphology in the emulsion.

Figure 7  
In the case of an emulsion the foreign surface will be water, the crystal will be the solid lipid and the liquid the oil from which the fat is crystallizing. $\gamma_s$ is the interfacial tension between the liquid and the foreign surface, $\gamma_{cs}$ the interfacial tension between the crystal and the foreign surface and $\gamma_{lc}$ the interfacial tension between the liquid and the crystal. This produces Young’s relation $\cos \theta = \frac{\gamma_{cs} - \gamma_{sc}}{\gamma_{lc}}$.

Many workers have discussed the complex issues that arise with regard to crystal wetting in emulsions (Bergenstahl & Alander, 1997; Boode, et al., 1991; Boode & Walstra, 1993b; Boode, Walstra, et al., 1993; Johansson & Bergenstahl, 1995a, 1995b; Johansson, Bergenstahl, & Lundgren, 1995; Ogden & Rosenthal, 1994, 1997, 1998). It is worth remarking that the surface energy concept itself may fail when the entities involved (nuclei, surfactant molecules and micelles and oil molecules) are all of comparable sizes in a system which may be kinetically stable but is not in thermodynamic equilibrium.
Surfactant causes a level of solubilisation of the dispersed liquid phase in the continuous phase, enabling transport of the otherwise insoluble liquid between droplets. In the presence of a wide range of particle sizes, a driving force exists which causes the large particles to grow at the expense of the smaller ones. This is called Ostwald ripening (Ostwald, 1897) and may have an impact on crystallization. For example, it can increase the likelihood of coalescence between two droplets, once crystallized and the other not, if they have very different sizes. This same transport mechanism may permit mixing of different oils between droplets of the same size but different composition (Dickinson, Goller, McClements, & Povey, 1991). This may impact on crystallization by alteration of the composition of each droplet. It has also been suggested that guest molecules and other catalytic impurities may be transported between droplets (Herhold, Ertas, Levine, & King, 1999).

The adsorbed layer at the oil-water interface may itself undergo crystallization (Fillery-Travis, 1995; Hianik, 1999) and finally, heat transfer processes between the crystallizing dispersed phase and the continuous phase may greatly alter the polymorphic form and crystal habit (Bedecarrats, Strub, Falcon, & Dumas, 1996; Dumas, Krichi, Strub, & Zeraouli, 1994; Dumas, Strub, & Broto, 1990; Dumas, Strub, & Krichi, 1990; Dumas, Zeraouli, & Strub, 1994; Dumas, Zeraouli, Strub, & Krichi, 1993, 1994; Gibout, et al., 2007); see also Section 2.3.

Room temperature thermal fluctuations generate surface displacements (Wang, Kim, Mir, & Popescu, 2013) of up to 50-nm with frequencies between 1 Hz and 1kHz and these surface fluctuations may have a big influence on nucleation in emulsion droplets with diameters below 100-nm (See Figure 1, Figure 2 and Figure 3).

Emulsions form a very convenient framework within which to study crystallization itself. The earliest example of this is the work of Vonnegut (Vonnegut, 1948). Turnbull and co-workers
formed dispersions of molten metal particles in order to study crystallization in bulk metals (Turnbull, 1950a) and employed normal alkane oils as relatively simple model systems (Turnbull, et al., 1961). As indicated above, by subdividing a bulk fluid into smaller and smaller particles, it is possible to control the probability that a nucleus will be found in a given particle of fluid. A careful study of nucleation kinetics in emulsions can tell us a great deal about the nature of the crystal nucleation. For example, it is possible to distinguish between homogeneous and heterogeneous nucleation and between nucleation at the droplet surface and nucleation which is volume dependent. In the case of heterogeneous nucleation it is possible to determine the nature of the nucleus, its Gibbs free energy for nucleation, the concentration of nuclei and even to get some idea of the size of nuclei and this will be illustrated in the next section.

