Structure and Mechanical Properties of Fat Crystal Networks

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What is this? How is it different from this?

margarine olive oil
So, what is a fat after all?

- *To the chemist and chemical engineer:* a complex mixture of high melting point triacylglycerols in low melting point triacylglycerols with complex phase behavior – all can be explained from knowledge of molecular composition and phase behavior (SFC and phase diagrams are king…)

- *To the crystallographer:* a metastable polycrystalline material prone to recrystallization and fractionation – all can be explained from knowledge of polymorphism (XRD is king and DSC is queen…)

- *To the colloidal scientist:* a colloidal gel (or colloidal crystal) composed of a network of polycrystalline fat particles which trap liquid oil within – all can be explained from knowledge of the mesoscale structure, i.e., colloidal sizes, interactions, distribution (rheometer is king and microscope is queen…)

- *To the consumer:* something that makes you fat, but tastes good (cookies and chocolate rule…)

- All agree on the last point only

Factors affecting the texture of fats and fat-structured foods

1. Solid fat content
2. Primary crystal habit (polymorphism)
3. Nano and Microstructure  
   a. crystallite morphology and size  
   b. spatial distribution of network mass
4. Interparticle interaction forces
### What controls hardness?

<table>
<thead>
<tr>
<th>Temperature (ºC)</th>
<th>G’ (Pa)</th>
<th>SFC (%)</th>
<th>F_y (N)</th>
<th>K (N/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>2.19E+07^a</td>
<td>90.5^a</td>
<td>602^a</td>
<td>231^a</td>
</tr>
<tr>
<td>15</td>
<td>2.64E+07^b</td>
<td>90.5^a</td>
<td>593^a</td>
<td>223^a</td>
</tr>
<tr>
<td>20</td>
<td>1.63E+07^c</td>
<td>80.5^b</td>
<td>312^b</td>
<td>90^b</td>
</tr>
<tr>
<td>24</td>
<td>4.08E+07^d</td>
<td>60.0^c</td>
<td>344^b</td>
<td>96^b</td>
</tr>
</tbody>
</table>

Means with a common superscript within a column are not significantly different (P>0.05).

![Diagram of fat structures](image_url)

- **Floc**: Helps increase hardness
- **Cluster**: Helps increase hardness
- **SFC**: Stabilizes fat structures
- **Domain Lamella**: Affects hardness
- **D**: Single crystallite
- **d**: Bulk fat

What controls hardness? The hardness is controlled by the structures and interactions of fats, such as the flocs, clusters, and crystallite domains. The specific interactions and their implications on hardness are complex and depend on the temperature and other factors.
Triacylglycerols—Molecular Structure

Triacylglycerol = glycerol + 3 fatty acids
Fatty Acids and Triacylglycerol Types

Fatty Acids
- Long-Chain Saturated: 14:0, 16:0, 18:0
- Medium-Chain Saturated: 8:0, 10:0, 12:0
- Short-Chain Saturated: 4:0, 6:0
- Mono- Unsaturated: 18:1
- Poly-Unsaturated: 18:2, 18:3, 22:6
- Geometric Isomers: (cis vs. trans)
- Positional Isomers: (ω-3,6,9)

Triacylglycerols
- Simple Homogeneous
- Mixed
- Complex and varied positional distribution of fatty acids on TAG molecule.

Triacylglycerol Crystallization Process

\( T > T_m \)
- Isotropic Melt
- Decrease temperature below melting point of solid into metastable region (undercooled or supersaturated)

\( T < T_m \)
- Crystalline Solid
Crystallization Process – more to the story?

Isotropic Melt $\rightarrow$ Structured Liquid?

Amorphous Solid? $\rightarrow$ Crystalline Solid

Gibbs-Thompson Equation

$$\Delta G_n = A_n \gamma - V_n (\Delta \mu / V_m)$$

Diagram:
- $\sigma = 30 \text{ mJ m}^{-2}$
- $\Delta G_n = 150 \text{ J mol}^{-1}$
- $V_n = 8.5 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}$
- $\Delta G_n = 1.46 \times 10^{-14} \text{ J/nucleus}$
- $r_c = 3.4 \times 10^{-7} \text{ m}$
Long Spacings (001)

2L

Long Spacings (001)

3L
Polymorphism

$\rightarrow$ Same chemical composition but different solid-state structure

Melt-mEDIATE and/or solid-state phase transitions (polymorphic transformations)

Lower melting point  $\rightarrow$ Higher melting point
Lower density  $\rightarrow$ Higher density
Lower stability  $\rightarrow$ Higher stability
The Crystalline State – The Subcell
(Polymorphism)

Characteristic short spacings:

- \( \beta \): 4.6Å (Triclinic)
- \( \beta' \): 3.8Å and 4.2Å (orthorhombic \( \perp \))
- \( \alpha \): 4.15Å (Hexagonal)

Stability, melting point and packing density:

\[ \alpha < \beta' < \beta \]

Also: \( \gamma \) (orthorhombic \( \perp \)), \( \delta \) and several \( \beta' \) polymorphs

Subforms possible
Rigaku Multiflex
\[ n\lambda = 2d \sin \theta \]
Differential Scanning Calorimeter
TA Q1000
### Cocoa Butter

- Predominant fatty acids include: palmitic acid (16:0), stearic acid (18:0) and oleic acid (18:1)

- Mainly composed of symmetrical triacylglycerols POP, SOS and POS

**Triacylglycerol (TAG) Molecule**

**Double- and triple-chain-length structures**
Table 3: Fatty Acid Composition of Cocoa Butter

<table>
<thead>
<tr>
<th>Fatty Acid</th>
<th>Cocoa Butter (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16:0</td>
<td>28.1 ± 0.45a</td>
</tr>
<tr>
<td>18:0</td>
<td>34.4 ± 0.47a</td>
</tr>
<tr>
<td>18:1</td>
<td>32.6 ± 0.28b</td>
</tr>
<tr>
<td>18:2</td>
<td>2.81 ± 0.06a</td>
</tr>
<tr>
<td>18:3 and 20:0</td>
<td>1.95 ± 0.21a</td>
</tr>
</tbody>
</table>

aData represents the average of seven replicates ± standard error.

