



Quantitative Microstructure Characterization of a NMC Electrode

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Outline

Characterization of NMC (already segmented) microstructures with a focus on numerical methods, bias/assumption, RVE size, and voxel size dependence

- Introducing original “level of details” parameters
- Volume fractions and connectivity
- Particle size
 - Calendaring effect
 - Correlate RVE size with standard deviation
 - Results from different methods compared
- Tortuosity factor
 - Voxel size and RVE analysis (including isotropy)
 - Introducing original two-step homogenization method
 - Calendaring effect
 - Spatial variation along electrode thickness.

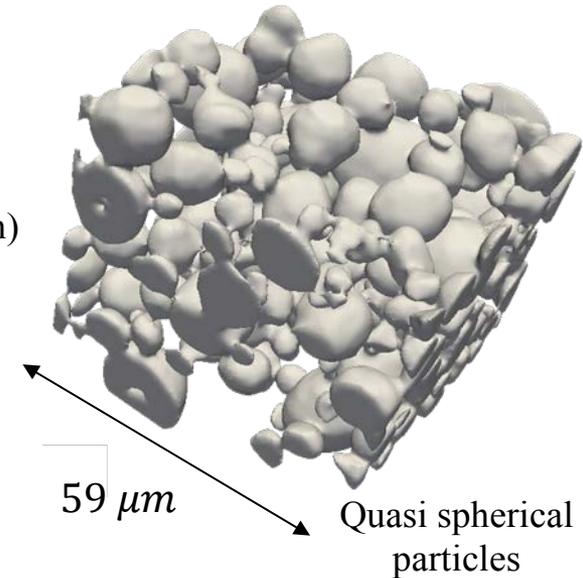
Surface area results are in the annexes slides

- **Un-calendared (UC) & Calendared (C) positive NMC** ($\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$) electrode, with different composition of active material (wt 90%, 92%, 94%, and 96%).
Raw (X-ray tomographic microscopy) and binarized image available online (**open-source data**) on the ETH (Swiss Federal Institute of Technology Zurich) website.

Ebner et al. Adv. Energy Mater. 2013, 3, 845–850

- Secondary phase has not been identified (considered as pore)

- Total of **16 Volumes**



Analyzed domain size: $328.9 \times 328.9 \times A \mu\text{m}^3$
Equivalent domain size: $B \times B \times B \mu\text{m}^3$

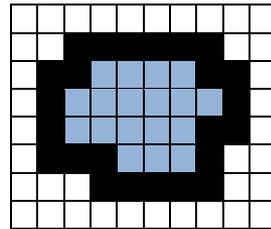
| Composition of the active material (%) | Un-calendared electrode | Calendared electrode (300 bar) | Calendared electrode (600 bar) | Calendared electrode (2,000 bar) |
|--|-------------------------|--------------------------------|--------------------------------|----------------------------------|
| 90 | 50.3 (176) | 52.2 (178) | 47.7 (173) | 57.0 (183) |
| 92 | 45.9 (171) | 77.3 (203) | 58.8 (185) | 61.1 (188) |
| 94 | 65.9 (192) | 78.8 (204) | 74.0 (200) | 64.8 (191) |
| 96 | 98.1 (220) | 94.7 (217) | 101.0 (222) | 87.7 (212) |

Voxel size: $370 \times 370 \times 370 \text{ nm}^3$

Level of details of a microstructure

Introducing parameters dedicated to evaluate the image quality

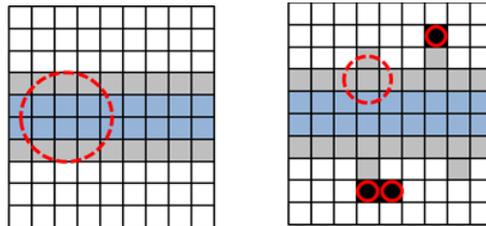
$$\text{Edge volume ratio} = \begin{cases} 1 - \frac{\text{Edge "volume"}}{\text{Phase volume}} \\ 1 - \frac{\sum \blacksquare}{\sum \blacksquare + \sum \blacksquare} \end{cases}$$



≤

$$\text{One voxel particle volume ratio} = 1 - \frac{\text{Volume}(\textit{particle described by 1 voxel})}{\text{Phase volume}}$$

Will increase if smooth interface

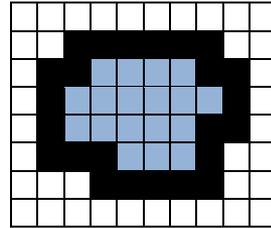


- Based upon edge detection
- Easy to interpretate: values ranges from 0 (poor) to 1 (ideal)
- Ideal to compare different data set image quality and different obs. techniques

Level of details of a microstructure

Introducing parameters dedicated to evaluate the image quality

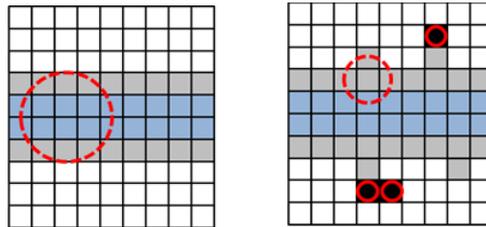
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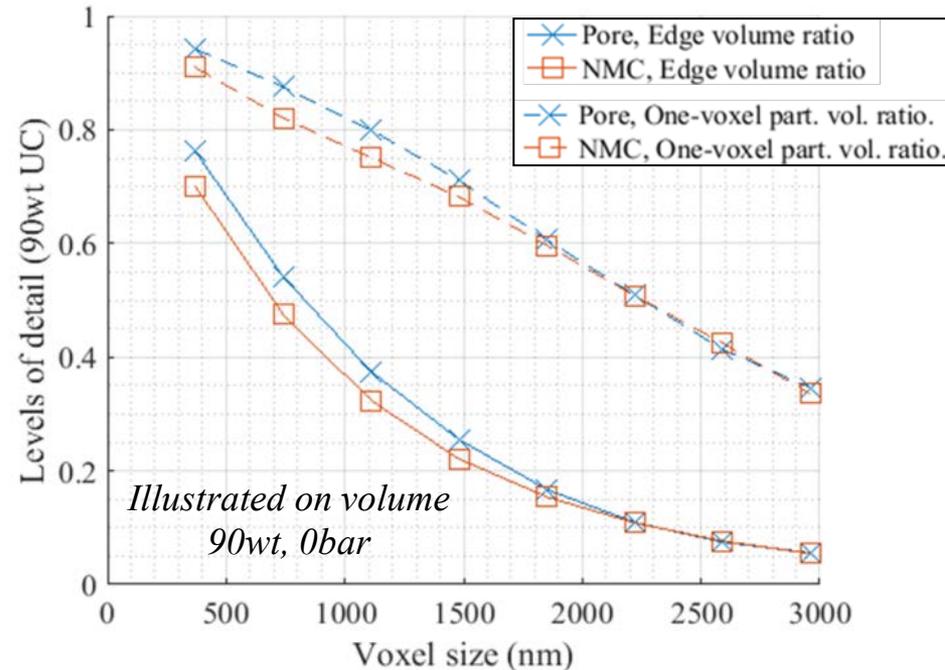
≤

$$\text{One voxel particle volume ratio} = 1 - \frac{\text{Volume}(\text{particle described by 1 voxel})}{\text{Phase volume}}$$