2.5 Characterizing nucleation by the oil-in-water emulsion crystallization method

2.5.1 Surface and volume nucleation

Nucleation rates in emulsified fats can be determined by measuring the volume fraction of solid fat ($\phi$) as a function of time ($t$). Solid contents in the work quoted in this paper have all been determined by the speed of sound method. (Povey, 1997) and also see (Dickinson, Goller, McClements, Peasgood and Povey, 1990; Dickinson, McClements and Povey, 1991; Dickinson et al., 1991; Coupland, Dickinson, McClements, Povey and de Mimmerand, 1993; Dickinson et al., 1993; Dickinson et al. 1996; Hindle et al., 2000; Hindle et al., 2002; McClements et al., 1990; McClements et al., 1991; McClements, Povey and Dickinson, 1993; Povey, 2001; Povey, Hindle and Smith, 2001; Povey et al., 2006; Povey et al., 2007; Povey et al., 2009). A crystal nucleation event at the droplet surface will have the same effect as an
event in the bulk because following the onset of nucleation complete crystallization of colloidal particles is effectively instantaneous; hence, the crystallization rate is determined by the nucleation rate (Turnbull, 1952; Turnbull, et al., 1961; Turnbull, et al., 1949).

In the case of homogeneous nucleation, in the bulk volume or at the droplet boundary, the isothermal crystallization rate is determined by only one fit parameter, i.e., $J$, the nucleation rate. Taking into account droplet size distribution, the volume fraction of solid fat is

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

where $k$ is the reaction rate constant and $\varphi_d^0$ is the differential volume fraction of droplets with sizes between $d$ and $d + \delta d$. $k$ is expressed as a function of $J$ such that

$$k = Jv_d$$

$v_d$ being the droplet volume or

$$k = Ja_d$$

$a_d$ being the droplet area.

Finally, the surface Gibbs free energy of the nucleating surface can be determined by taking the gradient of a plot of $ln J_0$ against $1/T_\Delta T^2$, and $T_\Delta T^2$ is the difference between the crystallization temperature and the melting temperature of the $\alpha$ polymorph of the nucleating surface.

In Figure 8 an attempt is made to fit volume and surface homogeneous and heterogeneous nucleation models to the measured solid content in a cocoa butter emulsion without success, even when the droplet size distribution is accounted for properly (Hindle, Povey, & Smith, 2002). In circumstances like this it might be concluded that a nucleation rate does not exist.
and empirical modelling is required. (Sear, 2012; Sear, 2013). However, what the data of Figure 8 shows is that nucleation has occurred rapidly in a proportion of droplets and then in the remaining uncrystallised droplets a proportion of collisions with crystallized droplets induces nucleation. In Figure 9, heterogeneous volume particle size distribution models fit the experimental data well, indicating that a proportion of droplets contain catalytic impurities, in this case cocoa butter seed crystals.

Figure 8 Plot of solids against time for a 20.75% vol/vol West African cocoa butter (WACB) oil-in-water emulsion (1.00 wt% sodium caseinate) crystallized isothermally at 15.0°C (■ experimental data). The following nucleation models are fitted based on particle size distribution; ■ volume heterogeneous, × surface heterogeneous, ◇ volume homogeneous and Δ surface homogeneous. (Hindle, et al., 2002)
Figure 9 Plot of solids against time for 20.75% vol/vol WACB oil-in-water emulsions (1.00 wt% sodium caseinate) crystallized at □ 14.2, ◊ 15.0, △ 15.5, and ○ 15.8°C. Heterogeneous volume particle size distribution nucleation models are fitted to experimental data (shown as solid lines) (Hindle, et al., 2002).

For abbreviations see Figure 8.