Table 4: Triacylglycerol Composition of Cocoa Butter

<table>
<thead>
<tr>
<th>Triacylglycerol (carbon number)</th>
<th>Experimental Results (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>19.8 ± 0.27b</td>
</tr>
<tr>
<td>52</td>
<td>47.6 ± 0.21b</td>
</tr>
<tr>
<td>54</td>
<td>31.4 ± 0.33b</td>
</tr>
<tr>
<td>56</td>
<td>1.11 ± 0.13b</td>
</tr>
</tbody>
</table>

bData represents the average of four replicates ± standard error.

Table 6.1 Triglyceride composition (%) of cocoa butters from different growing areas
(Reprinted with the permission of Loders Croklaan)

<table>
<thead>
<tr>
<th>Triglyceride</th>
<th>Brazil</th>
<th>Ghana</th>
<th>Malaysia</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSS</td>
<td>1.0</td>
<td>1.4</td>
<td>2.3</td>
</tr>
<tr>
<td>SOS</td>
<td>63.7</td>
<td>76.8</td>
<td>84.0</td>
</tr>
<tr>
<td>SSO</td>
<td>0.5</td>
<td>0.4</td>
<td>0.5</td>
</tr>
<tr>
<td>SLS</td>
<td>8.9</td>
<td>6.9</td>
<td>6.8</td>
</tr>
<tr>
<td>SOO</td>
<td>17.9</td>
<td>8.4</td>
<td>5.1</td>
</tr>
<tr>
<td>OOO</td>
<td>8.0</td>
<td>6.1</td>
<td>1.3</td>
</tr>
</tbody>
</table>

S = Saturated fatty acids (mainly palmitic and stearic), O = oleic acid, L = linoleic acid.
Table 2: Characteristic short spacings as determined by XRD for the various polymorphic forms of cocoa butter (Larsson, 1994).

<table>
<thead>
<tr>
<th>Polymorphic Form</th>
<th>Short Spacings (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma ) (sub-( \alpha ))</td>
<td>3.87 (m), 4.17 (s)</td>
</tr>
<tr>
<td>( \alpha ) (II)</td>
<td>4.20 (vs)</td>
</tr>
<tr>
<td>( \beta ) (III)</td>
<td>3.87 (vw), 4.20 (vs)</td>
</tr>
<tr>
<td>( \beta ) (IV)</td>
<td>3.75 (m), 3.88 (w), 4.13 (s), 4.32 (s)</td>
</tr>
<tr>
<td>( \beta ) (V)</td>
<td>3.65 (s), 3.73 (s), 3.87 (w), 3.98 (s), 4.22 (w), 4.58 (vs), 5.13 (w), 5.38 (m)</td>
</tr>
<tr>
<td>( \beta ) (VI)</td>
<td>3.67 (s), 3.84 (m), 4.01 (w), 4.21 (vw), 4.53 (vs), 5.09 (vw), 5.37 (m)</td>
</tr>
</tbody>
</table>

The relative intensity: very strong (vs), strong (s), medium (m), weak (w) or very weak (vw).

Table 1: Polymorphic forms of cocoa butter as determined by various research groups

<table>
<thead>
<tr>
<th>Wille and Lutton (1966)</th>
<th>Merken and Vaeck (1980)</th>
<th>as reported by van Malssen et al. (1996a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymorphic Form (Tm (°C))</td>
<td>Polymorphic Form (Tm (°C))</td>
<td>Polymorphic Form (Tm (°C))</td>
</tr>
<tr>
<td>I (17.3)</td>
<td>( \gamma ) (16-18)</td>
<td>( \gamma ) (-5-+5)</td>
</tr>
<tr>
<td>II (23.3)</td>
<td>( \alpha ) (20.7-24.2)</td>
<td>( \alpha ) (17-22)</td>
</tr>
<tr>
<td>III (25.5)</td>
<td>( \beta )' (26-28)</td>
<td>( \beta )' (20-27)</td>
</tr>
<tr>
<td>IV (27.5)</td>
<td>( \beta ) (33.7-34.9)</td>
<td>( \beta ) (29-34)</td>
</tr>
<tr>
<td>V (33.8)</td>
<td>( \beta ) (33.7-34.9)</td>
<td>( \beta ) (29-34)</td>
</tr>
<tr>
<td>VI (36.3)</td>
<td>( \beta ) (33.7-34.9)</td>
<td>( \beta ) (29-34)</td>
</tr>
</tbody>
</table>
SAXS+WAXS+DSC Setup

Sample: 20 μl
Lin. glass Capillary (I = 1.4 ± 0.1 mm)

X-Ray
A = 1.5 Å

Calorimeter

Linear Detector
Wide angles
8 < 2θ < 13°

Linear Detector
Small angles
0 < 2θ < 5°

Cobalometre Control
Electronic Counting

Short spacings

Longitudinal
Long spacings

Techniques de caractérisation 2. DSC

Triglyceride Polymorphism
PPO
1,2-diPalmitoyl, 3-Oleyl glycerol:
Monotropic transitions

Temperature (°C)

Time (min)

0 5K/min
1K/min

120 0 -120

Thermal flux (mV)

endo
An example of lipid polymorphism: PPO Triacylglycerol

- **Unstable form**
  - α (3L) 75 Å
  - 20°C

- **Intermediate form**
  - β<sub>y</sub> (2L) 39-41 Å
  - 30°C

- **Stable form**
  - β<sub>y</sub> (3L) 64-66 Å
  - 21°C

- **Liquid**
  - 35°C

Ollivon et al., 2005, NATAS proceedings + J. Therm. Anal. and Cal. in press

Montecellati lab 2007
Microcalix

T range: -30 to +230°C
Scan rates: 0.01–20°C/min
Sample: 0.5–30 mg (µl)
Sample change: 2 sec.

