About myself:
what I like to work on
and how I do it

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Algorithms + Geometry + Physics/Math/Chemistry

Event-driven hard sphere numerics

Correlation fct, elasticity of hard-sphere crystals:
towards discrete differential operators of elasticity

Delaunay/Voronoi tessellations:
variant with different sizes
variant with inside/outside spheres
measure volumes, surfaces, and arcs
measure connectivity

connection with physics: pressure and chemical potential of hard-sphere sys
connection with chemistry: plastics degradation

The Compatibility problem:
distances between points
Ideals, modules, Gröbner bases

towards a discrete notion of “strain”

Example:

A geometric model for enzymatic degradation of plastic waste

Model: a simple ODE with complicated right-hand-side
Numerics: Voronoi/Delaunay tessellation with several extensions
Insights: Statistics of overlapping spheres
Application: parameters mapped to experimental data

Experimental facts: Enzymatic de-polymerisation of polyester waste

	PET bottle waste		96% yield after 24h
	PET textile waste swimwear lining		82%
	PET fiber waste automotive scrap		36%
	PET/PBT textile swimwear trunk		15%
	PBT		0%

Experimental facts: Preparing and treating the polyesters. Phase diagram

enzymes act only at the **surface**

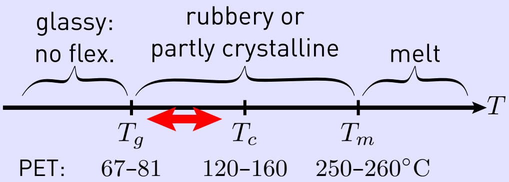
they "need space" to act:
- **amorphous** substrate (avoid crystals!)
- substrate **mobility** (avoid glass!)

natural temperature range (enzymes are proteins!)
- roughly 40–$70°\mathrm{C}$

water

prepare:
- melt + quench
- mill + sieve: break into pieces $\sim 300\,\mu m$

de-polymerise:



- initial crystallinity + nucleation
- **crystal growth!**

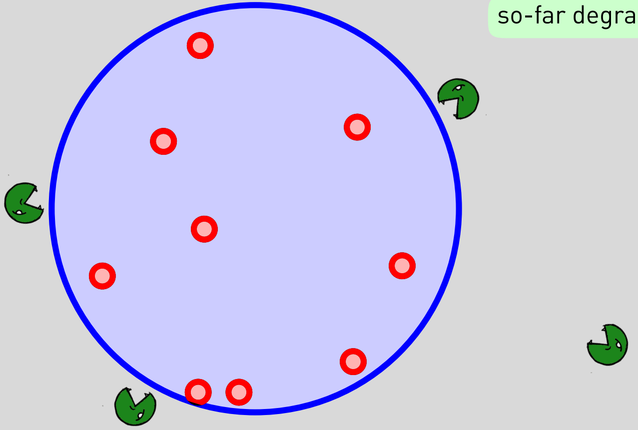
The growing crystallites are a problem!

Geometric model: de-polymerisation vs. crystal growth

model: one shrinking sphere: amorphous material: degradable

many growing spheres: (partly) crystalline material: not degradable

so-far degraded amorphous material



parameters: N_s, $\dot{R}_s/\dot{R}_h$, R_{s0}/R_{h0}, ($\dot{N}_s$)

depend on material, composition, preparation, processing temperature, . . .

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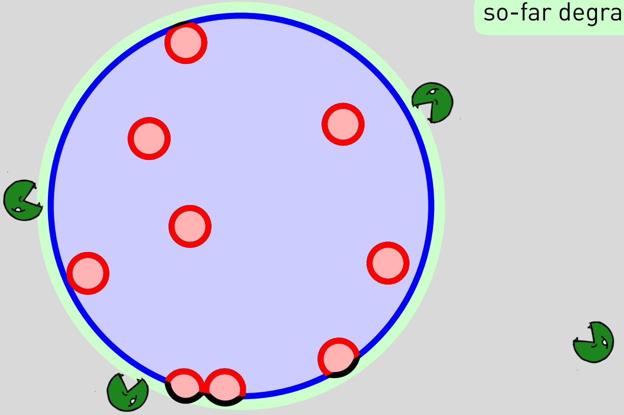