Will increase if smooth interface



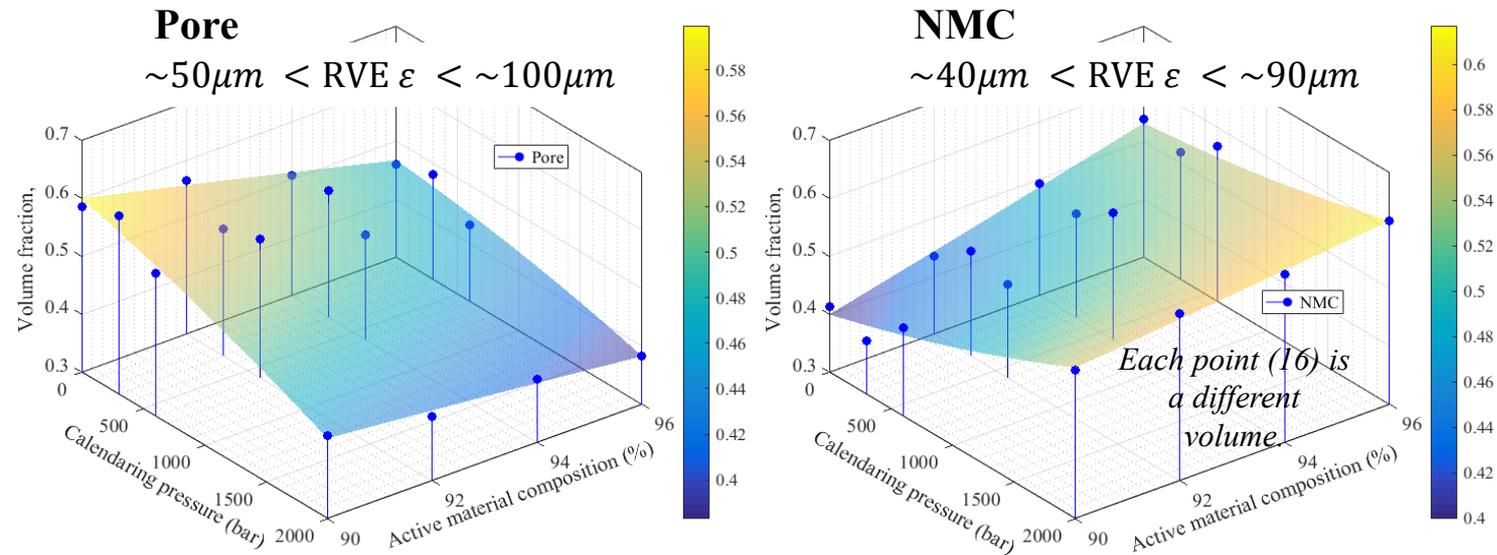
- Based upon edge detection
- Easy to interpretate: values ranges from 0 (poor) to 1 (ideal)
- Ideal to compare different data set image quality and different obs. techniques



- As expected, level of details are degrading monotonously with image resolution.
- High level of details have been achieved by Ebner group.
- Both phases exhibits similar values (2-phase data-set).

Volume fraction & connectivity

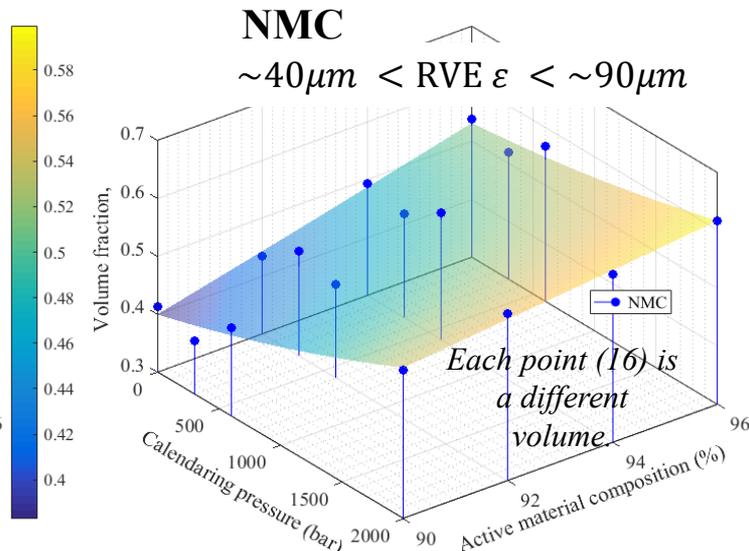
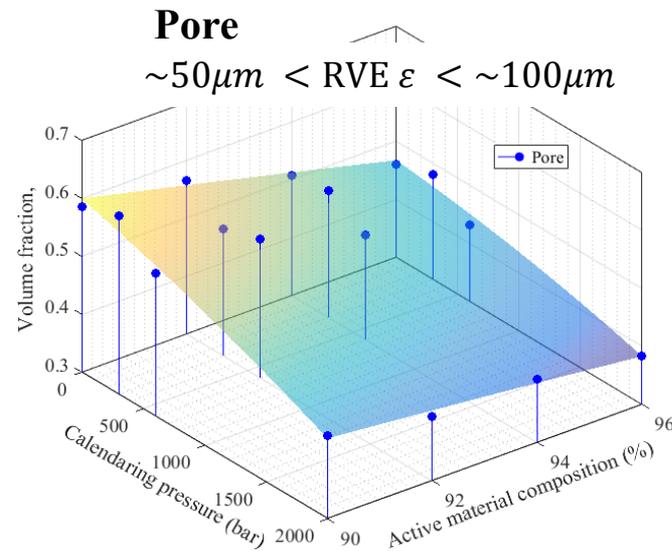
Results obtained on the 16 volumes (4 calendaring X 4 active material composition)