Coupled synchrotron time-resolved XRD/DSC (SAXS and WAXS)
Insertion of a calorimeter cell on D22 beamline (LURE, Orsay, France)


Calorimeter Cell

X-Rays

Sample

O.D.= 1.4mm

JCAT Montpellier juin 2007
Phase Behavior

Fats are mixtures of lipids, predominantly triacylglycerols, but also contain minor polar components such as diacylglycerols, monacylglycerols, free fatty acids, phospholipids, sterols, etc.

Continuous solid solution (mixed crystals), eutectic, monotectic (partial solid solution), compound formation phase behaviors are commonly observed

Conditions for fat compatibility

1. Equivalent thermal properties
   Melting points
   Melting and solidification ranges
   SFC
2. Similar molecular size, shape and packing
   To allow isomorphous replacement or formation of a single lattice unit in mixtures
3. Similar polymorphism
   Transformation from stable to unstable forms should occur as readily for binary mixtures as with individual components
Continuous solid solution – compatible

Eutectic – incompatible (minima)

Monotectic – significant amounts of lower melting component solubilized by higher melting component. Eutectic point close to m.p. of lower melting component; partial solid solution

Compound formation (maxima)

Liquidus lines predicted by Hildebrand equation

\[ T = \left( \frac{R \ln(x_i)}{\Delta H} - \frac{1}{T_m} \right)^{-1} \]

\[ \ln(x_i) = \frac{\Delta H_i}{R} \left( \frac{1}{T_m} - \frac{1}{T} \right) \]
Continuous solid solution: SSS/ESS, POS/SOS

Eutectic behavior: PPP/SSS, EEE/SOS, POS/PSO, PPP/LLL, PPP/SOS

Compound formation: SSO/SOS, POP/OPO

Monotectic behavior: SSS/OOO, SSS/LLL, PPP/POP, SSS/SOS

Bruker Minispec pNMR
Magnetization Signal Intensity vs. Pulse Time (μs)

Solid – liquid components (total hydrogen content)
Liquid component only

Isosolid Diagrams (Phase Diagrams?)

SFC vs. temperature profile for AMF/Cocoa Butter

- 0% AMF
- 10% AMF
- 20% AMF
- 30% AMF
- 40% AMF
- 50% AMF
- 60% AMF
- 70% AMF
- 80% AMF
- 90% AMF
- 100% AMF
SFC influences hardness…

- **Composition (%w/w milkfat fraction)**
- **Dropping Point (°C)**
- **Tempering Time (hours)**
- **Penetration Depth (1/10 mm)**
Ideal Solubility – Fact or fiction?

\[ \ln(x_i) = \Delta H_i / R \left(1/T_m - 1/T \right) \]

Polymorphism and Microstructure
The α form

A

B

C

D
The $\beta'$ form

The $\beta$ form
Cocoa butter crystallized at 0°C

α
(1 day)

α → β'
(5 days)

α → β'
(7 days)

β'
(14 days)

β'
(21 days)

β'
(28 days)

Cocoa butter crystallized at 20°C

β'
(1 day)

β’ → β
(7 days)

β’ → β
(21 days)

β’ → β
(21 days)

β
(35 days)

β
(35 days)

β
(35 days)
Cocoa butter crystallized at 26°C

Growth of a Polycrystalline Fat Crystal Network
Growth of a fat crystal network
Effect of cooling rate

1.2°C/min

0.4°C/min

6.0°C/min

Effect of Surfactant Addition

0.1% vs. 0.5% Tween 60
Temperature Effect

Effect of film size on slide

170µm  20µm
Cocoa Butter Fat Crystal Network Visualized using AFM

Cryo-TEM Isobutanol-extracted SSS
Relationship between structure and crystallization behavior

1. Growth mode (Avrami model)

\[
\frac{\text{SFC}(t)}{\text{SFC}(\infty)} = 1 - e^{-kt^n}
\]

- \( k \) - rate constant of crystallization
- \( n \) - dimensionality of growth and the type of nucleation

2. Nucleation (\( \tau, \Delta G_c \)- Fisher-Turnbull model)

\[
J = \frac{NkT}{h} e^{-\frac{(\Delta G_c + \Delta G_d)}{kT}}
\]

- \( \Delta G_c \) - activation free energy of nucleation
- \( \Delta G_d \) - activation free energy of diffusion

Table 6: Avrami exponent values for the different types of growth and nucleation (Sharples, 1966)

