

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



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# Algorithms + Geometry + Physics/Math/Chemistry

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## 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

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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°C

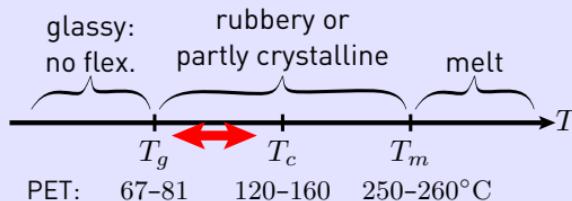
water

**prepare:**

melt + quench

mill + sieve: break into pieces  $\sim 300\mu\text{m}$

**de-polymerise:**



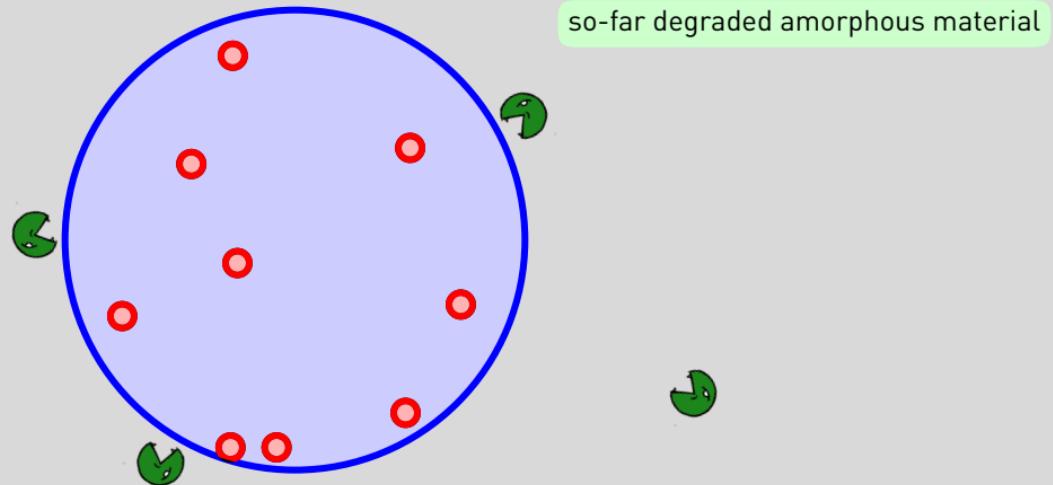
**The growing crystallites  
are a problem!**

initial crystallinity + nucleation  
**crystal growth!**

## Geometric model: de-polymerisation vs. crystal growth

**model:** one shrinking sphere: amorphous material: degradable

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



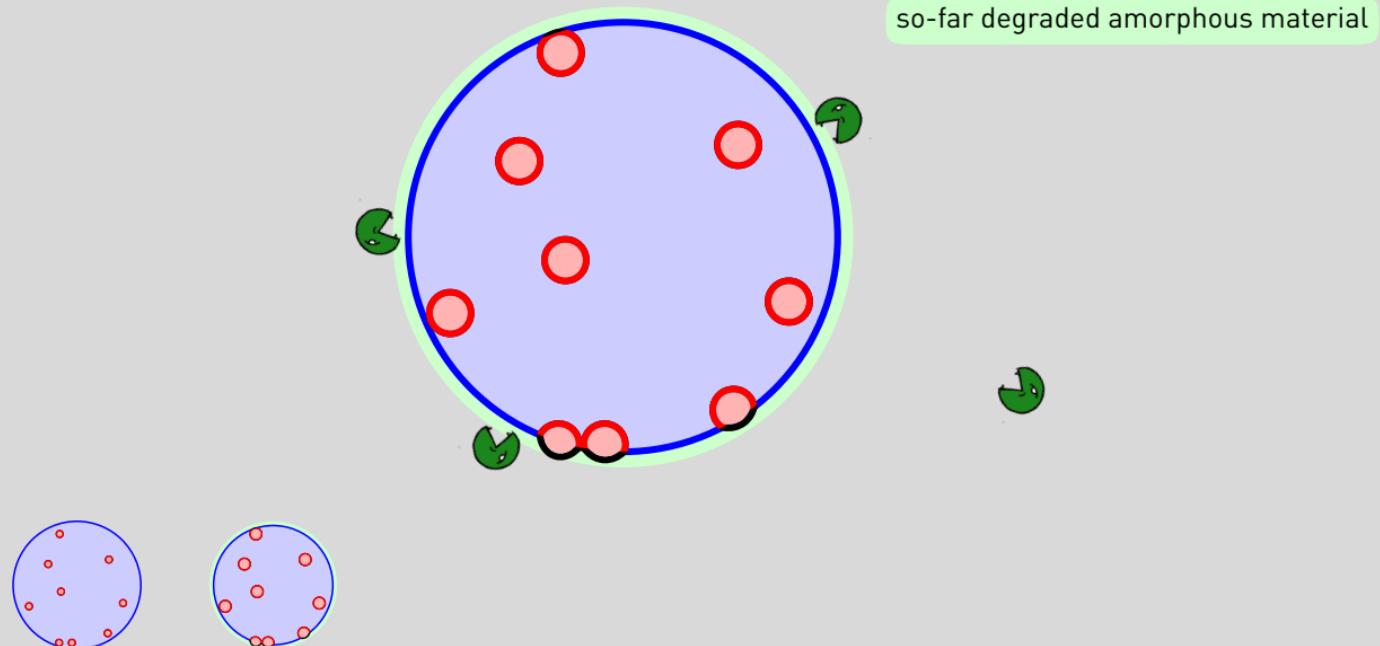
**parameters:**  $N_s, \dot{R}_s/\dot{R}_h, R_{s0}/R_{h0}, (\dot{N}_s)$