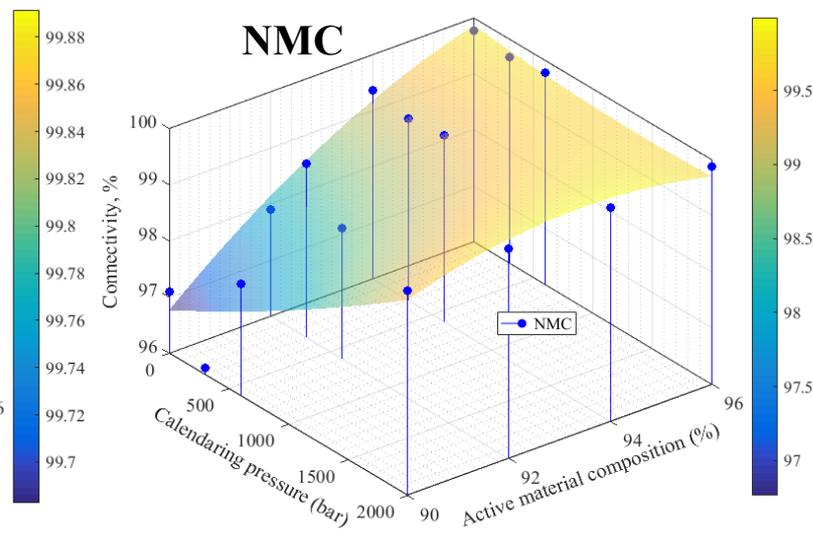
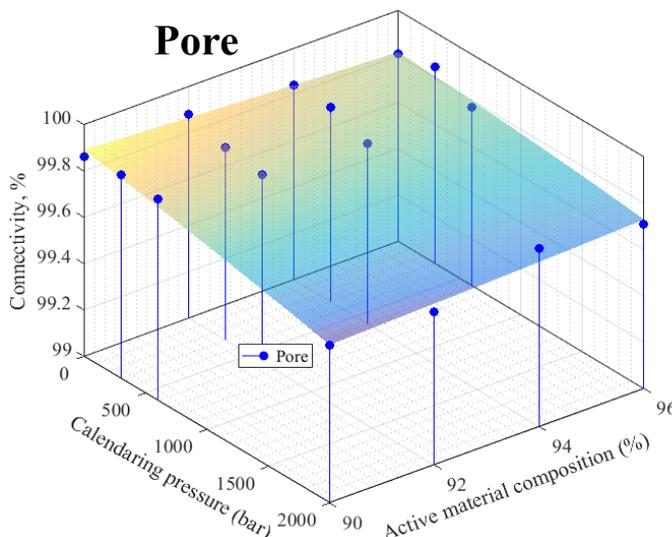
Porosity is \searrow when active material composition is \nearrow (because secondary phase has been identified as pore) and when calendaring pressure is \nearrow

Volume fraction & connectivity

Results obtained on the 16 volumes (4 calendaring X 4 active material composition)



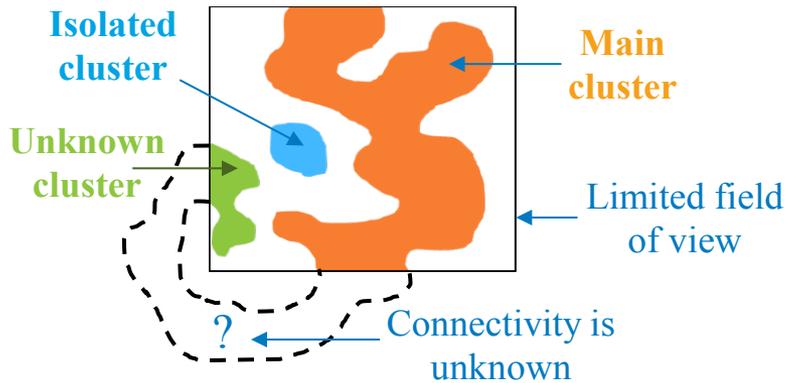
Porosity is \searrow when active material composition is \nearrow (because secondary phase has been identified as pore) and when calendaring pressure is \nearrow



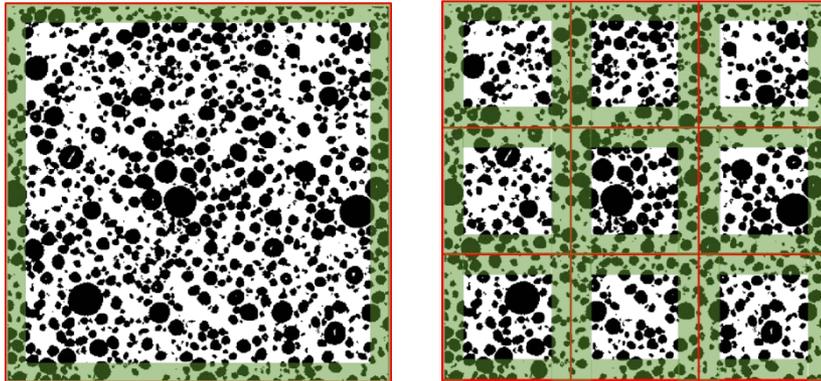
Very high connectivity (percolation) is achieved. Solid particles have a better connectivity when calendaring pressure is \nearrow and when active material composition is \nearrow

Volume fraction & connectivity

Edge effect induce a loss of percolation on small domains, especially for NMC



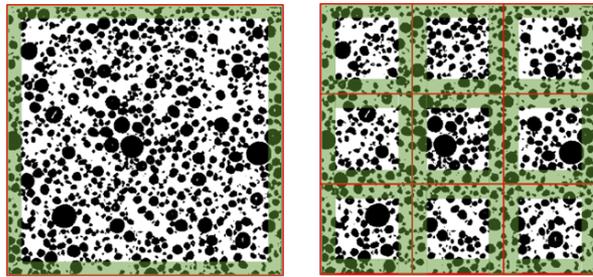
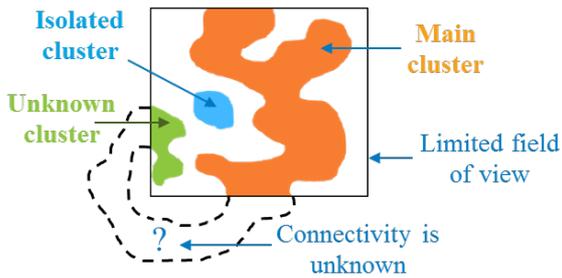
J. Joos et al., *Journal of Power Sources* 246, 819–830 (2014).



Unknown clusters are accumulating on subdomains → global amount of unknown voxel is increasing.