<table>
<thead>
<tr>
<th>Avrami Exponent</th>
<th>Various types of growth and nucleation</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 + 1 = 4</td>
<td>Spherulitic growth from sporadic nuclei</td>
</tr>
<tr>
<td>3 + 0 = 3</td>
<td>Spherulitic growth from instantaneous nuclei</td>
</tr>
<tr>
<td>2 + 1 = 3</td>
<td>Disc-like growth from sporadic nuclei</td>
</tr>
<tr>
<td>2 + 0 = 2</td>
<td>Disc-like growth from instantaneous nuclei</td>
</tr>
<tr>
<td>1 + 1 = 2</td>
<td>Rod-like growth from sporadic nuclei</td>
</tr>
<tr>
<td>1 + 0 = 1</td>
<td>Rod-like growth from sporadic nuclei</td>
</tr>
</tbody>
</table>
n=4

n=1

k=0.00103 min^{-1.5}

SFC_{\infty}=67.7\%
Avrami Exponent vs. Crystallization Temperature

Phase Technology Cloud Point Analyzer
$\tau_{\text{nucleation-A}}$

$\tau_{\text{nucleation-B}}$

**Time (min)**

**Signal (a.u.)**

**Slope = 221100**

$R^2=0.99$

$\frac{1}{T} (\Delta T)^2$

$\ln(\tau) T$

**Crystallization Temperature (°C)**

**$\Delta G_c$ (kJ/mol)**
Avrami Exponent vs. Crystallization Temperature

Induction Times as Determined from Crystallization Curves at Various Temperatures
Rheology of Fats

Small Deformation Dynamic Controlled Stress Rheometer
TA AR2000
Viscoelasticity of Fats

$\frac{G''}{G'} \sim 0.1$

Shear strains of $\sim 0.1\%$ or less

$G'$ frequency-independent
Large Deformation Mechanical Tests
Modeling the microstructure of a fat
MECHANICAL PROPERTIES OF PLASTIC-DISPERSE SYSTEMS AT VERY SMALL DEFORMATIONS

M. Van den Tempel

Unilever Research Laboratory, Vlaardingen, Netherlands

Received August 8, 1960; revised November 15, 1960

Abstract

A system containing secluded solid particles in a liquid shows viscoelastic behavior at very small deformations. A model is described by means of which the elastic modulus of the system can be correlated with the forces acting between the particles. It is assumed that these forces are due to van der Waals-London attraction, and their contribution to the modulus is calculated. A method is indicated which allows the contribution of the van der Waals-London forces to the modulus of the material to be measured under specified conditions. Experiments on materials containing ice crystals in sediments between layers predicted and experimental values for the contribution, if it is assumed that the solid particles in the aggregate approach each other at a distance of about 10 Å.

The energy content of the van der Waals-London bonds in these materials has been estimated from measurements of their rate of boiling in vacuum experiments, i.e., under the influence of a constant, low shearing stress. The energy content of about 30 kcal/mole is in satisfactory agreement with the results of stiffness measurements.

List of Symbols

$A$ = Hamaker constant determining van der Waals-London attraction (nm$^2$).

$r_0$ = Interparticle distance (nm).

$\Delta U_i$ = Free energy of activation for breaking a bond of type $i$.

$\Delta E_i$ = Average force exerted on bond of type $i$.

$G$ = Elastic modulus (Gyres, etc.).

$G = \frac{5AD^{0.5}}{24\pi H_0^{rac{3}{2}}} \Phi$


$E = \frac{A}{2\pi d_o^3} \Phi$

For small deformations only

There also exists a modification of van den Tempel's model by Sherman (1968).
The rheological properties of sufficiently concentrated dispersions in small or slow deformations are mostly determined by colloidal interactions forces between the dispersed particles. Viscous properties and flow behavior of suspensions in which attraction prevails over at least a certain range of interparticle distances. The average modulus, the yield value, and the strength of these materials have been expressed in terms of a network model (1-6). In this model the stress is carried by chains of particles, and the deformation is determined by the maximal stress occurring across the sample gap between consecutive particles in a chain.

The particle network model necessarily leads to a storage modulus and a yield value proportional to the first power of the dispersed volume fraction. Moreover, these properties are not or are weakly dependent on the particle size. Note that the yield value, or strength, is here measured as the maximum stress occurring across the sample gap as described in Ref. (1) and is a quite different property.

Experiments have shown that the viscoelastic properties and the yield value depend much more strongly on volume fraction and particle size than would be predicted on the basis of the simple network model (5, 7). Although this would make the model unsuitable for practical application, it has been found that the results obtained in the case of two-phase systems exhibit particulate breakage and remolding of interparticle bonds (7) and flow of solid along and between particles. Moreover, despite its deficiencies, the simple network model was found to correctly predict the macroscopic properties of the average modulus in a number of systems. The present paper attempts to improve the network model by taking into account the presence of particle aggregates.

2. THEORY

There is abundant evidence that flow of concentrated dispersions is governed by a mechanism in which two types of interaction are present: primary particle-particle interactions and aggregate-particle interactions. The main feature of the network model is the presence of primary particle-particle and aggregate-particle interactions. The network model needs to take into account the presence of particle (crystal) aggregates.
for single particle network does not provide satisfactory description of system's behavior

Rather: $G = \Phi \mu$

Several parameters that determine the state of aggregation are lumped together into one dimensionless 'scaling factor'

He also suggests that $\mu \sim N$

Good agreement with experiments

The low values of the correction factor in dispersions containing a smaller number of larger particles suggest the presence of aggregates containing up to 10^4 particles. This is what one would expect on the basis of kinetic arguments: The initial rate of aggregation is proportional to the square of the particle concentration. In a sufficiently concentrated suspension (i.e., large $N$) the aggregation is essentially finished before the particles have had time to migrate toward centers of aggregation. The result is a uniform distribution of single particles in the network. If aggregation proceeds more slowly there is ample time for the formation of the inhomogeneous structure that is commonly found in flocculated dispersions.