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

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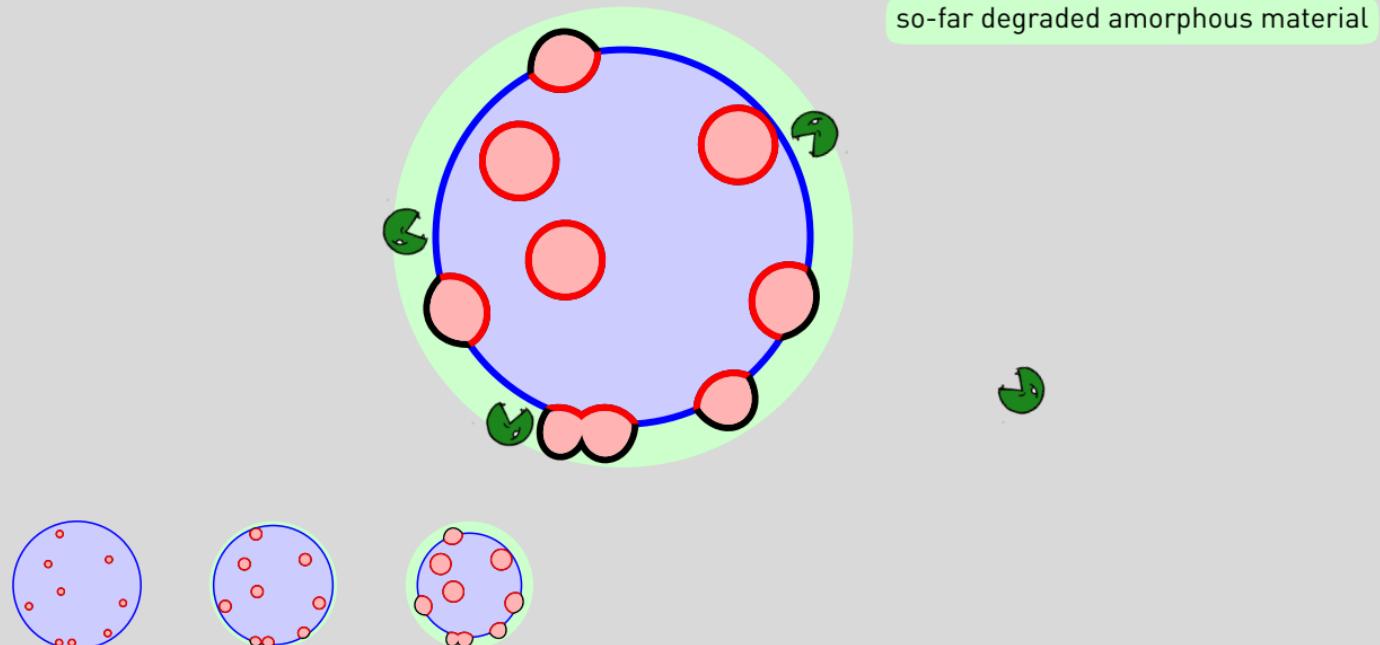
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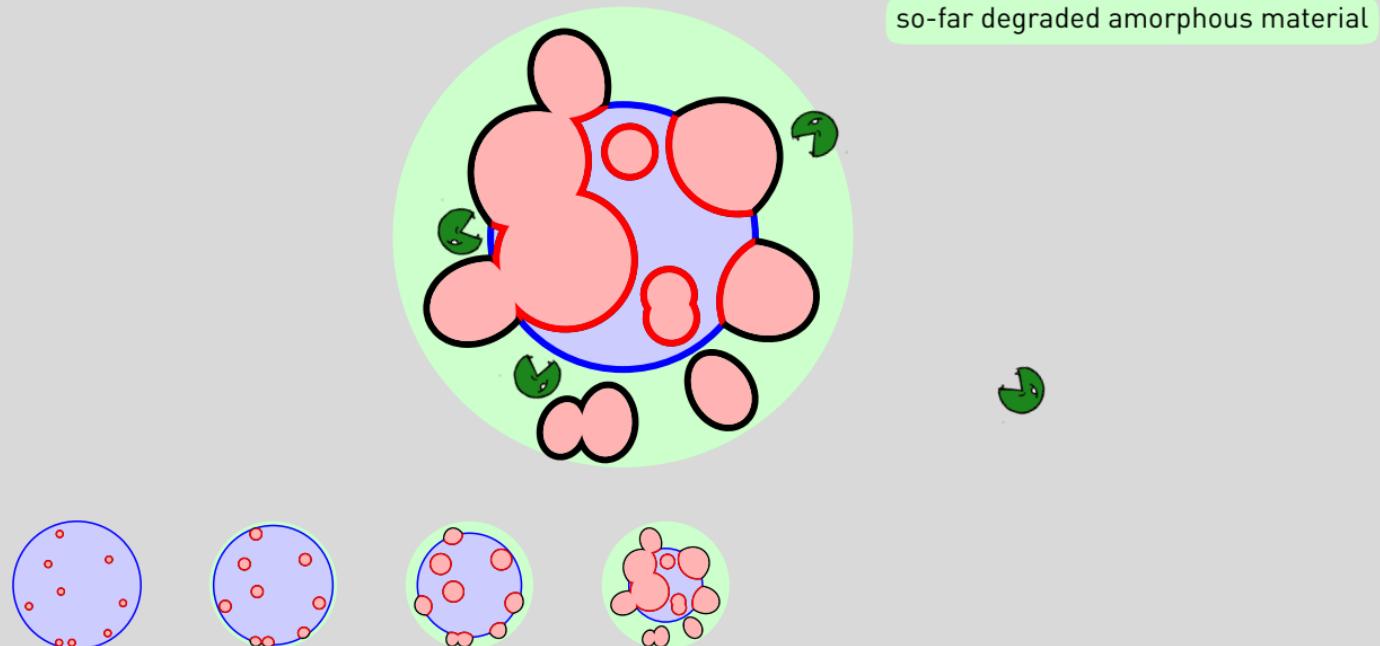