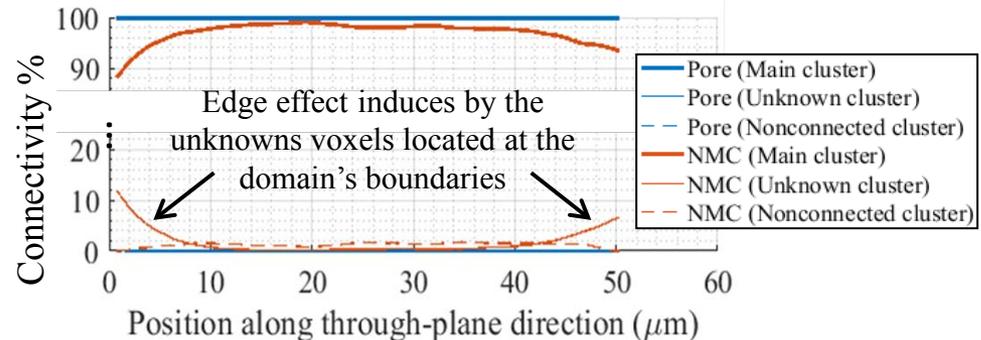
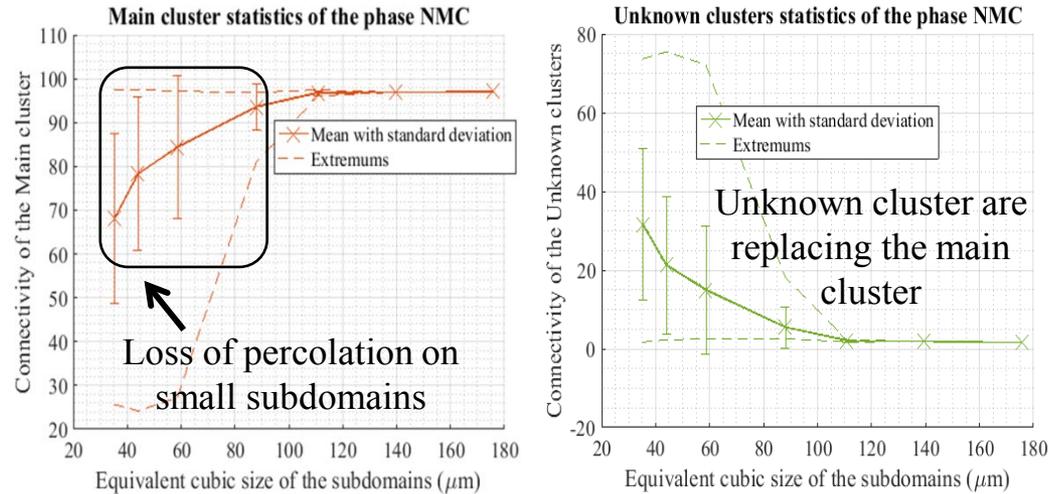
Volume fraction & connectivity

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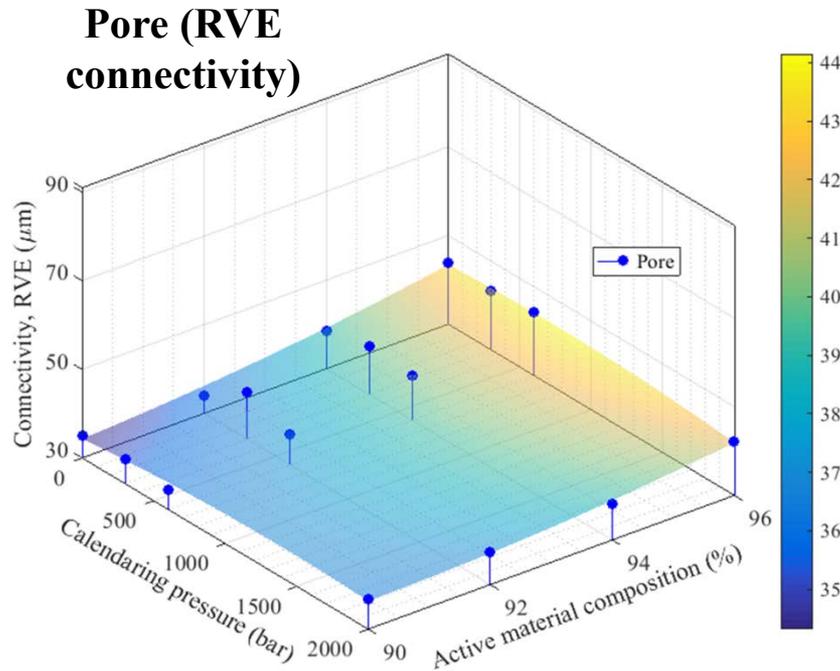
Illustrated on NMC, 90 wt, 0 bar



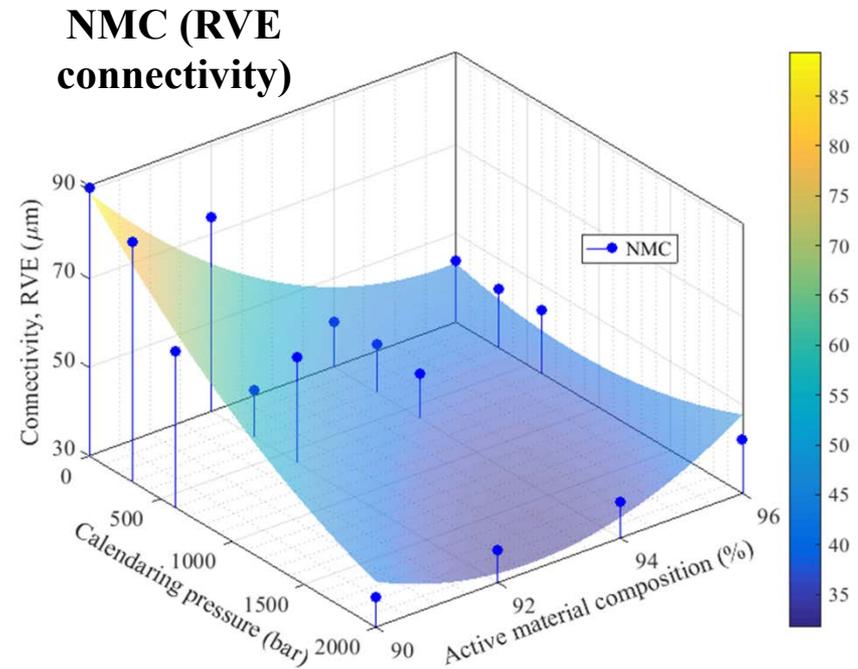
NMC small subdomains suffer from loss of percolation due to this edge effect. Pore is untouched.