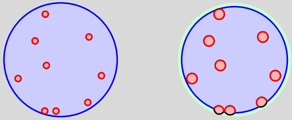

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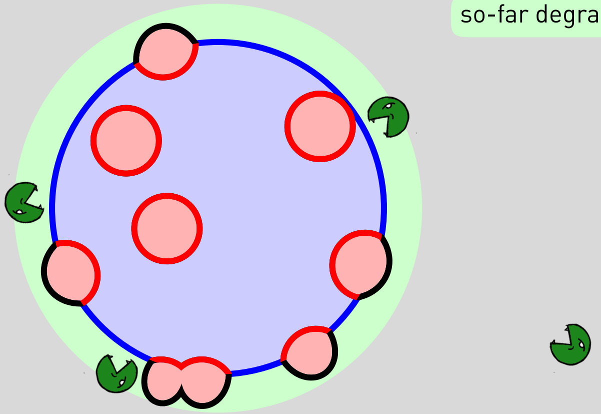

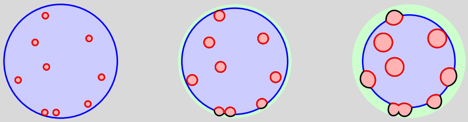

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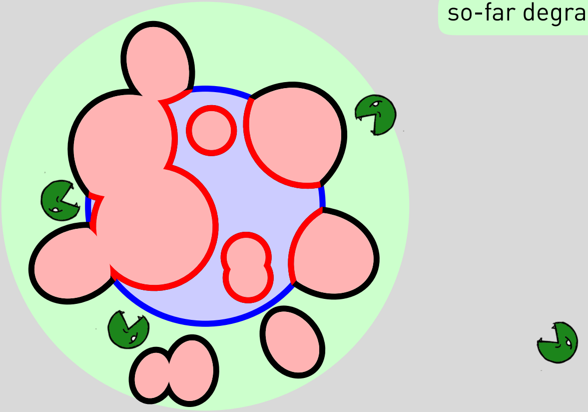

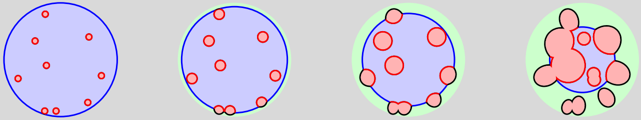

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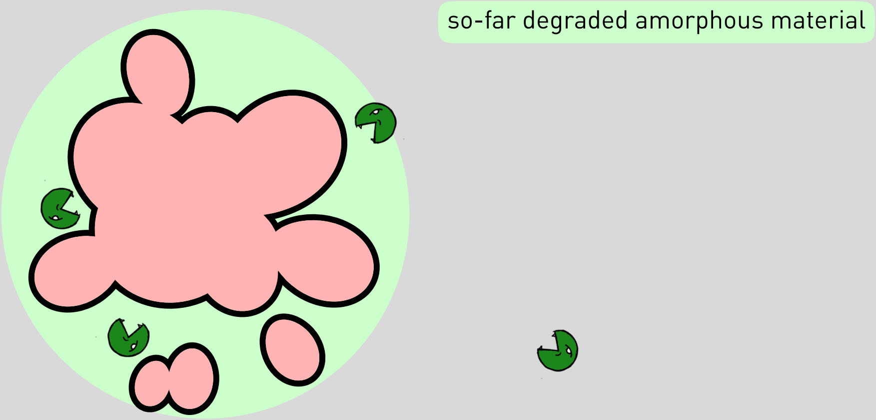
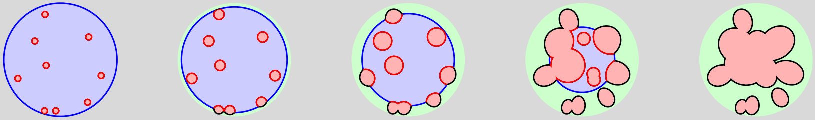


