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Fractal Growth of Milk Fat Crystals Is Unaffected by Microstructural Confinement

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Ⓦ This paper contains enhanced objects available on the Internet at http://pubs.acs.org/crystal.

ABSTRACT: The fractal dimension of growing milk fat crystal clusters was determined for samples 20 and 170 μm thick. The mass fractal dimensions for the thin and thick samples were not significantly different ($P > 0.05$), with an average value of $D = 1.44$. This work demonstrates that milk fat crystal growth is fractal in nature and that this fractal growth is not affected by confinement at the microstructural level in the range 20−170 μm.

Fractal objects are best known as self-similar patterns that cannot be explained by classical geometry. Fractals are scale invariant, meaning that an object will look statistically similar at different length scales. For example, if a piece of a fractal object is cut out and magnified, the resulting object will, on average, look the same as the original one. This so-called self-similarity is characteristic of fractal objects. To determine the fractal dimension of a growing object,[1] it is necessary to measure the variation in the object's volume (V) with its linear size (R): $V(R) \sim R^D$. Here D is typically a noninteger number called the fractal dimension, which is smaller than the Euclidean dimension (d) of the space the fractal is embedded in: $D < d$. If the space is completely or homogeneously filled, then $D = d$. The volume term can be replaced with mass of that cluster (M), assuming, as is usual in the field of mass fractals, that $M \sim V$.

If a crystal cluster grows in a fractal fashion, then M will be proportional to time (t); namely, $M \sim t$. This linear mass accumulation arises if the amount of mass accrued in time is proportional to the number of random steps, $j(t)$, performed by the diffusing molecules:[2] $j(t)$ is directly proportional to t. For fractal objects, the cluster mass scales to the cluster diameter (ξ) as $M \sim \xi^D$. Consequently, the diameter of the growing cluster scales in time as $\xi \sim t^{1/D}$. Thus, if an object obeys the linear mass deposition condition, and its growth is fractal in nature, a log−log plot of ξ vs t will be linear with a slope equal to $1/D$. For the case where the growth of the cluster is Euclidean, the fractal dimension would equal d, and its value would be 2 or 3, depending on the type of crystal growth mechanism (two- or three-dimensional). The slope of the log−log plot of ξ vs t for these two cases would then be 1/2 or 1/3.

For example, Rothschild studied the electrodeposition of silver. The radius (r) of the growing deposits was measured over time (t) and plotted on a log−log scale. The fractal dimension for silver agglomeration was then calculated from the inverse of the slope. The results of this graph method were in agreement with the theoretical value for the fractal dimension for silver agglomeration[2] of $D = 2.53$.

Crystallization of materials under spatial confinement has been found to change their bulk properties. For example, materials confined to nanoscale dimensions display properties that differ from those of the corresponding unconfined case, due to their reduced dimensionality and large interfacial effects.[3] Phase transition pressures and temperatures are shifted from their bulk values, and new phases can appear due to surface forces. A study on polymer confinement found that the crystallinity was greatly reduced and the crystallization rate was much slower under confinement.[4] Moreover, heterogeneous nucleation on the surface governed the crystallization process.

The impetus for this project comes from the recent experimentally obtained relationship between the nucleation rate (J) and the box-counting fractal dimension (D) of cocoa butter crystal networks;[5] namely

$$D - D^* = \beta \ln J \tag{1}$$

where D^* is the fractal dimension of the network at $J = 1$. This equation could be obtained using the relationships $N = C\xi^D$ and $\xi = kt^{1/D}$ by assuming $M \sim t$ and $M \sim \xi^D$), where N is the number of particles within a fractal cluster, C is a system-specific proportionality constant, k is the rate constant for cluster growth, M is the mass of the fractal cluster, ξ is the diameter of the fractal cluster, and D is the mass fractal dimension. Combining these expressions, one obtains $N = Ck^Dt$, where the differential of N with time ($J = \partial N/\partial t$) has the form $J = Ck^D$. Taking the natural log of the above expression yields

$$\ln J = \ln C + D \ln k \tag{2}$$

Upon rearrangement, eq 2 can be expressed as eq 1, where $\beta = 1/\ln k$, and $D^* = \ln C/\ln k$.

Ultimately, this expression can be related to the free energy of nucleation using the Fisher−Turnbull equation. The nucleation rate (J) is related to the free energy of nucleation (ΔG_n) by

$$\ln J = \alpha - \frac{\Delta G_n}{k_B T} \tag{3}$$

where T is the absolute temperature (K) and k_B is Boltzmann's constant (J mol^{-1} K^{-1}).