Volume fraction & connectivity

This edge affects mainly the solid phase when calendaring pressure is not applied, as a result RVE for the connectivity is much more higher for the NMC



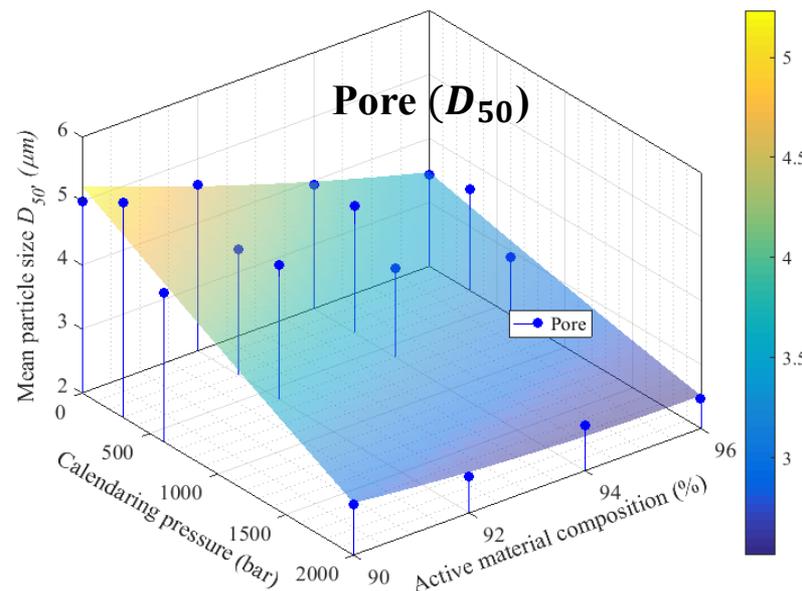
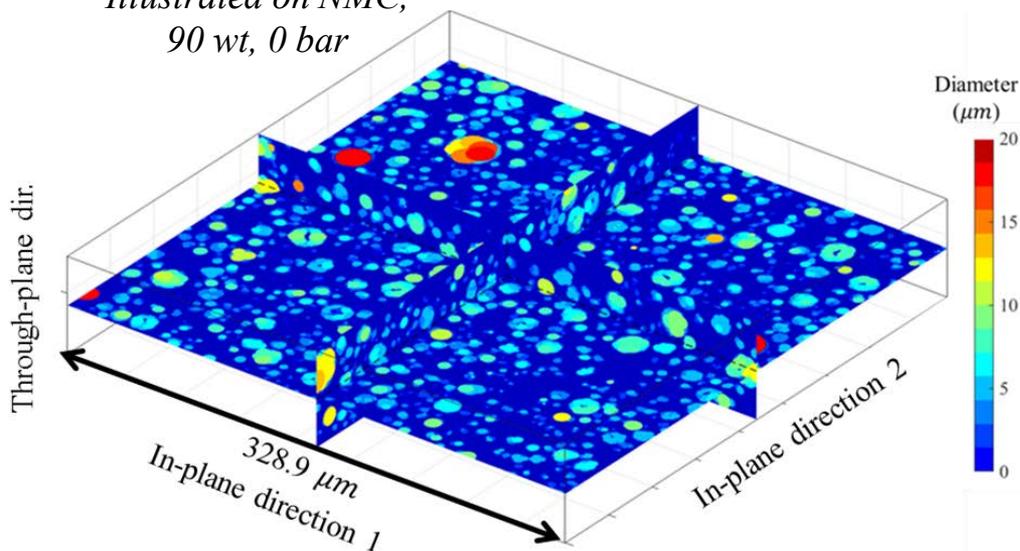
Pore exhibits excellent connectivity even for small volume (RVE is $< 45 \mu\text{m}$ for all volumes)



On the contrary, NMC need a larger volume to get connected. High calendaring pressure and active material composition reduce the RVE.

Particle size: spherical assumption (C-PSD)

Illustrated on NMC,
90 wt, 0 bar

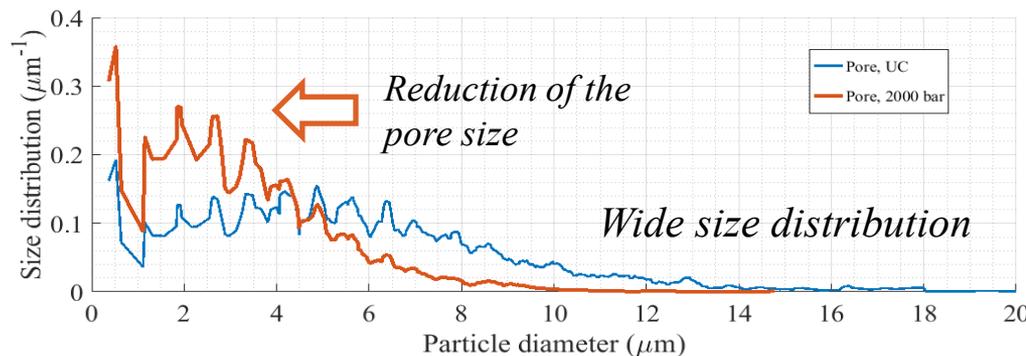


Voxels are attributed to the largest sphere that contains them.

L. D. Gelb and K. E. Gubbins, Langmuir 1999, 15, 305-308

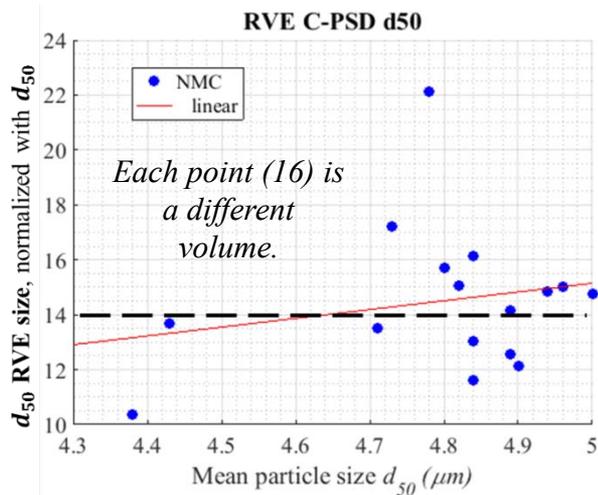
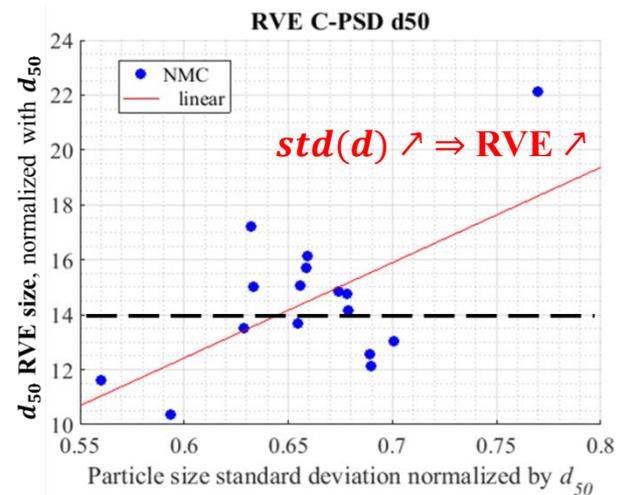
Underestimation of the size distribution is expected due to this particle shape assumption