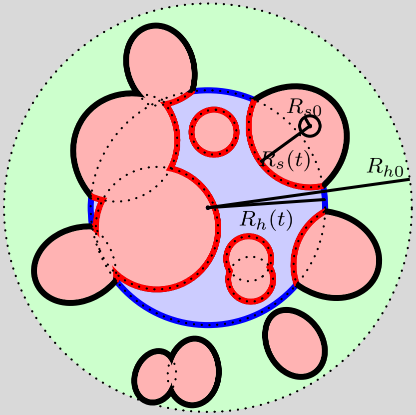


parameters: N_s, $\dot{R}_s/\dot{R}_h$, R_{s0}/R_{h0}, ($\dot{N}_s$)
depend on material, composition, preparation, processing temperature, . . .

Geometric model: ordinary differential equation (ODE) of detailed geometry

Init: place growing spheres randomly in shrinking sphere.
An ordinary differential equation for the three volumes:

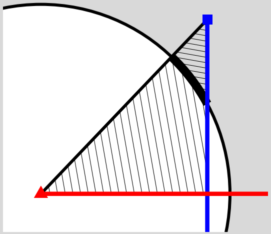
$$R_h(t) = R_{h0} + \dot{R}_h t, \quad \text{with const } \dot{R}_h < 0$$
$$R_s(t) = R_{s0} + \dot{R}_s t, \quad \text{with const } \dot{R}_s > 0$$
$$\frac{d}{dt} V_{\mathsf{sph}}(t) = \dot{R}_s \, S_{\mathsf{am,sph}}(t)$$
$$\frac{d}{dt} V_{\mathsf{deg}}(t) = |\dot{R}_h| \, S_{\mathsf{am,deg}}(t)$$
$$V_{\mathsf{am}}(t) + V_{\mathsf{sph}}(t) + V_{\mathsf{deg}}(t) = V_{\mathsf{tot}} \quad \text{const}$$



$R_h(t)$: radius of shrinking (amorphous) sphere
$R_s(t)$: radii of growing (crystal) spheres
$V_{\mathsf{sph}}(t)$: volume of (crystal) spherulites
$V_{\mathsf{deg}}(t)$: volume of so-far degraded (amorphous) material
$V_{\mathsf{am}}(t)$: volume of remaining amorphous volume
$V_{\mathsf{tot}} := \frac{4\pi}{3} R_{h0}^3$

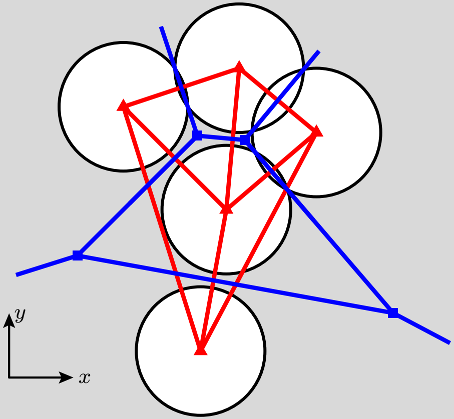
We need the areas of interfaces $\mathrm{S}_{\mathsf{am,sph}}$ and $\mathrm{S}_{\mathsf{am,deg}}$: numerically!
We need a special version of Delaunay/Voronoi tessellation

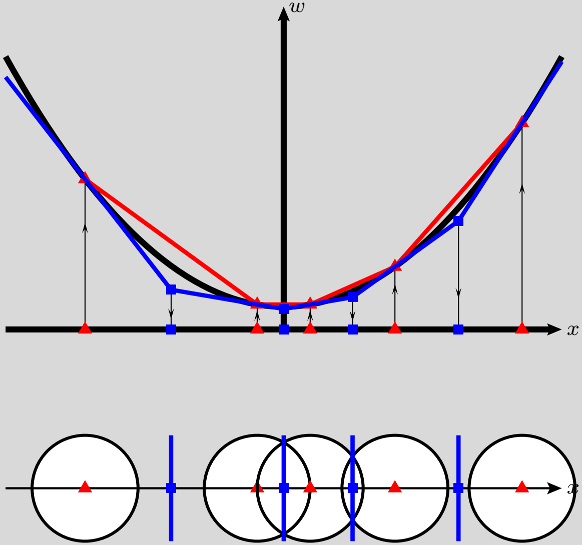
Excursion 1: *standard* Delaunay/Voronoi tessellation