The state of aggregation in a flocculated suspension must depend on the conditions prevailing during and immediately prior to its production. In particular, the amount and type of agitation and the magnitude of the attractive force will affect the aggregation parameters and hence the mechanical properties of the material obtained. The results presented in Fig. 1 had been obtained with a minimum of agitation during flocculation. Dispersions of carbon particles in oil or in water, and emulsions, require more agitation. It is, therefore, not surprising that such dispersions exhibited less aggregation than would be expected on the basis of the correlation shown in Fig. 1.

REFERENCES
The fractal nature of fat crystal networks

R. Verkerk, L.L. Hoekstra, D.C. den Boer and W.G.M. Aptom

Erasmus Research Laboratories, Erasmus University, P.O. Box 1738, 3000 DR Rotterdam, The Netherlands

Abstract

General review papers are often given to have a fractal nature. They include features that are self-similar at different scales. However, it is not always clear how self-similar features are observed, and how the fractal parameters are determined. In this paper, the fractal nature of fat crystal networks is presented in the framework of fractal theory. It is shown how the fractal dimension of the fat crystal networks and the yield stress vary with particle concentration according to a power law. From the power law parameters the fractal dimension of the fat crystal network is determined and well with the results of light scattering experiments.

\[
G' \sim \Phi^\mu
\]

\[
\mu = \frac{d + x}{d - D}
\]

\[
\mu \approx \frac{4.3}{3 - D}
\]

Introduction

In many foood products, the formation of a network of crystalline fat particles is essential. The fat network provides texture and stability to products such as margarine or spreads. The mechanical properties of fat crystals have been extensively reviewed in terms of a simple network model, developed originally by van der Tempel [1] and modified by others [2-4]. In this model, the network is composed of straight chains of aggregated particles held together by attractive van der Waals forces. The model correctly predicts the order of magnitude of the elastic modulus for a number of systems and has been the basis for a number of applications in texture measurements. However, the simple network model also shows some deviations. For example, the elastic modulus and the yield strength of the network are predicted to vary linearly with the volume fraction of dispersed particles, whereas experiments have shown a much stronger dependency [5,6]. It was realized that this discrepancy is related to the assumption that the fat particles are connected into straight chains. In reality, the network is built from aggregates of fat particles. Several attempts have been made to improve the network model by taking into account the presence of aggregates [7-9]. A qualitative description of the network properties, however, was hampered by the relatively simple and often arbitrary treatment of the aggregates.

A comprehensive approach has been made recently after the introduction of the fractal concept [10]. This approach provides a quantitative description of the structure of aggregates through the fractal dimension \(d\), which characterizes the way in which the mass, \(M\), of a cluster increases with its area \(A\). The fractal dimension of the aggregates is given by \(d = 1.75\), and aggregates grown by the diffusion-limited mechanism have a higher fractal dimension, \(d = 2.1\) [5]. Light scattering has shown that the fractal nature of the aggregates is preserved.

Heertje, I. (1993)

Microstructural Studies in Fat Research

Food Structure 12, 77-94
Support for the view of fats as crystallite fractal gels grows
Johansson also shows that:

$$\xi \sim \Phi^{1/(D-d)}$$
Fractal analysis explains the softening observed in milkfat upon chemical interesterification.
Structural view – a colloidal gel?

Fractality and the Fractal Dimension
Characterization of the Spatial Distribution of Mass within the Fat Crystal Network

Fractal Geometry

Fat crystal networks display statistical self-similarity and scaling behavior characteristic of stochastic fractal systems
Statistical Self similarity – you guess!
Self-similarity?

Scaling Behavior and Fractional Dimensionality

Scaling behavior $G \sim \Phi^\mu$

Scaling behavior $N \sim L^D$
\( \xi \sim \Phi^\mu \)

$\xi \sim t^{1/D}$

Milkfat Spherulites at 20°C

for $M \sim t$

Batte and Marangoni, 2005, Crystal Growth and Design 5: 1703-1705

Fracal Structural-mechanical model
The view
Structure-mechanical model
Thermodynamic arguments

\[ E = \frac{6\delta}{a\varepsilon^*} \Phi^{3-D} = \frac{A}{2\pi a\varepsilon^* d_o^2} \Phi^{d-D} \]

\[ G = \frac{1}{3} E \]

Marangoni and Rogers, 2003, Appl. Phys. Lett. 82, 3239

Structure-mechanical model
Particle-spring arguments

\[ G = \frac{A}{6\pi cad_o^3} \Phi^{3-D} \]

Narine and Marangoni, 1999, Phys. Rev. E 60, 6991
The Yield Stress (Compression)

\[ \sigma^* = E \cdot \varepsilon^* \]

\[ \sigma^* = \frac{6\delta}{a} \Phi^{\frac{1}{3-D}} \]

Marangoni and Rogers, 2003, Appl. Phys. Lett. 82, 3239

Model simulations
Methods of Determination
Processing procedure for calculation of scaling fractal dimensions of fat crystal network

Original polarized light microscopy image

Adjust contrast of the images

Threshold it to binary image

Calculate $D_b$ by Benoit 1.3, $D_f$ by particleCounting.m, and $D_{F,T}$ by Photoshop

Fractal Dimension by Microscopy - particle counting

- $D_f$ is related to the spatial distribution of mass
- higher $D_f$ → more orderly distribution
Mass Fractal Dimension (D) by particle counting (sensitive to order)

\[ N = cL^D \]

N = number of particles  
L = length of ROI  
c = constant of proportionality

\[ \log N = D \log R + \log c \]
\[ Y = mX + b \]

Narine and Marangoni, 1999, PRE 59:1908

Fractal Dimension Determination by Particle Counting

![Graph showing log(N) vs log(length)](image)

D=2.01 (0.06)  
\[ r^2=0.994 \]
Artifacts!