Calendaring pressure significantly reduces the pore size. Slight effect on the NMC



Particle size: Representative volume element (RVE) size

Correlating RVE size of d_{50} with particle size: d_{50} & $std(d)$

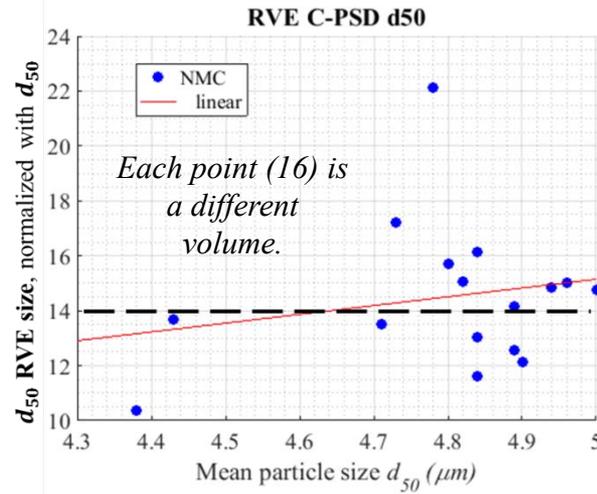
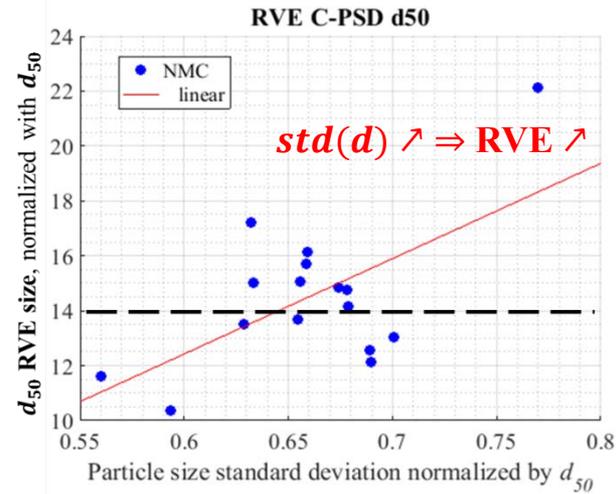


NMC (RVE D_{50}) normalized with d_{50}

Each point (16) is a different volume.

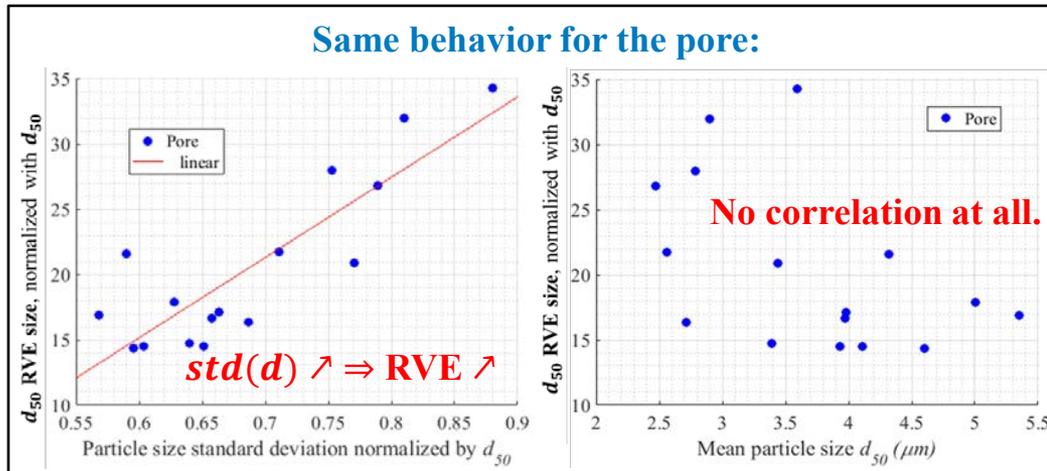
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NMC (RVE D_{50}) normalized with d_{50}

Each point (16) is a different volume.



RVE, by definition, must catch all heterogeneities of the medium → the more heterogeneous the medium is, the larger the RVE will be.

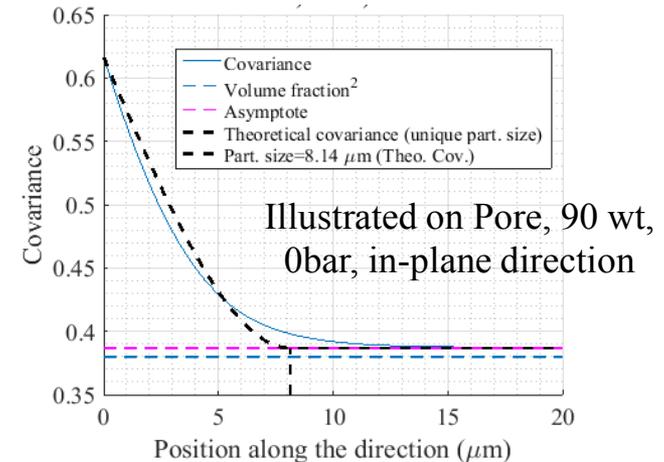
Simple rule $RVE = 14 \times d_{50}^*$ is not enough for medium with a wide size distribution

Particle size: statistical approach & watershed method

Alternative methods to avoid particle size underestimation

Statistical approach

- Based upon a two-point correlation (covariance) function.
- **Spherical assumption is no more used.** But less detail are available (no size distribution)
- **Refinement added to the classic method to improve the determination of the mean particle and pore size.**



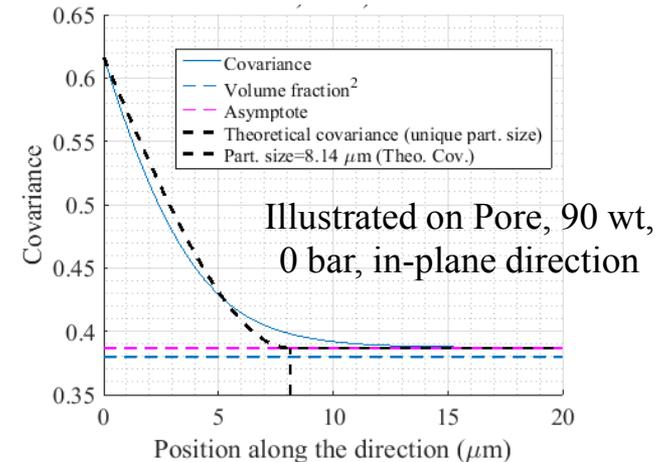
Detailed in the back-up slides to save presentation time, and in the upcoming ECTS article