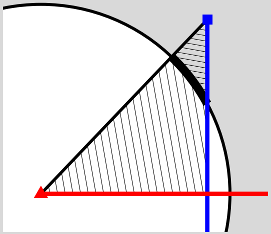
Delaunay/Voronoi tessellation
dissects space into orthogonal tetrahedra,
in each use analytical formulae for volumes, surfaces, arclengths, orientations

Delaunay/Voronoi is equivalent to a lower-convex-hull problem:





Excursion 1: *weighted* Delaunay/Voronoi tessellation



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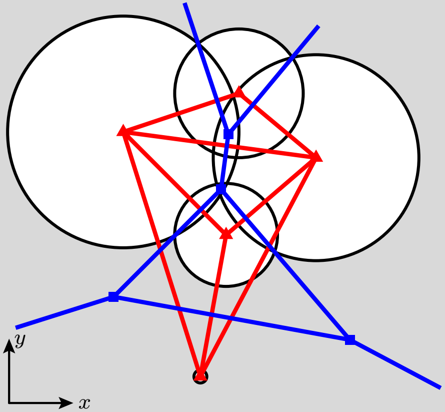
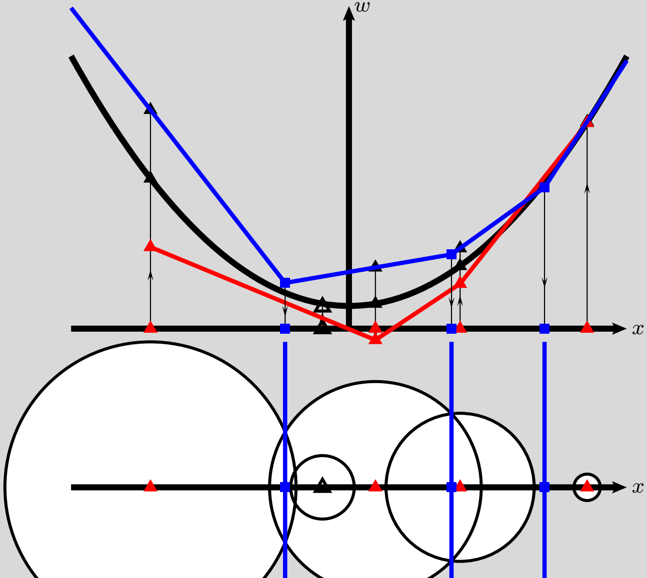
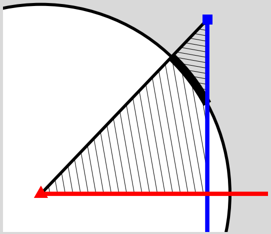




