Skeletons in the Labyrinth

Medial surfaces and off-surface properties of triply periodic minimal surfaces of cubic and non-cubic symmetries
Non-cubic TPMS

- **Cubic TPMS:** G, D, P, I-WP, C(Y), F, S, …

- Families of **non-cubic** TPMS: tD, tP, tG, rPD, rG, H, …

- Transition pathways between cubic G, D, P
rPD – a rhombohedral TPMS family

✓ minimal
✓ bicontinuous
✓ embedded
✗ not isometric

0.51
(departure point to rG family)

1/sqrt(2)
(Cubic P surface)

sqrt(2)
(Cubic D surface)

Skeletons, Graphs and Domain Sizes

- Definition of Point-wise Domain Size
- Packing frustration in copolymers
Medial Surface

- Shrink labyrinth to its 2D skeleton
- collapsing parallel surfaces
- skeletal graph = spine
- medial surface = spine plus rib cage

Gyroid with line graph

Medial Surface

• Amenta, Choi, Kolluri, Comp. Geom: Th & Appl **19** (2-3), 127 (2001)
Formal definition of Medial Surface

‘Reduce objects to their symmetric axes or skeletons’

... is the locus of centres of maximal spheres

... is the set of points with 2 or more nearest boundarypoints.

\[ \forall p \in S : ms(p) = p + d(p) n(p) \]

\[ d(p) \text{ gives thickness/depth of labyrinth at point } p. \]

First description of MS in context of biological shape description and in 2D:
Some simple examples
Computing the Medial Surface

as a subset of the Voronoi diagram

Triangulated Object

Delaunay Triangulation

Voronoi Diagram

Medial Surface

(Amenta et al, 1998)
2D Medial Surface Skeleton

- Medial surface maximally distant to minimal surface
- Line graphs contained in medial surface for P, D, G
- Shrink 2D Medial Surface to 1D skeletal graph?
Skeletal graph on MS

- Distance contours $d(p)$ on Medial Surface
- Skeletal graph = ridge line of distance profile
- Connect saddles of $d$ to maxima

Maximally distant line network with topology of labyrinth
Skeletal graph on MS

Connect saddles to maxima of radius function

Maximum

Saddle

MS with distance contours

Distance on circle vs Angle
Medial Surface

- Parallel surfaces collapsed to 2D skeleton
- Maximally distant points to minimal surface

Skeletal graph

- Reduce medial surface to 1D graph
- Traces lines furthest away from TPMS

... interesting graphs in non-cubic TPMS?
Nodes not always widest points

Nodes = widest points

Nodes = saddles of distance

Edge midpoints = widest points

The centered graph has curved edges

Transition from 6- to 4-nodes

Nodes not defined by symmetry R3c

[Schröder-Turk, Sheppard, Hyde, in prep.]
Changes in Coordination number

4-coordinated → 3-coordinated
“Alternative” 3 → 4 transition in tG family

tG = retain 4-fold symmetry of cubic Gyroid, but not the 3-fold symmetry.

3-nodes → normal points, mid-edge → **asymmetric** 4-nodes

4-node
Medial Surfaces and Skeletal Graphs

- TPMS → Medial Surface → Skeletal graph
- Symmetry alone not sufficient to define graph
- Centeredness of medial surface
- 4-coordinated to 6-coordinated transition in rPD
- Alternative 4- to 3-coordinated transition in tG

Schröder-Turk, Sheppard, Hyde, in prep.
Part II: Packing frustration in self-assembly processes

... and what we can learn about them from non-cubic minimal surfaces!
Self-Assembly in Lipid-Water Systems

- **hydrophilic head group**
- **hydrophobic tail**

Channel diameter: ~ 20-100 nm

Cubic Q230 and Q214 phases  

[LUZATTI, 1960s]
AB-copolymers: “Ia3d core-shell Gyroid”

“A”

“B”

Strong covalent bond

A and B are immiscible. They would like to phase-segregate! 
.... much like oil and water

Macroscopic phase-separation impossible because the strong bond holds A’s and B’s together!

bulk phase of “A” separated from a bulk phase of “B”
Covalent bonds cannot be broken, hence ...

“Micro-phase separation”

“Hexagonal” (sphere/cylinder)

“Lamellar”

“Bicontinuous”
Gyroid Phase in Hard Pears

Shown are
• half the pears
• those in 1 domain

Also shown (in green):
• Gyroid “Medial Surface”
• similar to skeletal graphs
• details later

• 10000 hard pears
• Box with fixed volume V
• Periodic boundary conditions

Ellison, Cleaver et al, PRL 97, 237801 (2006)
Identical particles assemble into homogeneous (point-wise similar) structures.

How can Medial Surface help us understand…

Ubiquitous P, D and G structures are cubic

Why cubic symmetry?

Why (in co-polymers) only the Gyroid?

Transitions D → G in lipid
Point-wise Domain Size from Medial Surface

∀ \( p \in S \) : \( ms(p) = p + d(p)n(p) \)

\( d(p) \) gives thickness/depth of labyrinth at point \( p \).
“Energetics” for *monodisperse* strongly-segregated co-polymer Gyroid phases

Thickness variations of structure ⇔ stretching penalty of chains

- Minimise interface between moieties A, B ⇒ interface (parallel to) minimal surface
- Polymer coils have to fill space ⇒ one end on TPMS, the other on MS
- Coils incur entropic penalty for stretching/squashing ⇒ \((d-\langle d\rangle)^2\) (frustration)

AB copolymer

“Coreshell” Gyroid

⇒ search for structure with least amount of thickness variations (“Homogeneity”)
Is there a labyrinth of \textit{constant} thickness?