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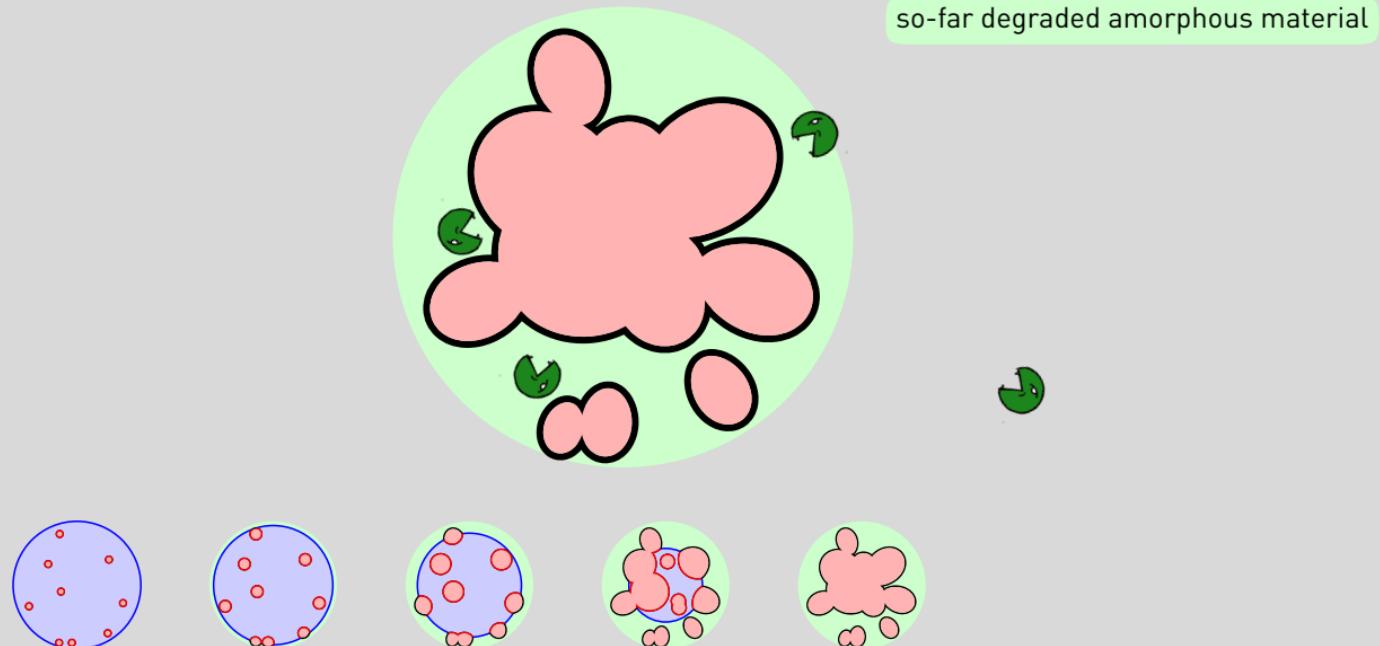
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depend on material, composition, preparation, processing temperature, ...