Excursion 1: *double weigthed* Delaunay/Voronoi tessellation



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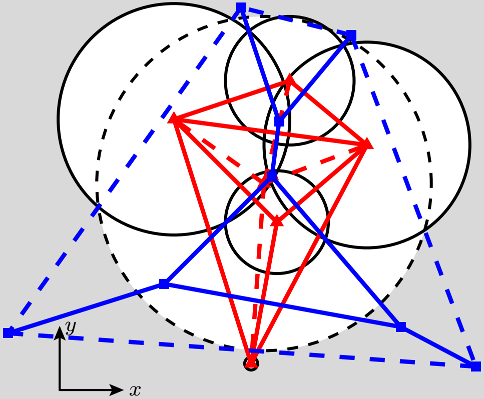
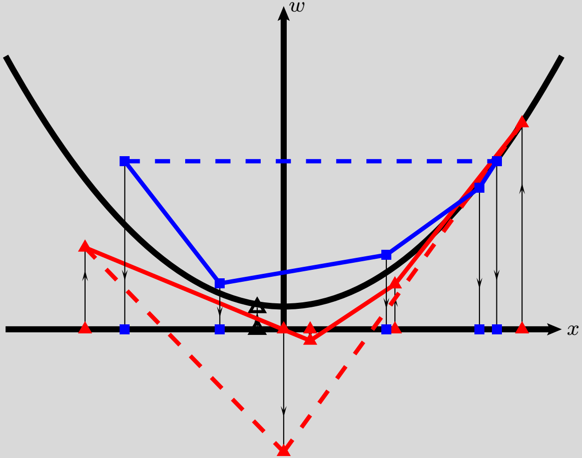
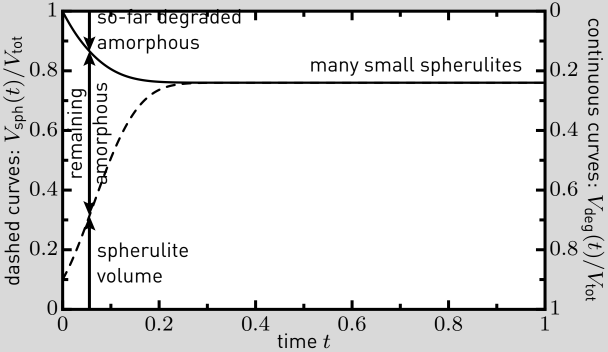
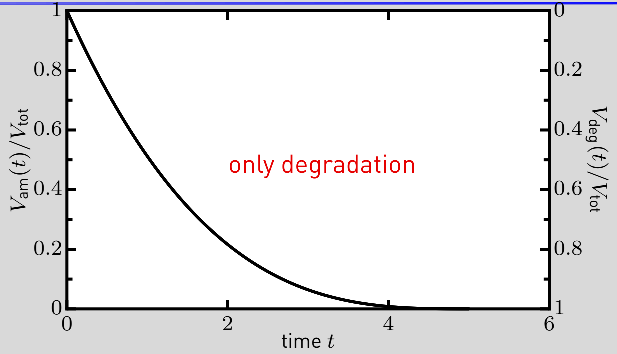


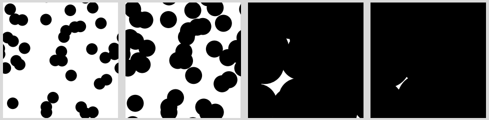


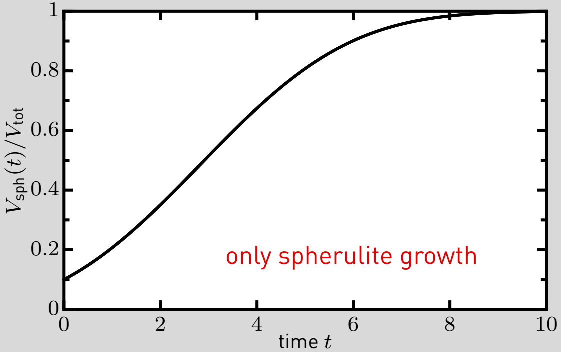
Solution of the model: volume evolution

competition:
spherulite growth
vs. degradation of amorphous:









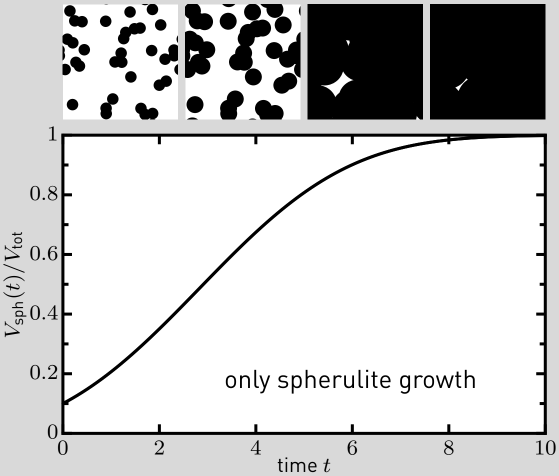
Excursion 2: The Avrami problem revisited

Without degradation, the growth curve is known analytically.
The dominant viewpoint in the literature is that of a *fitting* function $1-\exp(at^b)$ – but there is much more to it!