Particle size: statistical approach & watershed method

Alternative methods to avoid particle size underestimation

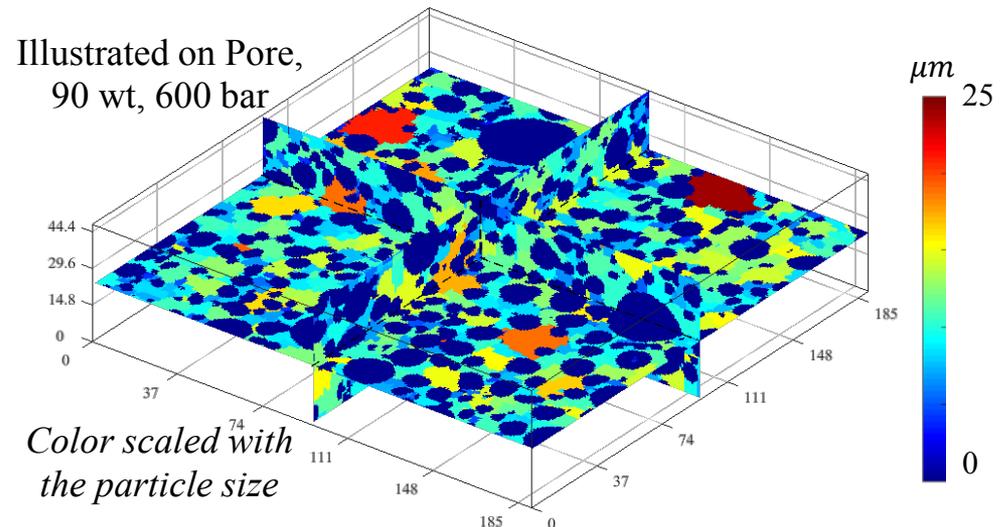
Statistical approach

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Watershed method

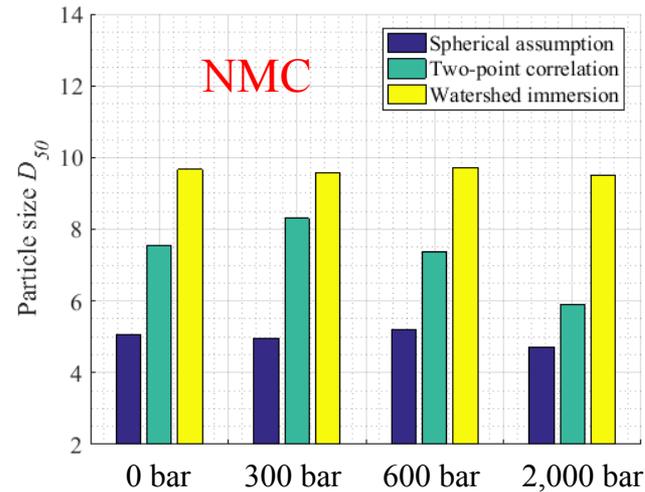
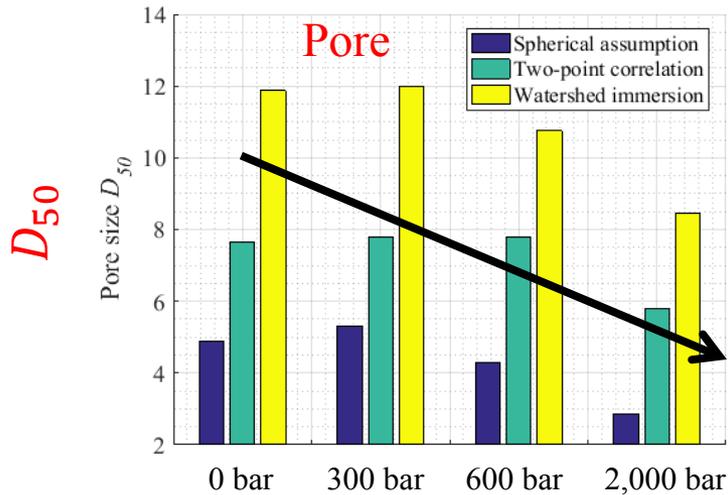
- Based upon an immersion approach, with a **refinement to handle over-segmentation**
- Distinct particles are identified without any shape assumption.



Detailed in the back-up slides to save presentation time, and in the upcoming ECTS article

Particle size: all three methods compared

Particle size difference illustrated on the 90 wt electrode with different compression level

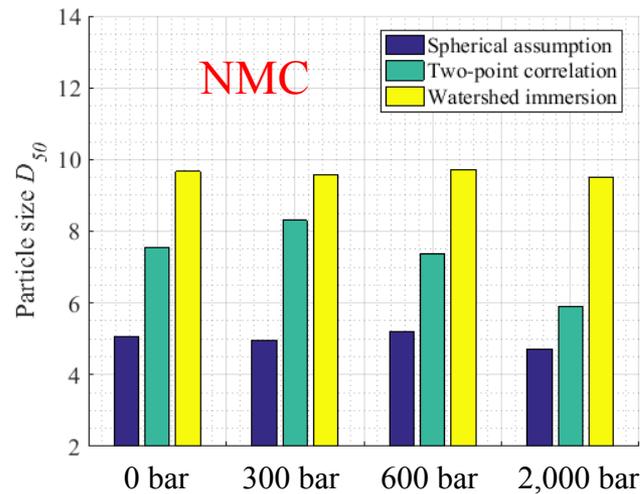
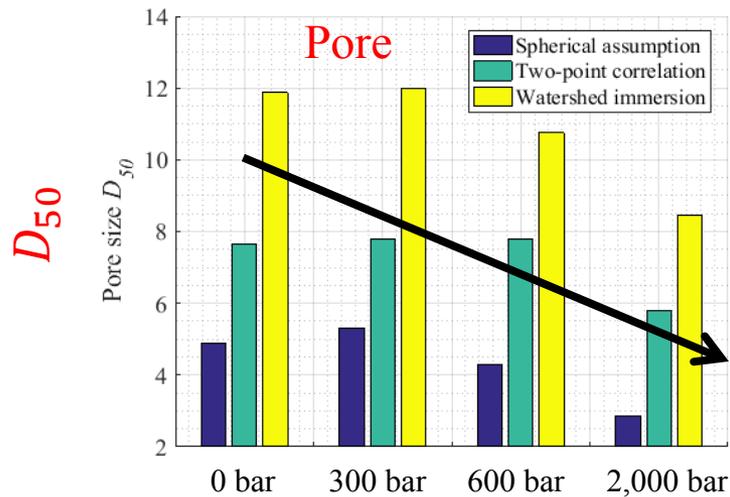