## 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:

$$R_h(t) = R_{h0} + \dot{R}_h t, \quad \text{with const } \dot{R}_h < 0$$

$$R_s(t) = R_{s0} + \dot{R}_s t, \quad \text{with const } \dot{R}_s > 0$$

$$\frac{d}{dt} V_{\text{sph}}(t) = \dot{R}_s S_{\text{am,sph}}(t)$$

$$\frac{d}{dt} V_{\text{deg}}(t) = |\dot{R}_h| S_{\text{am,deg}}(t)$$

$$V_{\text{am}}(t) + V_{\text{sph}}(t) + V_{\text{deg}}(t) = V_{\text{tot}} \quad \text{const}$$

$R_h(t)$  : radius of shrinking (amorphous) sphere

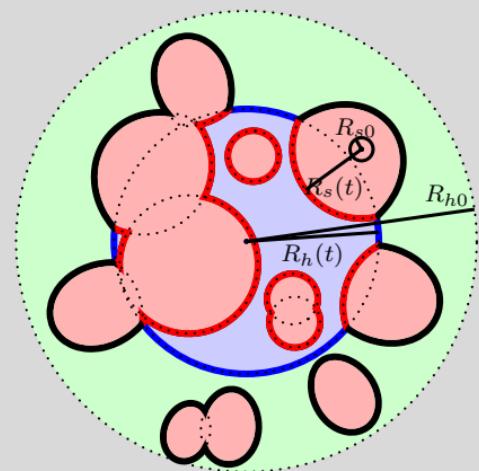
$R_s(t)$  : radii of growing (crystal) spheres

$V_{\text{sph}}(t)$  : volume of (crystal) spherulites

$V_{\text{deg}}(t)$  : volume of so-far degraded (amorphous) material

$V_{\text{am}}(t)$  : volume of remaining amorphous volume

$$V_{\text{tot}} := \frac{4\pi}{3} R_{h0}^3$$

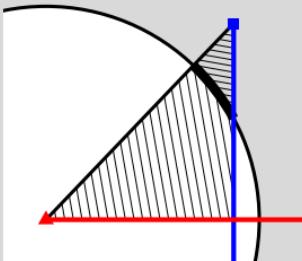


We need the areas of interfaces  $S_{\text{am,sph}}$  and  $S_{\text{am,deg}}$ : numerically!