Circle or sphere \hspace{2cm} Parallel planes \hspace{2cm} Cylinder

… these are perfectly homogeneous shapes for elliptic, planar and parabolic geometries!

\textbf{NO:} a labyrinth with constant MS distance (or constant curvature*) does not exist

* Hilbert knew that already
Optimal labyrinthine shape?

... analyse thickness variations of minimal surfaces!

Start with three candidate structures (of cubic symmetry):

- Primitive,
- Diamond and
- Gyroid

Gyroid best!

Harmonic approximation of an energy that penalises

1. Deviations from a preferred curvature (bending)
2. Deviations from a preferred radius (stretching)

\[ H(S) = \int_S \left[ \alpha (K(p) - K_0)^2 + \beta (d(p) - d_0)^2 \right] dS \]

Borrows from Helfrich and concept of preferred molecular shape
(assuming minimal surface interfaces and \( H_0 = 0 \))

\[ \Delta K = \sqrt{\langle (K - \langle K \rangle)^2 \rangle} \quad \Delta d = \sqrt{\langle (d - \langle d \rangle)^2 \rangle}. \]
Non-cubic TPMS

- **Cubic TPMS**: G, D, P, I-WP, C(Y), F, S, …

- **Families of non-cubic TPMS**: tD, tP, tG, rPD, rG, H, …

- Transition pathways between cubic G, D, P
Is the most “homogeneous” TPMS cubic?

- Investigate all (*) Minimal Surface families of tetragonal & rhombohedral symmetry
- Plot std dev of Gaussian curvature histogram as function of free surface parameter

\[\Delta K = \sqrt{\langle (K - \langle K \rangle)^2 \rangle}\]

⇒ Curvature fluctuations minimal for cubic TPMS

[(* of the “regular class”, see Fogden&Hyde, Acta Cryst A, 1992]
Cubic cases minimise curvature and thickness fluctuations

\[ \Delta K = \sqrt{\langle (K - \langle K \rangle)^2 \rangle} \quad \Delta d = \sqrt{\langle (d - \langle d \rangle)^2 \rangle}. \]

Channel thickness variations
Why do bicontinuous soft-matter structures have *cubic symmetry*?

- Because they are more homogeneous!
- Minimal variations of channel diameter and Gaussian curvature
Cubic-To-Cubic Transitions in Lipids

Polysaccharid-induced


Pressure-induced


What is transition pathway?
Transition structures $D \rightarrow G$

- Tetragonal pathway
- Rhombohedral pathway

Curvature fluctuations

- Tetragonal and rhombohedral pathways
- Tetragonal transition has smaller energy barrier

Channel thickness variations
Which is the optimal transition pathway between D and G?

- Tetragonal symmetry!
- Minimal energy barrier (homogeneity)

Resolve symmetry of transition structure by time-resolved scattering?
“Isotropic” hexagonal TPMS

Hexagonal TPMS family with symmetry P6m2 – one free parameter A

For which A is H surface most homogeneous?
For which A is H surface most “isotropic”?

[Source: Brakke]
Value for which curvature variations are minimised

Channel radius variations

Curvature variations

Value for which channel radius variations are minimised
Min/Max Eigenvalue ratio of "surface tensor"

Unit tensor

Equal surface density for x, y and z direction

"Isotropic"

"Isotropic" c/a very different from Hexagonal closed-packed spheres

Min/Max Eigenvalue ratio of "surface tensor"
Distribution of surface normals

\[ \int_{\partial K} N(r) \otimes N(r) \]
\[ = \int_{S} w(N') \ N' \otimes N' \]

with \( w(N') = \int_{\partial K} \delta(N'-N(r)) \)

Surface area of that part of \( \partial K \) that has surface normal \( N' \)

Identical eigenvalues (isotropic)  
Different eigenvalues (not isotropic)
Min/Max Eigenvalue ratio of “surface tensor”

Equal surface density for x, y and z direction

“Isotropic”

“Isotropic” c/a very different from Hexagonal closed-packed spheres

Min/Max Eigenvalue ratio of “surface tensor”

\[ \int_{\partial K} \vec{N} \otimes \vec{N} \, dS = \text{Unit tensor} \]
“Isotropic” Hexagonal bicontinuous structure?

Hexagonal TPMS with single free parameter A. The values for A with

(a) smallest curvature variations

(b) smallest channel radius variations

(c) most “isotropic” distribution of surface directions

are very close to each other.

⇒ Likely geometry for a bicontinuous hexagonal lipid phase
Could “isotropic” H-surface be misidentified as cubic TPMS?

Simulated scattering pattern of simple biphasic H surface

Conclusions

- Medial Surfaces as Centered Skeletons
- TPMS $\rightarrow$ Medial Surface $\rightarrow$ Line Graph
- Homogeneity and Packing frustration

Non-cubic minimal surfaces and their homogeneity:

Fogden & Hyde, EPJB, 7, 91-104 (1999)


Medial Surface construction and homogeneity Gyroid versus Diamond, Primitive:


Isotropy analysis of general phases using Minkowski curvature integrals:


http://www.theorie1.physik.uni-erlangen.de/gerd/