Turn it into a **sampling problem**:
(here: no degrading particle, growth is unimportant, just overlap of spheres).
Pick any point $\mathbf{x}$ and place spheres randomly:

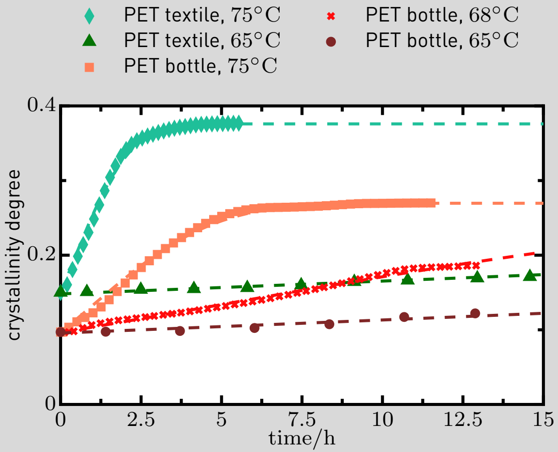
$$
\begin{aligned}
\xi := & \,\mathrm{Prob}[\mathbf{x} \text{ is covered}] \\
= & \,1-\mathrm{Prob}[\mathbf{x} \text{ is not covered}] \\
= & \,1-\prod_{i=1}^{N}\mathrm{Prob}[\mathbf{x} \text{ is not covered by sphere i}] \\
= & \,1-\prod_{i=1}^{N}\left(1-\frac{4\pi R_s^3}{3V}\right) \\
= & \,1-\left(1-\frac{4\pi R_s^3}{3V}\right)^N = 1-\left(1-\frac{1}{N}N'\frac{4\pi R_s^3}{3}\right)^N \\
\overset{N\to\infty}{\to} & \,1-\exp\left(-N'\frac{4\pi R_s^3}{3}\right)
\end{aligned}
$$

$$N' := N/V$$



The same sampling can be done on the surface of the shrinking sphere, to simplify the ODE to just a few variables.

Mapping to experiments: parameters



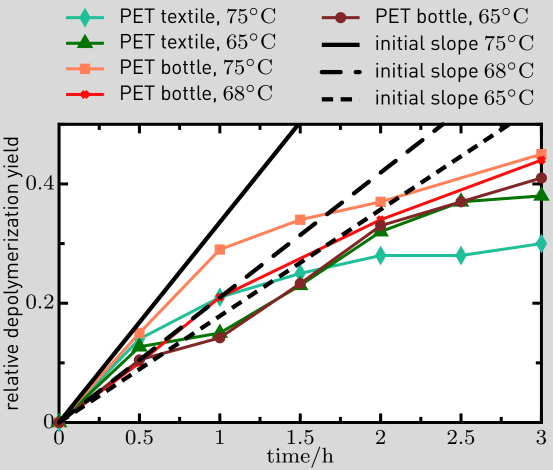
spherulite parameters from fit to

$$A\left[1-\exp\left(-\frac{4\pi}{3}(B+Ct)^3\right)\right]$$

$B=(N')^{1/3}R_{s0}$,
$C=(N')^{1/3}\dot{R}_s$.

Need further input for N': haze

A remains undetermined!