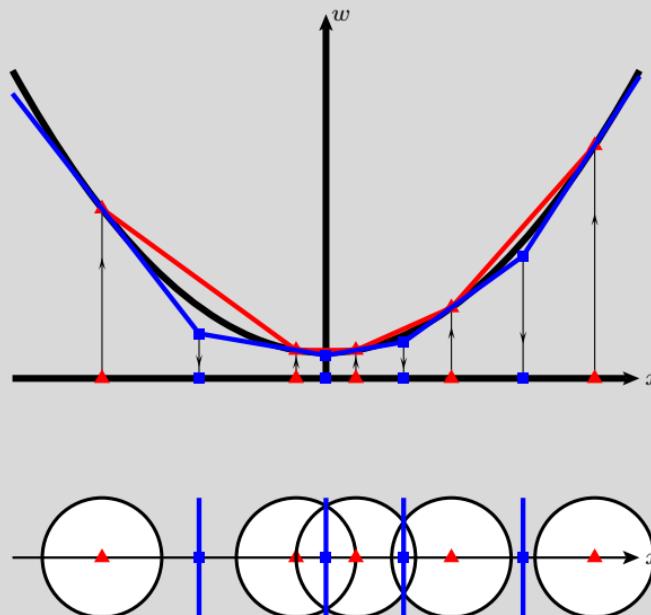
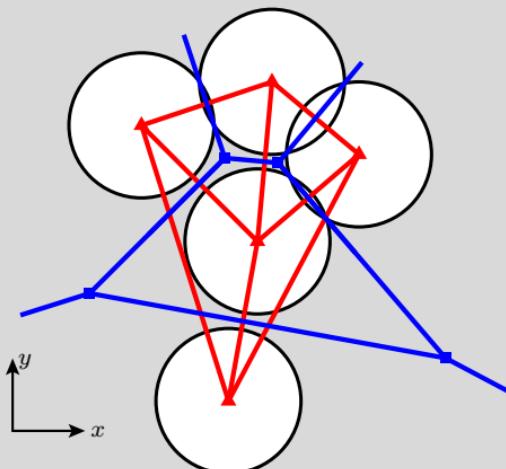
We need a special version of Delaunay/Voronoi tessellation

## Excursion 1: standard Delaunay/Voronoi tessellation

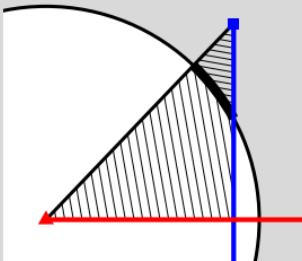
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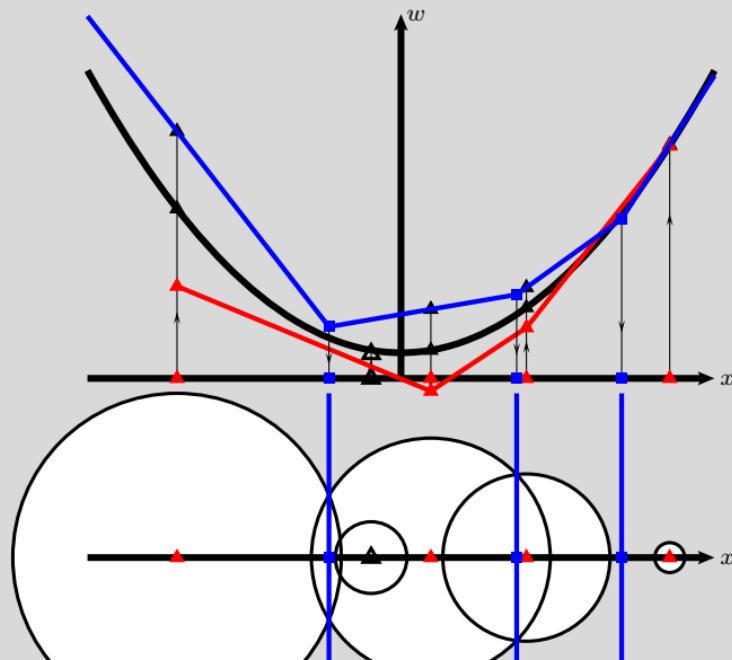
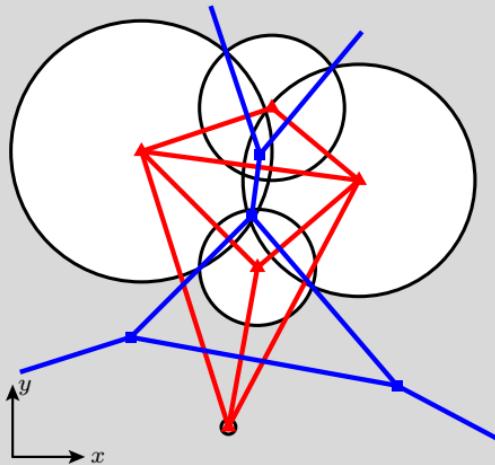
Delaunay/Voronoi tessellation  
dissects space into orthogonal tetrahedra,  
in each use analytical formulae for volumes, surfaces, arclengths, orientations  
Delaunay/Voronoi is equivalent to a lower-convex-hull problem:



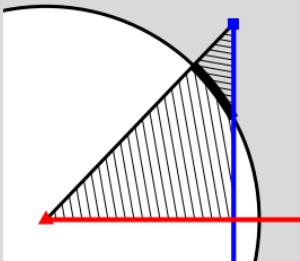
## Excursion 1: weighted Delaunay/Voronoi tessellation