The parameter α includes the contributions from the free energy of diffusion (ΔG_d), which is considered to be constant during nucleation, and has the form

$$\alpha = \ln\left(\frac{Nk_B T}{h}\right) - \frac{\Delta G_d}{k_B T} \tag{4}$$

Combining eqs 1 and 4 therefore leads to the expression

$$D - D^* = \kappa - \beta\frac{\Delta G_n}{k_B T} \tag{5}$$

where $\kappa = \alpha\beta$. This equation predicts that the excess mass

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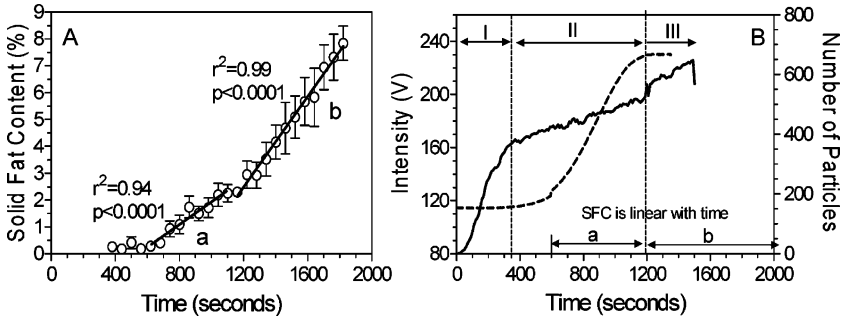

Figure 1. (A) Changes in solid fat content (SFC) with time for milk fat cooled to 21 °C. (B) Changes in the number of particles (—) and scattered light intensities (- - -) over time for milk fat cooled to 21 °C.

fractal dimension ($D - D^*$) of a fat crystal network is a function of the nucleation energetics of the crystallizing system.

The objectives of this study were to determine whether the growth of fat crystals is fractal in nature and whether the thickness of the crystallizing layer can affect the dimensionality of the growth process as well as final microstructure.

Anhydrous milk fat was crystallized under constant conditions using two thicknesses, 20 and 170 μm. The milk fat was heated to 80 °C for 20 min before a drop was placed on a preheated (80 °C) glass microscope slide and covered by a preheated (80 °C) glass coverslip. The slides were cooled under the microscope at 5 °C/min to 21 °C.

Polarized micrographs were obtained for single milk fat crystal clusters and nucleation studies using a 40× objective lens and a 10× objective lens, respectively, on an Olympus BH microscope (Olympus, Tokyo, Japan). The microscope was equipped with an XC75 CCD camera and LG-3 capture board (Scion Corp., Frederick, MD). Scion Image 1.62 was used to take PLM at specific time intervals, average each image over 16 frames, and subtract off the background. The images were manually thresholded using the same value for each image in that particular run. The threshold level was determined by the value that best distinguished the grayscale images from the background. Once thresholded, the images were inverted and the diameter was manually measured in ImageJ (image processing and analysis in Java).

Phase transition analysis recorded the changing intensity of light in 2 s intervals of the crystallizing milk fat. The data storage began once the sample completed cooling from 60 to 21 °C at 5 °C/min. The Automatic Petroleum Analyzer (Phase Technology, Richmond, Canada) was used for this purpose. Solid fat content (SFC) of the crystallizing milk fat was measured to verify the approximation of mass proportional to time. The SFC tubes were cooled with the equivalent cooling rate to milk fat on the glass slides from 80 to 21 °C, and then the SFC was measured every 30 s with pulsed nuclear magnetic resonance (pNMR) using a Bruker mq20 series NMR analyzer (Bruker, Milton, Ontario, Canada).

The first approximation to calculating the fractal growth of a milk fat crystal cluster assumes the mass of the growing cluster is proportional to the time ($M \sim t$). This was verified using pNMR of milk fat cooled under the same conditions as for milk fat on a glass slide. The pNMR measurements, shown in Figure 1A, have a linear region between 600 and 1200 s (a) and between 1200 and 1800 s (b) from when the milk fat was cooled to 21 °C.

These two linear regions suggest that mass deposition is directly proportional to time after 600 s. However, this linearity may have existed at earlier times, in the region where the pNMR spectrometer was not sensitive enough to detect small amount of solids in the sample. Figure 1B shows the existence of three major growth regions. The first region (I) corresponds to the time period where nucleation took place. No SFC was detected in this region, due to the low concentration of solids. The second region (II) shows a slower increase in the number of nuclei. Here, the energy in the system was mostly devoted to crystal growth. It can be noted that the time dependence of the SFC in Figure 1A and the time dependence of the scattered light intensity (Figure 1B) are almost identical. Thus, both of these methods are more sensitive to crystal growth than nucleation events. The small but abrupt increase in the number of particles at the boundary of regions II and III corresponds to the time at which the transition between regions a and b took place (Figure 1A). This jump in the number of particles may have been caused by a polymorphic transformation in the material or may be due to the crystallization of a particular fraction with different chemical composition: i.e., a different phase. The scattered light intensity signal becomes saturated in region III; however, crystal growth is still occurring at this point, as shown in region b of the SFC curve. Mass deposition in this region is also linear in time. The sudden decrease in the number of particles observed in region III is due to the crystal impingement (i.e., they touch), where their merging leads to an effective reduction in the number of identifiable crystals in the sample. Figure 1 illustrates that the mass of the growing crystal clusters is proportional to crystallization time after 600 s at 21 °C. The linear region used for calculating the slope in the following analyses went from 600 to 1200 s, representing region a of the SFC curve.

