Clustering of Triacylglycerols in the Molten State

"From Biomembranes to Chocolate"

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Overview

- Fitting Planar Stacks of Lipidic Layers
- Previous Models of TAGs in the Molten State
- X-ray Scattering Evidence for TAG Clusters
- New TAG-cluster Model and Structural Results
- Recent Simulation Studies
From Cells to Vesicles

Life bases on Biomembranes

Liposome (MLV)

Phospholipid Membrane Stack

Electron Density Profile

1 - 5 mm
The Global Fitting Approach


Fitting Cocoa Butter Polymorphs (α-phase)

EDP: 2 peak reconstruction (lab-source)

EDP: 5 peak reconstruction (synchrotron)

EDP: global fitting
Cocoa Butter (CB) Source

Lipidic fraction obtained from the cacao nibs.

(Theobroma cacao)

West African CB provided by Nestlé, PTC, York, U.K., was used without additional refining.
Cocoa Butter Composition

<table>
<thead>
<tr>
<th>TAGs</th>
<th>FFA’s</th>
<th>DAGs</th>
<th>PL’s</th>
<th>Glycolipids</th>
</tr>
</thead>
<tbody>
<tr>
<td>ca. 97</td>
<td>0.87-1.04</td>
<td>0.81-1.39</td>
<td>&lt;0.1-0.3</td>
<td>0.3-1.5</td>
</tr>
</tbody>
</table>

TAG: Triacylglycerol  
FFA: Free Fatty Acids  
DAG: Diacylglycerol  
PL: Phospholipids

Saturated chains:  
- Palmitic (P)  
- Stearic (S)

Mainly three types of TAGs:  
- SOS, POS, POP

Saturated

\[ \text{Saturated} = \begin{align*} 
\text{H}_2\text{C} & \text{O} \text{C} \\
\text{H} & \text{O} \text{C} \\
\text{H}_2\text{C} & \text{O} \text{C} 
\end{align*} \]
Polymorphism of TAGs

molten state

β’ phase

α-phase

β-V phase
(A) **Smectic**\(^1\) (B) **Nematic**\(^2\) and (C) **Discotic**\(^3\) arrangements of TAGs in the molten state.

2 Cebula, D. J.; McClements, D. J.; Povey, M. J. W.; Smith, P. R. J. Am. Oil Chem. Soc. 1992, 69, 130–136.
X-ray Scattering Evidence

SAXS: Water

SAXS: TAGs from cocoa butter

2D fit (decay with $q^2$)
20 °C
Our Approach: Modelling with Gaussians

Fluid Bilayer Modelling

Rappolt, M. (2019)
50 Years of Structural Lipid Bilayer Modelling
Advances in Biomembranes and Lipid Self-Assembly (ABiLSA) 29, 1-21.
New TAG-cluster Model: Temperature Trends

**A**

![Graph showing intensity vs. q (nm⁻¹) with a marked temperature increase](image)

**B**

![Graph showing D-spacing vs. temperature (°C)](image)

**C**

![Graph showing FWHM of peak vs. temperature (°C)](image)
New TAG-cluster Model: Core and Cluster Thickness

A

Cluster thickness
Core thickness

-3 -2 -1 0 1 2 3

z (nm)

B

Cluster Thickness (nm)

C

Core Thickness (nm)

20 40 60 80 100

Temperature (°C)
New TAG-cluster Model: The Second Shell
New TAG-cluster Model: 1D vs 2D Embedding
New TAG-cluster Model: Summary

- TAGs assemble through the glycerol group
- A single percolating network forms
Sadeghpour, A., Ladd Parada, M., Vieira, J., Povey, M., Rappolt, M.
Global Small-Angle X-ray Scattering Data Analysis of Triacylglycerols in the Molten State (Part I).

Ladd Parada, M., Sadeghpour, A., Vieira, J., Povey, M., Rappolt, M.
Global Small-Angle X-ray Scattering Data Analysis of Triacylglycerols in the α-Phase (Part II).