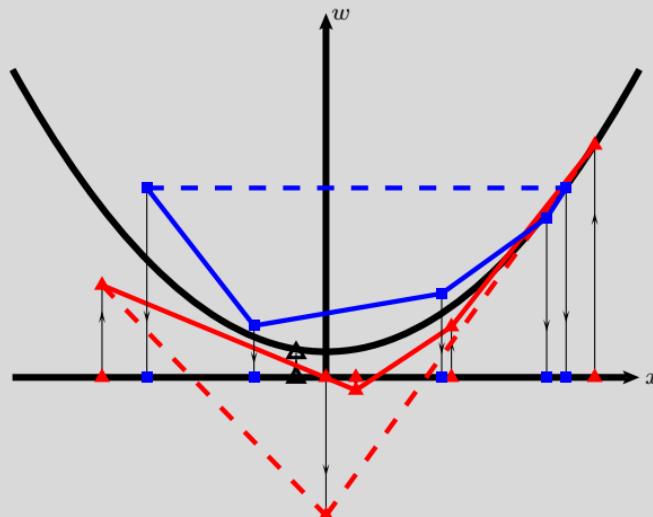
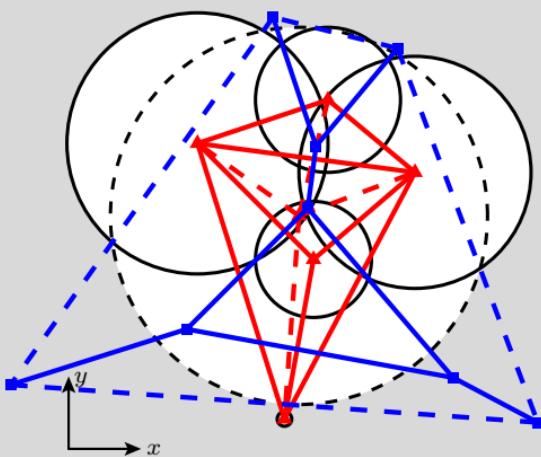
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## Excursion 1: double weighted Delaunay/Voronoi tessellation

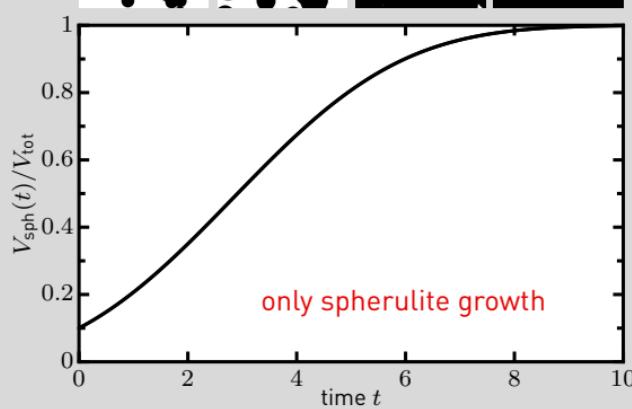
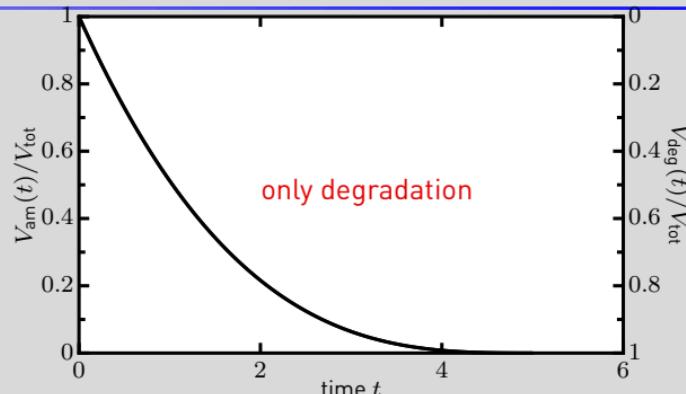
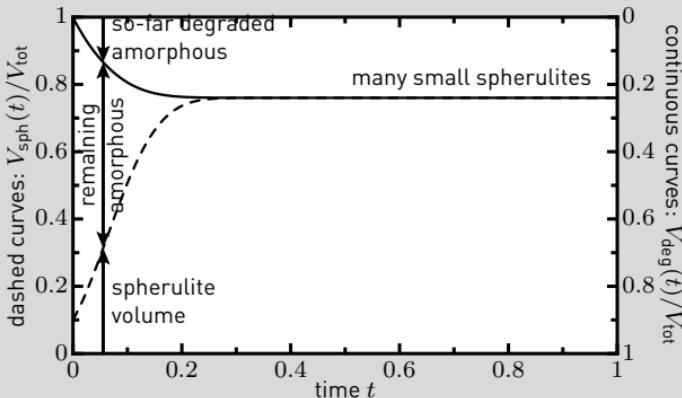