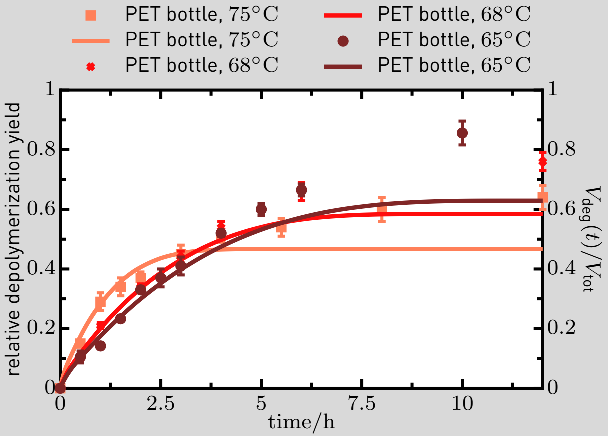
depolymerisation parameters from initial slope

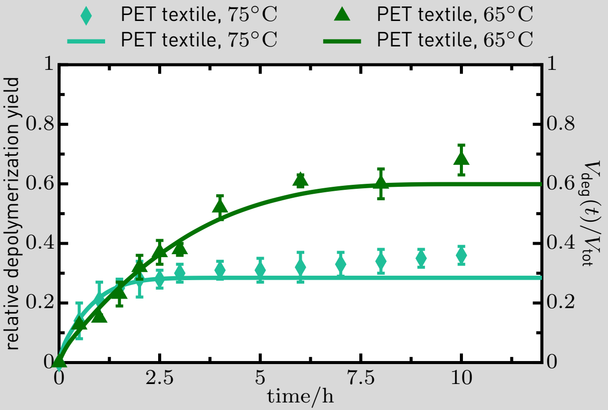
$$D\left[1-(1-Et)^3\right]$$

$3DE=(-3\dot{R}_h/R_{h0})\exp(-\frac{4\pi}{3}N'R_{s0}^3)$

Initial covering by spherulites is important
Take only one slope per temperature!

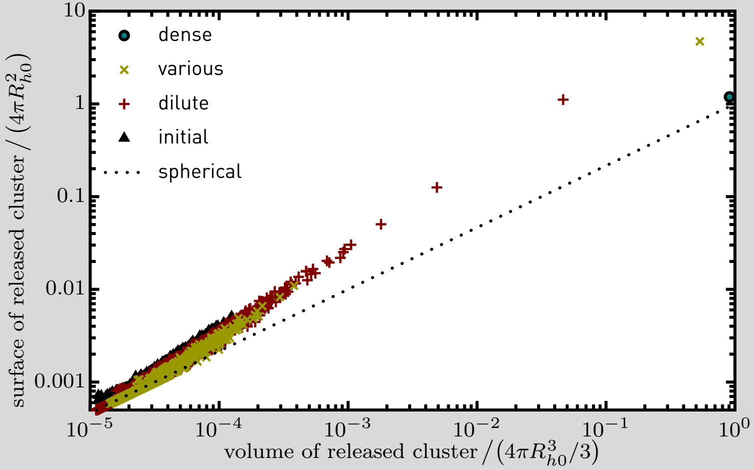
Comparing experiments and numerics

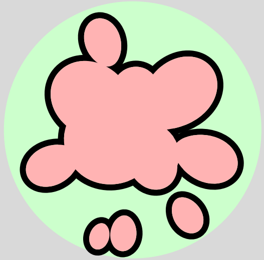




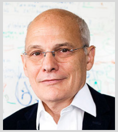
Additional slow degradation of spherulites happens also . . .

Clustering of spherulites: volume, surface, number, ...



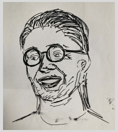


Enzyme genetics + physico-chemistry + modeling:



Ludwik Leibler (Gulliver lab, CNRS)

Hernan Garate (SIMM lab, ESPCI/CNRS/PSL)



. . . and me (Gulliver lab, CNRS). . .

Andrew Griffiths (Biochemistry lab, ESPCI)

Yannick Rondelez (Gulliver lab, ESPCI)

and Costantino Creton (SIMM lab, CNRS)

and Clément Freymond (SIMM lab, ESPCI)

and Louise Breloy (SIMM lab, ESPCI)

. . . plus industrial contacts . . .

Experiments published in PNAS
Numerics currently under review at Macromolecules