Polarized light micrographs of milk fat clusters crystallized at 20 °C in 20 and 170 μm sample thicknesses are shown in Figure 2.

The 20 μm thick sample (Figure 2A) is more defined and more sharply focused than the 170 μm sample (Figure 2B). The thick sample appeared hazy due to the extra mass in the z axis of the specimen. Material above and below the focal plane causes haze due to the scattering of light from crystallites. The sizes of the crystal clusters were generally similar for thick and thin samples; however, there were many more movement and agglomeration processes taking place in the 170 μm samples. Movies of the growing thick and thin crystal clusters can be accessed via the link in the caption to Figure 2.

The log−log plot of the diameter of the cluster versus time for the thick and thin samples was linear in time from 170 s after reaching 21 °C onward (Figure 3). The slope of each line was calculated using linear regression in the region of time from 600 to 1200 s, since this satisfies the linear mass deposition condition $M \sim t$ (for all linear regressions, $0.96 < r^2 < 0.99$). However, the entire range was linear. The values obtained using the entire range were not significantly different from those in the 600−1200 s range. The dimensionality of growth is fractal in each

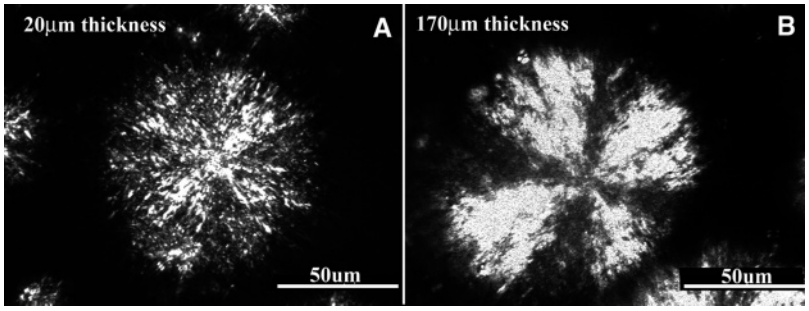

Figure 2. Polarized light micrographs of 20 μm (A) and 170 μm (B) samples of milk fat.

Ⓦ Polarized light microscopy movies in QuickTime format of the growth of milk fat crystal clusters in Ⓦ 20 μm and Ⓦ 170 μm samples are available.

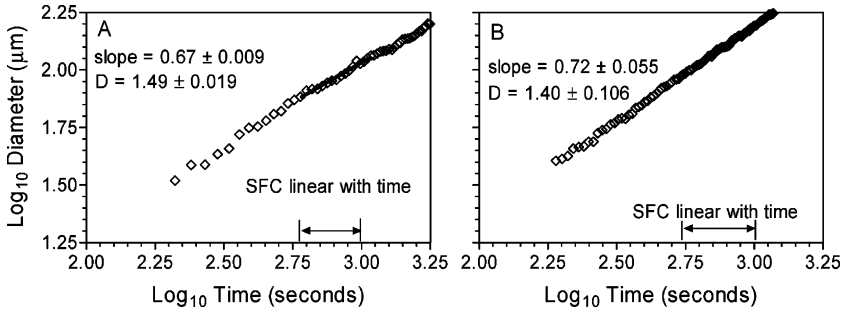

Figure 3. Log−log plot of diameter of the cluster versus time for 20 μm (A) and 170 μm (B) samples of milk fat. Values reported correspond to the mean of standard errors of three replicates.

graph, suggesting milk fat crystals grow in a fractal fashion. The average fractal dimensions for the 20 and 170 μm samples were 1.49 ± 0.019 and 1.40 ± 0.106, respectively. There was more variability in the 170 μm samples, which was expected because of material movement and haze in the images. There were, however, no statistically significant differences between the fractal dimensions obtained at the two thickness ($P > 0.05$). The average fractal dimension was $D = 1.44$. Moreover, microstructural confinement did not affect the growth fractal dimension for milk fat crystal clusters.

To conclude, we have shown that milk fat crystal clusters grow in a fractal fashion, and this growth was unaffected by microstructural confinement in the range 20−170 μm. This includes the usual range of sample thicknesses used in microscopy studies of crystallizing materials.

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