Mass Fractal Dimension by Box Counting (sensitive to degree of occupancy of embedding space)

Benoit 1.3 (Truesoft Int’l Inc.)
Effect of crystallization temperature on cocoa butter microstructure
Effect of crystallization temperature on milkfat microstructure

![Graph showing effect of crystallization temperature on milkfat microstructure.](image)

Cooling rate effects on milkfat microstructure

![Graph showing cooling rate effects on milkfat microstructure.](image)
Fractal Dimension by Microscopy: box counting

- $D_b$ is sensitive to the degree of fill in the network:
  higher $D_b$ $\rightarrow$ higher degree of fill

What is the fractal dimension?

\[
\Phi = N_p V_p / NV \sim (\xi/a)^D / (\xi/a)^d
\]

\[
\Phi \sim (\xi/a)^D / (\xi/a)^d = (\xi/a)^{(D-d)} \quad \xrightarrow{\xi \sim a\Phi^{1/(D-d)}}
\]
Fractal dimension from the characteristic slope of FFT power spectrum

\[ D = 2 + \frac{\text{slope}}{2} \]

Fractal dimension - rheology

\[ G' = \lambda \left( \frac{SFC}{100} \right)^\mu \]

\[ \ln G' = \ln \lambda + \mu \ln \left( \frac{SFC}{100} \right) \]
Weak-link Theory - Fat Crystal Networks

Developed for colloidal gels and adapted to fat crystal networks:

\[ G' \sim \Phi^\mu \sim \lambda \Phi^{1/(d-D)} \]

\( G' \) = dynamic shear elastic modulus (storage modulus)
\( \lambda \) = constant which depends on particle properties and particle-particle interactions
\( \Phi \) = solids’ volume fraction of fat sample

Narine and Marangoni, 1999, PRE 59:1908

Using the Weak-Link Theory to Calculate Fractal Dimensions Rheologically

\[ G' \sim \lambda \Phi^{\frac{1}{d-D}} \]

\[ \log G' = \left[ 1/(3-D) \right] \log \Phi + \log f_c \lambda \]
Dilute fat with vegetable oil under conditions where fat is not dissolved significantly in the oil?

Milkfat
Palm Oil

Cocoa Butter
Strain at the limit of linearity always increases with SFC, thus fats are always in the weak-link rheological regime and thus:

$$\mu = \frac{1}{(3-D)}$$


Effect of D on the Elastic Modulus

$G'/\lambda (\phi=0.5)$
Relationship to Large Deformation Rheological Behavior?

Effects of shear on $D_r$ (AMF)

\[ D_{\text{max}} - D = \frac{\beta}{SR} \]

\[ \ln \frac{\lambda}{\lambda_0} = -\alpha (SR) \]

Crystallization behavior and structure

\[ D = D^* + \beta \ln J \]

Marangoni and McGauley, 2003, Crystal Growth and Design 3, 95
\[ \sigma^* = \frac{6\delta}{a} \Phi^{\frac{1}{d-D}} = \frac{6\delta}{a} \Phi^{\frac{1}{d-D^* - \beta \ln J}} \]

Thermomechanical Method for the Determination of the Rheology Fractal Dimension
CB SFC vs. Temperature vs.

Temperature (deg Celcius)

SFC (%)

CB G' vs. Temperature

G' (Pa)

Temperature (deg Celcius)
CB $G'$ vs. SFC

$G'$ (Pa) vs. SFC (%)

Thermo
- $r^2=0.98$
- $D=2.40$

Dilution
- $r^2=0.92$
- $D=2.43$
Dongming Tang’s project

- Determine the physical basis of the scaling fractal dimensions used to quantify the microstructure of fat crystal networks in 2D and 3D

- Compare the scaling fractal dimensions of fat crystal networks in 2D and 3D space

- Use fractal dimensions in 3-dimensional space to explain the rheological properties of fat crystal networks

Common methods to determine fractal dimensions

- $D_b$
- $D_f$
- $D_{FT}$

$D_{FT}$ in 2D = (4+slope)/2
2D simulation images of fat crystal networks

Sample images generated by computer simulation. The shape, crystal size, area fraction and the distribution orderliness for the images are (A) Line, 13 pixels, AF=10%, 100% randomly distributed; (B) disk, 29 pixels, AF=10%, 100% evenly distributed; (C) square, 49 pixels, AF=15%, 100% randomly distributed; (D) diamond, 25 pixels, AF=8%, 30% evenly distributed; (E) diamond, 25 pixels, AF=10%, 50% evenly distributed; (F) diamond, 25 pixels, AF=8%, 70% evenly distributed.


2D simulation on \( D_b \)

The effects of area fraction on \( D_b \) for different crystal sizes. \( R \) is the radius of fat crystals.

The effects of crystal size on \( D_b \). Solid symbols are for 100% randomly distributed crystals, and open symbols are for 100% evenly distributed crystals.
2D simulation on $D_f$

Radial distribution pattern of simulation images with different $D_f$. (A) $D_f = 0.998$; (B) $D_f = 3.052$.


2D simulation on $D_{FT}$
Different measures of fractality cannot agree since they are sensitive to different structural features within the network.