In inter-droplet heterogeneous nucleation, it is assumed that a collision occurs between a single liquid and a single solid droplet, and, as a reactive pair, that crystallization occurs spontaneously. It is also assumed that both the newly formed and the original solid droplet have equal reactivity. Thus, the change in the fraction of liquid oil $(1 - \varphi)$ remaining after time $t$ is given by:

$$\frac{d(1-\varphi)}{dt} = -k_{ls}\varphi(1 - \varphi)$$

(12)

where $\varphi$ is the volume fraction of solidified oil and $k_{ls}$ is the second-order rate constant giving degree of reactivity. Integration of Equation 12 gives:
\[
\ln \left( \frac{1 - \phi}{\phi} \right) = \ln \left( \frac{1 - \phi_0}{\phi_0} \right) - k_{ls} t \tag{13}
\]

where \( \phi_0 \) is the initial volume fraction of solidified droplets. The rate constant, \( k_{ls} \), can be calculated from the slope of a plot of \( \ln(1 - \phi)/\phi \) against time (Dalgleish & Leaver, 1991; Dickinson, et al., 1993; McClements, Dickinson, et al., 1993; McClements, et al., 1990) and is dependent upon the collision frequency of the droplets and the effectiveness of the collisions that (von Smoluchowski, 1917) promote secondary heterogeneous nucleation.

\[
n_c = \frac{8k_BTn_0^2}{3\eta} \tag{14}
\]

Where \( n_c \) is the number of collisions per second, \( n_0 \) is the total number of droplets per unit volume of emulsion and \( \eta \) is the viscosity of the continuous phase. The fraction of collisions that produce nucleation is then

\[
\frac{1}{W} = \frac{k_{ls}}{n_c/n_0} \tag{15}
\]

And the potential barrier \( E \) to inter-droplet nucleation is

\[
E = k_BT\ln W \tag{16}
\]

The data presented in Figure 8 can be analysed in terms of an initial heterogeneous nucleation event in a minority of droplets (Figure 9) followed by collision induced nucleation using Equations 12, 13 and 14 (Figure 10).
Figure 10  Plot of solids against time for 20.75% v/v WACB oil-in-water emulsions (0.8% v/v Tween 20) crystallized isothermally at $\Delta$, 14.2°C; $\bigtriangleup$, 15.0°C; $\blacklozenge$, 15.5°C; and $\blacklozenge$, 15.8°C. Closed symbols are experimental data and open symbols are heterogeneous volume particle size distribution models fitted over the time period 0–150 min. Insert: Corresponding particle size distribution (Hindle, Povey, & Smith, 2000).

Given the ability to measure nucleation rate in a minority of droplets it is possible to study in detail the catalytic impurities responsible for nucleation and this can be done simply by reducing the size of the droplets until the probability that a catalytic impurity will be found in the droplet is vanishingly small. This has been done for cocoa butter seed crystals (Hindle, et al., 2002) and in many instances in fats the properties of the catalytic impurities are temperature dependent (Kloek, 1998). Alternatively, if every drop contains a catalytic impurity then a heterogeneous model can be fitted to the data.
Solid content data such as that shown in Figure 11 can be plotted on a log-log plot using Equation 13 (Figure 12) from which the surface Gibbs free energy of the nucleating surface. A plot of $\frac{1}{T\Delta^2T}$, a supercooling term, yields a straight line with whose gradient is the surface Gibbs energy and the intercept a pre-exponential term (Zettlemoyer, 1969). This is exemplified in Figure 13 where the rate constant for nucleation is determined for a range of oil/surfactant combinations. Data such as this has been used to assemble the data presented in Table 4 (Discussed in the next section).
Figure 12 Data in Figure 11 plotted against the undercooling term $\frac{1}{T\Delta^2 T}$.
Figure 13 Analysis of a range of solid content vs time data using Equation 13 for a range of crystallizing oils and surfactants. The rate constant $k_0$ is shown on the Figure for each combination of oil and surfactant (Povey, Awad, Huo, & Ding, 2009)
2.5.2 Role of surfactant

Figure 14 Drawing of a triacylglycerol (TAG) liquid droplet with Tween 20 (polyoxyethylene 20 monolaurate) adsorbed at the oil/water interface.