Delaunay/Voronoi tessellation  
dissects space into orthogonal tetrahedra,  
in each use analytical formulae for volumes, surfaces, arclengths, orientations  
Delaunay/Voronoi is equivalent to a lower-convex-hull problem:



# 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:

$$\xi := \text{Prob}[\mathbf{x} \text{ is covered}]$$

$$= 1 - \text{Prob}[\mathbf{x} \text{ is not covered}]$$

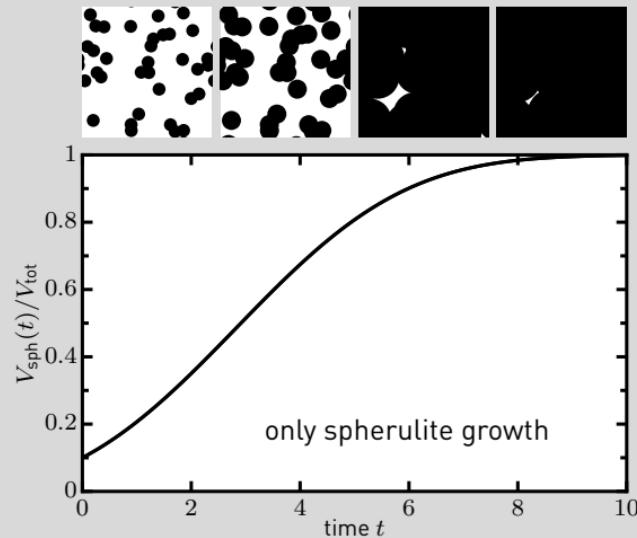
$$= 1 - \prod_{i=1}^N \text{Prob}[\mathbf{x} \text{ is not covered by sphere } i]$$

$$= 1 - \prod_{i=1}^N \left(1 - \frac{4\pi R_s^3}{3V}\right)$$

$$= 1 - \left(1 - \frac{4\pi R_s^3}{3V}\right)^N = 1 - \left(1 - \frac{1}{N} N' \frac{4\pi R_s^3}{3}\right)^N$$

$$\xrightarrow{N \rightarrow \infty} 1 - \exp\left(-N' \frac{4\pi R_s^3}{3}\right)$$

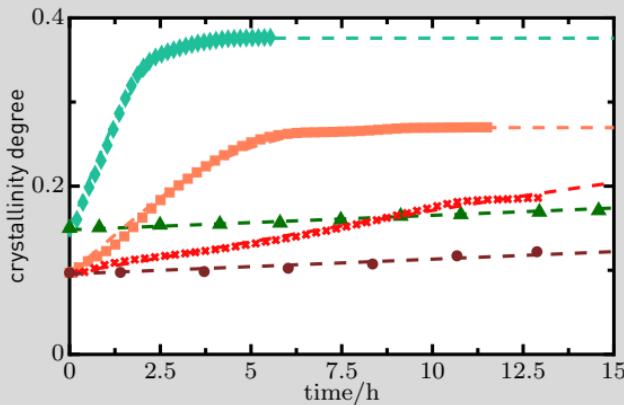
$$N' := N/V$$



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

◆ PET textile, 75°C    ★ PET bottle, 68°C  
▲ PET textile, 65°C    ● PET bottle, 65°C  
■ PET bottle, 75°C



spherulite parameters from fit to

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

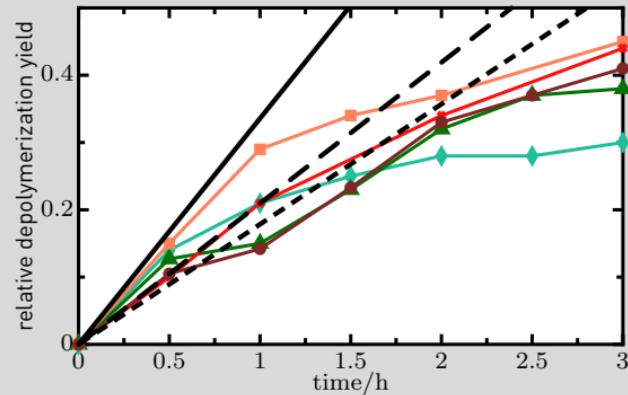
$$B = (N')^{1/3} R_{s0},$$

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

Need further input for  $N'$ : haze

$A$  remains undetermined!