Cannot use the argument that all values of the fractal dimension must be the same for the system to be fractal…….
2D fractal dimension vs 3D fractal dimension

Acquiring images of fat samples in 2- and 3- dimensional space

3-Dimensional Imaging of Bulk Fats by Wide-field Deconvolution Polarized Light Microscopy

Novel Approach: Wide-field Deconvolution

- traditional uses (confocal, fluorescence)
  - adapted to TLB (Holmes & O’Conner)
- allows for thicker samples (true volumes)
- 3-dimensional data sets (x, y, z)
- employs a deconvolution algorithm (removes haze from unfocussed portions of the specimen)
- 2D projection, 3D renderings
**Deconvolution Algorithm**

- **Openlab: Volume Deconvolution**
  - theoretical point spread function
  - uses 8 nearest neighbors (NN)
  - removes unfocussed haze from each plane

- **Autoquant: Autodeblur**
  - Estimates the point spread function
  - Uses the image data (Blind)
  - Removes unfocussed haze from each plane

- **sample:**
  high-melting fraction of milk fat (HMF) diluted in triolein (70:30), crystallized isothermally at 28°C for 15 minutes
Comparisons: 2D Projections

Comparisons: XZ and YZ
3D-FD

The main window of 3D-FD after the calculation of particle-counting dimension, \( D_f \). Note that the first data points on the left calculation graph was manually checked off.


3D simulation study on \( D_b \)

The effects of \( D_b \) for different crystal sizes. \( r \) is the radius of fat crystals.

The effects of crystal size on \( D_b \) of fat crystal networks with evenly distributed crystals. AF is area fraction of crystals.
2D vs 3D fractal dimension

(a) $D_b$ of 2D slices at different depths of a thick sample of the high melting fraction of milk fat in canola oil at a 7% solids' mass fraction (b) Comparison between the 2D and 3D box counting dimensions of samples of high melting fraction of milk fat in canola oil at 20°C at different mass fractions of solids ($\Phi$).


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Microscopy fractal dimensions of HMF

<table>
<thead>
<tr>
<th>SFC</th>
<th>Low SFC range ($&lt;10%$)</th>
<th>High SFC range ($&gt;10%$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2D $D_b$ average</td>
<td>1.34</td>
<td>1.65</td>
</tr>
<tr>
<td>3D $D_b$ average</td>
<td>2.06</td>
<td>2.37</td>
</tr>
<tr>
<td>2D $D_t$ average</td>
<td>1.99</td>
<td>1.90</td>
</tr>
<tr>
<td>3D $D_t$ average</td>
<td>2.76</td>
<td>2.67</td>
</tr>
</tbody>
</table>
## Rheology and microscopy fractal dimensions of HMF

<table>
<thead>
<tr>
<th>SFC</th>
<th>Low SFC range (&lt;10%)</th>
<th>High SFC range (&gt;10%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3D $D_b$ average</td>
<td>2.06</td>
<td>2.37</td>
</tr>
<tr>
<td>3D $D_r$ average</td>
<td>2.76</td>
<td>2.67</td>
</tr>
<tr>
<td>3D $D_t$ average</td>
<td></td>
<td>2.74</td>
</tr>
</tbody>
</table>

## Modified fractal model

**Heterogeneous Stress Distribution Principle**
Homogeneous factor and dynamic microstructure

Spatial distribution of strain energy in a perfectly connected DLCA network


Fat crystal network at high SFC
\[ G' = c \left(1 - e^{-k\Phi^b}\right) \frac{1}{3-D} \]

Tang and Marangoni, 2008, JCIS 318: 202
Modified fractal model of colloidal fat crystal networks

What about intermolecular interactions?
Van der Waals are the end-all?
Fat Crystal Network Model

\[ G' = \lambda \phi^{\frac{1}{3-D}} = \frac{A}{6 \pi \gamma d_0^2} \phi^{\frac{1}{3-D}} \]

<table>
<thead>
<tr>
<th>Variables</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \lambda )</td>
<td>Experimental value, obtained from a ln ( G' ) vs. ln ( \Phi ) plot</td>
</tr>
<tr>
<td>( a )</td>
<td>Diameter of particles</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>Strain at the limit of linearity</td>
</tr>
<tr>
<td>( d_0 )</td>
<td>Separation between the “flocs”</td>
</tr>
</tbody>
</table>

Hamaker constant

Material:
- Dispersed phase: Fully hydrogenated canola oil
- Continuous phase: High oleic sunflower oil

- McLachlan and Lifshitz approach
- Semi-classical approach
- Fat Crystal Network Model
McLachlan and Lifshitz approach

\[ A = A_{v=0} + A_{v>0} = \frac{3}{4} kT \left( \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_2 + \varepsilon_2} \right)^2 + \frac{3h\nu_e}{16\sqrt{2}} \left( \frac{n_1^2 - n_2^2}{n_1^2 + n_2^2} \right)^2 \]

\( k \) Boltzmann’s constant \( 1.38 \times 10^{-23} \text{ J/K} \)
\( h \) Planck’s constant \( 6.626 \times 10^{-34} \text{ J s} \)
\( T \) Temperature (K)
\( \varepsilon \) dielectric permittivity
\( n \) index of refraction
\( \nu_e \) electronic absorption frequency in the UV region \( 3 \times 10^{15} \text{ s}^{-1} \)

Index 1 and 2 are for dispersed and continuous phases

Permanent dipole-permanent dipole interaction are very important in fat crystal interactions!