The presence of surfactant may have a number of important consequences for crystallization. As the droplet gets smaller the role of the surface becomes more important and the complexity of the surface will dominate nucleation. Examination of Figure 14 indicates that the surfactant introduces two new interfaces into the droplet, separating the oil phase to a great extent from the aqueous phase. Thermal fluctuations will give rise to large surface displacements (Wang, et al., 2013). The surfactant itself may crystallize (Fillery-Travis, 1995; Hianik, 1999) for example. It is shown above that changes in surface energy may have a profound impact on nucleation (Figure 1, Figure 2, Figure 3) and modification of interfacial energy is discussed in Sections 2.3 and 2.4 above. The hydrophobic moiety may itself catalyse nucleation through chain length matching (Povey, 2001). The melting point of the
interfacial layer will be depressed through the formation of a solid solution of the hydrophobic moiety and the oil.
Table 4 List of the kinetic barrier properties of emulsions containing different surfactants, in units of $k_B T, E/k_B T$, and the probability that a collision event will lead to nucleation ($w^{-1}$) for a variety of oils, surfactants and particle sizes. The kinetic data were obtained through measurement of collision mediated nucleation. Crystallisation temperature is defined as the temperature at which the solids fraction is noted to rise above zero, at a given cooling rate. Undercooling is the difference between the bulk melting point and the crystallisation temperature. The cooling rate is 1 °C/min in all experiments apart from the cocoa butter, in which case the experiments were carried out isothermally, and the 123-nm Cafion-stabilised emulsion, which was cycled first at 1 °C/min then at 12 °C/min. The cocoa butter data (WACB) is also shown in Figure 13 and the longer time data represents collision mediated nucleation whilst the short time data is a result of seed crystal nucleation.

§ - data unavailable because nucleation was too fast.

± Data from a microemulsion.

† These data are consistent with dissolution of the surfactant (PGE) in the bulk of the oil.

$ The nucleation in this sample occurred too quickly to measure.
As colloid sizes reduce whilst keeping the dispersed phase volume constant a point is reached at which nucleation rates begin to rise again, having fallen from the bulk value due to emulsification and the reduction in the numbers of catalytic impurities per droplet. This rise is due (a) to increased surfactant and lower surface tension; (b) rapidly increasing inter-droplet collision rates; (c) van der Waals attraction between small droplets and larger surfaces, encouraging aggregation and an increased likelihood of inter-droplet nucleation. The details of these processes have still to be demonstrated experimentally. Nevertheless, a great deal of quantitative information regarding surfactants and the kinetic barriers that they present can be elicited (Table 4). A number of interesting features of the data may be highlighted. Firstly in the case of the different nucleation rates for West African Cocoa Butter (WACB – Figure 13 and Table 4), at short times (seconds) the rate is controlled by the presence of seed crystals in a minority of the droplets and at later times (hours) by collision mediated nucleation between those droplets that do not contain seed crystals and those that do and crystallised quickly. Secondly, Povey et al, 2009 suggest that the polyglycol ester L-7D (PGE) actually dissolves into the n-hexadecane oil phase, causing extensive surface melting during the heating phase arising from melting point depression in the mixture of oil and surfactant. Finally, the crystallisation temperature of the micro-emulsion is much higher than that of the emulsions and correspondingly, the undercooling is much lower. This suggests that nucleation is occurring at a higher rate in the micro-emulsion.

3 Conclusion

Crystal nucleation in food colloids is a complex subject, however here it is shown that classical nucleation theory provides a sound theoretical basis with which to understand the important phenomena. Emulsion crystallization and the measurement of solid content
provides a methodology whereby very many characteristics of crystal nucleation may be quantified – surface Gibbs energy for nucleation, determination of the nature of the nucleation (volume or surface homogeneous or volume or surface heterogeneous, interdroplet collision, partial coalescence, energy barrier to coalescence (Table 4) and combinations thereof). As colloidal particles get smaller many new physical phenomena appear which have an impact on nucleation, these phenomena are only partially understood and a great deal of careful and detailed scientific work will be needed to realise the full potential of emulsion crystallization in food colloids.