◆ PET textile, 75°C    ● PET bottle, 65°C  
▲ PET textile, 65°C    — initial slope 75°C  
■ PET bottle, 75°C    — initial slope 68°C  
★ PET bottle, 68°C    — initial slope 65°C



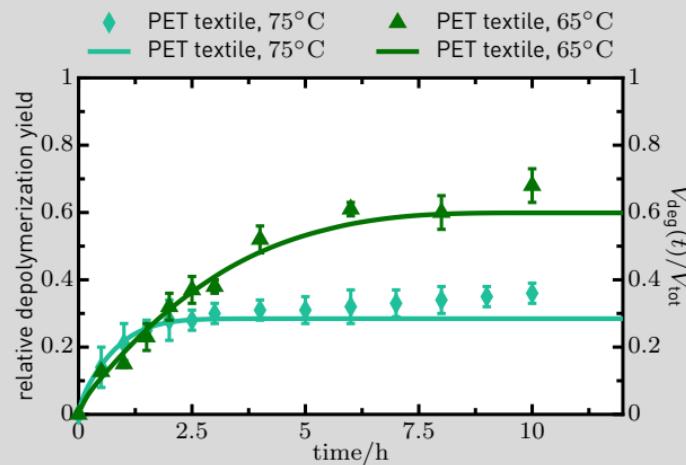
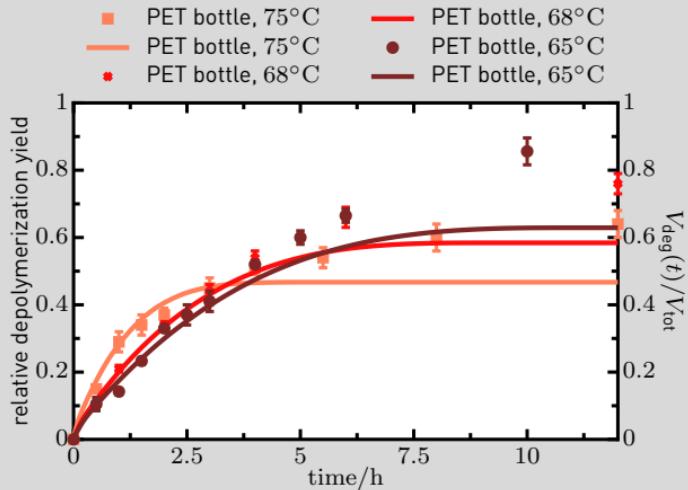
depolymerisation parameters from initial slope

$$D [1 - (1 - Et)^3]$$

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

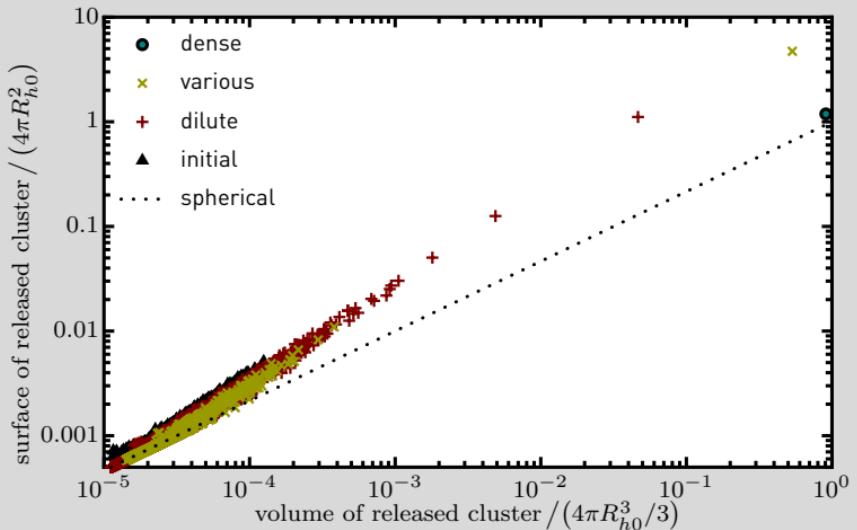
Initial covering by spherulites is important  
Take only one slope per temperature!

# Comparing experiments and numerics



Additional slow degradation of spherulites happens also ...

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



# Enzyme genetics + physico-chemistry + modeling:

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Ludwik Leibler (Gulliver lab, CNRS)



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

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



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