<table>
<thead>
<tr>
<th></th>
<th>( A_{v=0} )</th>
<th>% ( A_{v=0} )</th>
<th>( A_{v&gt;0} )</th>
<th>% ( A_{v&gt;0} )</th>
<th>Total A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Svaikauskas</td>
<td>3.5 ( 10^{-22} ) J</td>
<td>67%</td>
<td>1.70 ( 10^{-22} ) J</td>
<td>33%</td>
<td>5.2 \times 10^{-22} J (30°C)</td>
</tr>
<tr>
<td>Svaikauskas</td>
<td>9.1 ( 10^{-22} ) J</td>
<td>82%</td>
<td>1.77 ( 10^{-22} ) J</td>
<td>18%</td>
<td>1.1 \times 10^{-21} J (20°C)</td>
</tr>
<tr>
<td>Johansson</td>
<td>3.8 ( 10^{-23} ) J</td>
<td>12%</td>
<td>1.77 ( 10^{-22} ) J</td>
<td>88%</td>
<td>2.0 \times 10^{-22} J</td>
</tr>
<tr>
<td>(JAOC, Vol.69, 8 1992)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kloek</td>
<td>3.8 ( 10^{-23} ) J</td>
<td>8.5%</td>
<td>1.83 ( 10^{-21} ) J</td>
<td>91.5%</td>
<td>2.0 \times 10^{-21} J</td>
</tr>
</tbody>
</table>
### Semiclassical approach

\[ A = 24 \pi \delta d_0^2 \]

- \( \delta \) crystal-melt interfacial tension (30°C)
- \( d_0 \) equilibrium space between molecules

<table>
<thead>
<tr>
<th>( d_0 ) (nm)</th>
<th>( \delta ) (J/m²)</th>
<th>( A ) (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0.01 *</td>
<td>3.0x10^{-20}</td>
</tr>
<tr>
<td>0.2</td>
<td>0.005**</td>
<td>1.5x10^{-20}</td>
</tr>
</tbody>
</table>

1- Bailey’s Industrial Oil and fats Products (measured at 60°C)
2- Meeussen, Personal communication
3- Handbook of Chemistry and Physics, R.C East, 56th edn.

---

\[ \pi d_0^2 \delta = \pi d_0^2 \frac{\Delta z}{2} \]

- * Latifeh Ahmadi’s work

---

#### Table

<table>
<thead>
<tr>
<th>Hamaker from</th>
<th>( n_{SSS} )</th>
<th>( n_{OOO} )</th>
<th>( \varepsilon_{SSS} )</th>
<th>( \varepsilon_{OOO} )</th>
<th>( A )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Svaikauskas</td>
<td>1.503867</td>
<td>1.469903</td>
<td>1.68*</td>
<td>2.7</td>
<td>5.2x10^{-22} J (30°C)</td>
</tr>
<tr>
<td>(tristearin in sunflower oil)</td>
<td>1.51299</td>
<td>1.466420</td>
<td>1.926</td>
<td>3.17</td>
<td>1.1x10^{-21} J (20°C)</td>
</tr>
<tr>
<td>Johannson (JAOC, Vol.69, no8,1992)</td>
<td>1.44711</td>
<td>1.47351</td>
<td>23</td>
<td>2.53</td>
<td>2x10^{-22} J</td>
</tr>
<tr>
<td>(tristearin in soybean oil)</td>
<td>1.562</td>
<td>1.47351</td>
<td>23</td>
<td>2.53</td>
<td>2x10^{-22} J</td>
</tr>
</tbody>
</table>

---

* Estimated from 20 °C data.

---

#### Notes

- 1- Bailey’s Industrial Oil and fats Products (measured at 60°C)
- 2- Meeussen, Personal communication
- 3- Handbook of Chemistry and Physics, R.C East, 56th edn.
Fat Crystal Network Model

\[ A = \lambda \frac{6 \pi \gamma d_0^2}{\lambda} \]

\[ G' = \lambda \frac{A}{6 \pi \gamma d_0^2} \]

<table>
<thead>
<tr>
<th>Variables</th>
<th>Explanation</th>
<th>Experimental values</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \lambda )</td>
<td>Experimental value, obtained from the ( \ln G' ) vs. ( \ln \Phi ) graph</td>
<td>1.17 ( 10^7 ) Pa</td>
</tr>
<tr>
<td>( a )</td>
<td>diameter of particles</td>
<td>2( \mu )m, 1( \mu )m, 0.4( \mu )m, 0.2 ( \mu )m</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>Strain at the limit of linearity</td>
<td>1.9 ( 10^{-4} )</td>
</tr>
<tr>
<td>( d_0 )</td>
<td>separation between the “flocs”</td>
<td>0.2 nm</td>
</tr>
</tbody>
</table>

A = 3.35 \( 10^{-21} \) J when \( a = 2 \) \( \mu \)m

A = 1.68 \( 10^{-21} \) J when \( a = 1 \) \( \mu \)m

A = 6.7 \( 10^{-22} \) J when \( a = 0.4 \) \( \mu \)m

A = 3.35 \( 10^{-22} \) J when \( a = 0.2 \) \( \mu \)m

Summary of Hamaker values

<table>
<thead>
<tr>
<th>Temperature</th>
<th>M-L approach</th>
<th>Semi-classical</th>
<th>Fat Crystal Network Model</th>
<th>( d_0 ) (nm)</th>
<th>( a ) (( \mu )m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20°C</td>
<td>1.1 ( 10^{-21} ) J</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30°C</td>
<td>5.2 ( 10^{-22} ) J</td>
<td>1.5 ( 10^{-20} ) J</td>
<td>3.35 ( 10^{-22} ) J, 6.7 ( 10^{-22} ) J, 1.68 ( 10^{-21} ) J, 3.35 ( 10^{-21} ) J</td>
<td>0.2</td>
<td>0.2, 0.4, 1, 2</td>
</tr>
</tbody>
</table>
Thank You!