4 Acknowledgements

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during the transformations inside an emulsion .2. Melting of the crystallized droplets.

mechanism of formation of spherical grains obtained by the quasi-emulsion

Stabilized by 2 Physiological Surfactants - L-Alpha-Phosphatidylcholine and Sodium


Fredrick, E., Van de Walle, D., Walstra, P., Zijtveld, J. H., Fischer, S., Van der Meeren,

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For Food Hydrocolloids: Crystallization in colloids


• Speed of sound measurement is very sensitive to crystal nucleation.
• Isothermal nucleation rates are measured in a range of oil-in-water emulsions.
• Classical nucleation theory explains well all the measured data.
• Lowering interfacial energies may dramatically raise surface nucleation rates.
Figure 4
Click here to download high resolution image
Figure 10

Click here to download high resolution image
Figure 12

The graph shows the relationship between the supercooling term (in $10^{-5} \text{K}^{-3}$) and the logarithm of the initial nucleation rate ($\ln J_0$ in $\text{m}^3\text{s}^{-1}$). The linear regression equation is given by:

$$y = -0.1333x + 40.028$$

with a coefficient of determination $R^2 = 0.9505$. The data points are represented by an X symbol.
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**Table 3**
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1 Tables

Table 1 Entropy and enthalpy of fusion for some triacylglycerols and n-alkanes (Wesdorp, 1990). MMM – trimyristin, PPP – tripalmitin; StStSt – tristearin. .................................................. 14

Table 2 Melting temperature and enthalpies of fusion of pure triacylglycerols in polymorph i, together with the composition of fully hydrogenated palm oil (Wesdorp, 1990) ................. 14

Table 3 Particle volume, area and number together with estimates for single molecular layer coverage of emulsion particle with Tween 20, for 1 litre of 20 % v/v trilaurin oil-in-water emulsion. The choice of surface layer depth is based on the assumption that the lauric acid moiety of Tween 20 organises a trilaurin layer one unit cell deep. ........................................... 22

Table 4 List of the kinetic barrier properties of a range of emulsions containing different surfactants, in units of $k_BT, E/k_BT,$ and the probability that a collision event will lead to nucleation ($w^{-1}$) for a variety of oils, surfactants and particle sizes. The kinetic data were obtained through measurement of collision mediated nucleation. Crystallisation temperature is defined as the temperature at which the solids fraction is noted to rise above zero, at a given cooling rate. The undercooling is the amount by which the crystallisation temperature is reduced below the bulk melting point. The cooling rate is 1 °C/min in all experiments apart from the cocoa butter, in which case the experiments were carried out isothermally, and the 123-nm Caflon-stabilised emulsion, which was cycled first at 1 °C/min then at 12 °C/min. The cocoa butter data is also shown in Figure 13 and the longer time data represents collision mediated nucleation whilst the short time data is a result of seed crystal nucleation.

§ - data unavailable because nucleation was too fast.

± Data from a microemulsion.

† These data are consistent with dissolution of the surfactant (PGE) in the bulk of the oil.

$ The nucleation in this sample occurred too quickly to measure.

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1 Figure Captions

Figure 1 Plot of surface and volume energy as a function of particle radius for a trilaurin droplet, together with the number of molecules per droplet and the energy of formation of the nucleus. The surface tension in this plot is 30 mN/m and the enthalpy change of the trilaurin into the alpha form is taken as 167 J/kg. ................................................................................................. 8

Figure 2 Plot of surface and volume energy in units of $k_B T$ as a function of particle radius for a trilaurin droplet, together with the number of molecules per droplet and the energy of formation of the nucleus. The surface tension in this plot is 1 mN/m and the enthalpy change of the trilaurin into the alpha form is taken as 167 J/kg. ................................................................................................. 10

Figure 3 Plot of surface and volume energy in units of $k_B T$ as a function of particle radius for a trilaurin droplet, together with the estimated attachment energy per molecule in units of $k_B T$. The surface tension in this plot is 1 mN/m and the enthalpy change of the trilaurin into the alpha form is taken as 167 J/kg. ................................................................................................. 11

Figure 4 Velocity of sound and density plotted against temperature for a 20 vol. % n-hexadecane oil-in-water emulsions containing 2 wt % Tween 20. Closed circles, velocity on cooling; open circles, velocity on heating; closed squares, density on cooling; open squares, density on heating. Average volume-surface diameter of 800 nm. taken from (E. Dickinson, et al., 1993) ........................................................................................................................................ 18

Figure 5 Cocoa butter solids content plotted as a function of particle diameter crystallized at 14.2 °C (open squares), 15.0 °C (open diamonds), 15.5 °C (open triangles) and 15.8 °C (open circles). (S. Hindle, et al., 2000) ........................................................................................................................................ 20
Figure 6 Proportion of total volume of a trilaurin droplet occupied by a surface layer 6–nm deep. This choice of surface layer depth is based on the assumption that the lauric acid moiety of Tween 20 organises a trilaurin layer one unit cell deep. ........................................21

Figure 7 In the case of an emulsion the foreign surface will be water, the crystal will be the solid lipid and the liquid the oil from which the fat is crystallizing. \( \gamma_{ls} \) is the interfacial tension between the liquid and the foreign surface, \( \gamma_{cs} \) the interfacial tension between the crystal and the foreign surface and \( \gamma_{lc} \) the interfacial tension between the liquid and the crystal. This produces Young’s relation \( \cos \theta = \gamma_{ls} - \gamma_{cs} - \gamma_{lc} \). ..........................................................23

Figure 8 Plot of solids against time for a 20.75% vol/vol West African cocoa butter (WACB) oil-in-water emulsion (1.00 wt% sodium caseinate) crystallized isothermally at 15.0°C (■ experimental data). The following nucleation models are fitted based on particle size distribution; □ volume heterogeneous, × surface heterogeneous, ◇ volume homogeneous, and △ surface homogeneous. (Hindle, et al., 2002) ..........................................................................................................................27

Figure 9 Plot of solids against time for 20.75% vol/vol WACB oil-in-water emulsions (1.00 wt% sodium caseinate) crystallized at □ 14.2, ◇ 15.0, △ 15.5, and ○ 15.8°C. Heterogeneous volume particle size distribution nucleation models are fitted to experimental data (shown as solid lines) (Hindle, et al., 2002). For abbreviation see Figure 8. ..........................................................28

Figure 10 Plot of solids against time for 20.75% v/v WACB oil-in-water emulsions (0.8% v/v Tween 20) crystallized isothermally at ○, 14.2°C; △, 15.0°C; ◇, 15.5°C; and □, 15.8°C. Closed symbols are experimental data and open symbols are heterogeneous volume particle size distribution models fitted over the time period 0–150 min. Insert: Corresponding particle size distribution (S. Hindle, M. Povey, & K. Smith, 2000)..........................................................30

Figure 11. Plot of solids against time in which the first 10 minutes of the data in Figure 10 is ignored. A heterogeneous nucleation model now fits the data very well. (20.75% v/v WACB
oil-in-water emulsions (0.8% v/v Tween 20) crystallized isothermally at $\circ$, 14.2°C; $\triangle$, 15.0°C; $\diamond$, 15.5°C; and $\Box$, 15.8°C. Closed symbols are experimental data.) (S Hindle, et al., 2000)

Figure 12 Data in Figure 11 plotted against the undercooling term $1T\Delta T$ .................................................................32

Figure 13 Analysis of a range of solid content vs time data using (13, for a range of crystallizing oils and surfactants. The rate constant $k_{ls}$ is shown on the Figure for each combination of oil and surfactant (Povey, Awad, Huo, & Ding, 2009) ..................................................33

Figure 14 Drawing of a triacylglycerol (TAG) liquid droplet with Tween 20 (polyoxyethylene 20 monolaurate) adsorbed at the oil/water interface. .................................................................................34