All methods describe D_{50} for the pore with compression

C-PSD
<
statistical approach
<
watershed

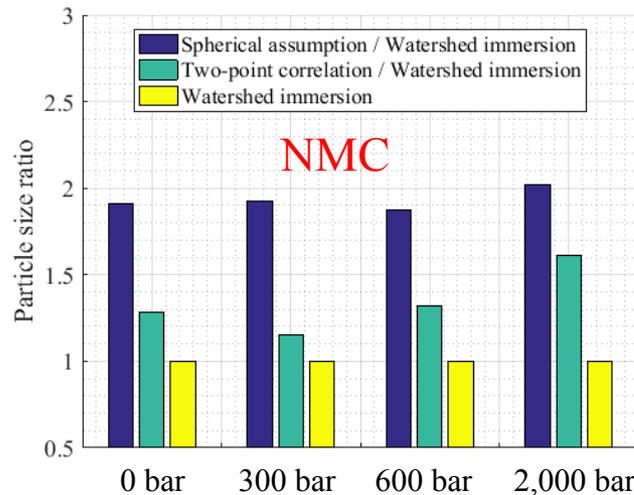
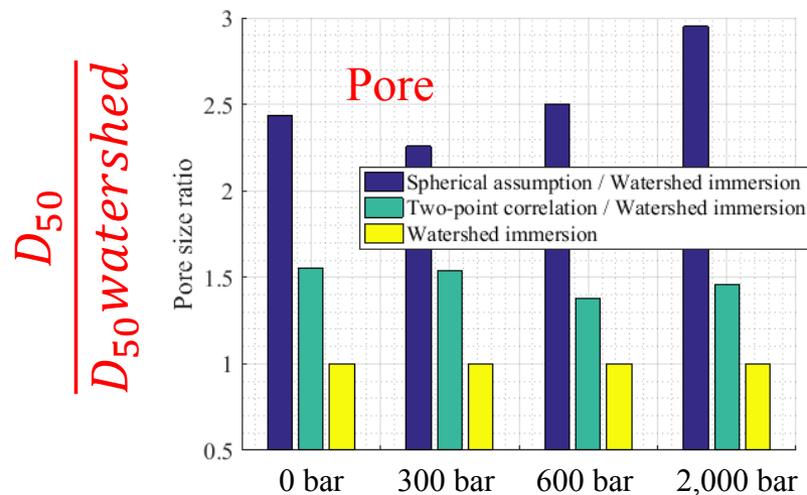
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Particle size difference illustrated on the 90 wt electrode with different compression level



All methods describe D_{50} for the pore with compression

C-PSD < statistical approach < watershed

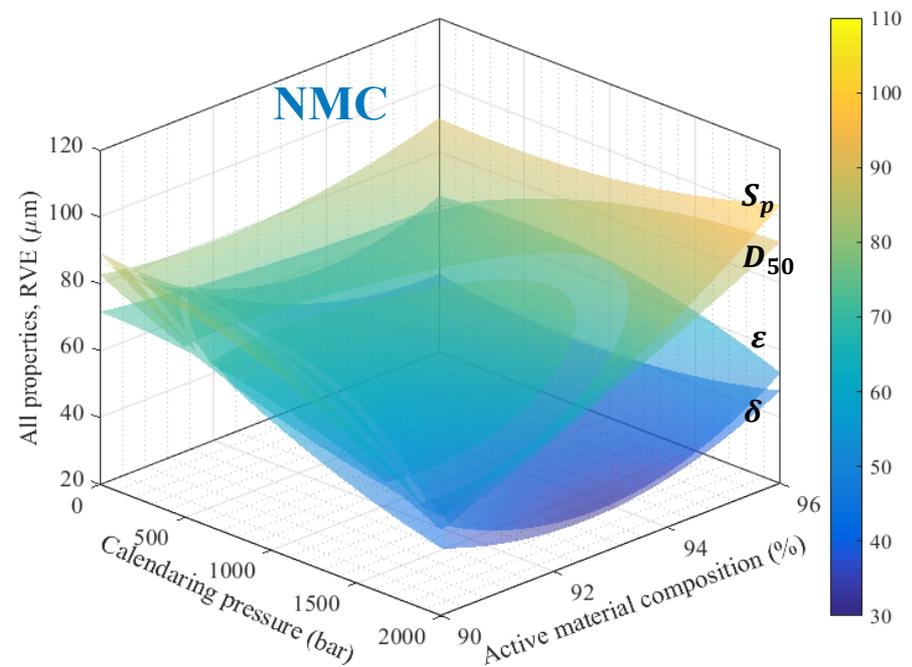
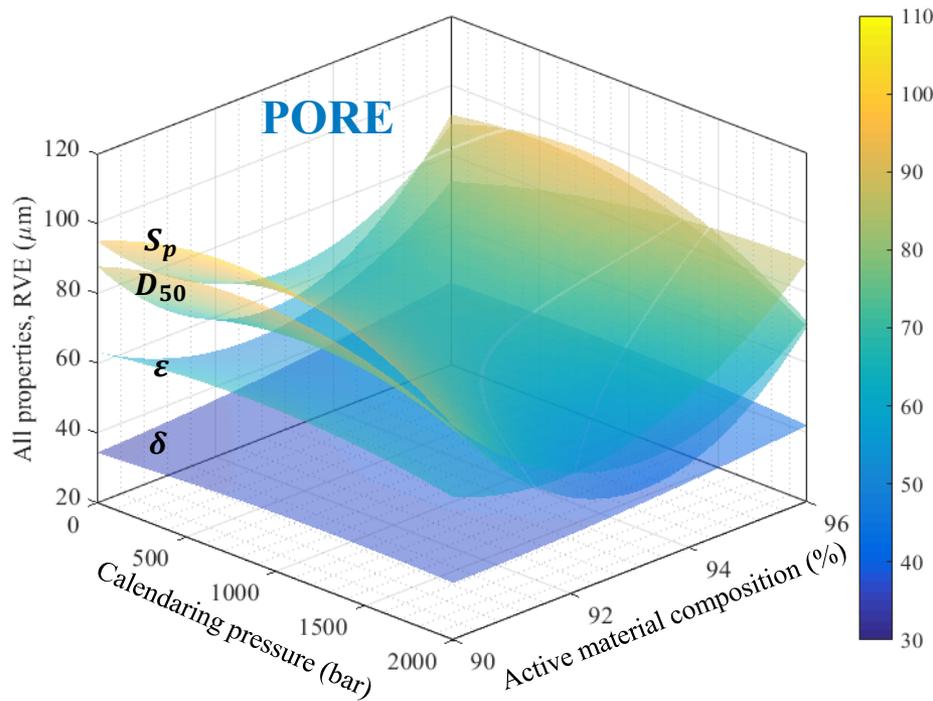


Ratio is quite high, but expected

~2.8 found by L. Holzer et al. JPS 196 (2011) 7076-7089

Ratio is higher for Pore than for NMC → Pore are less spherical than NMC particles. NMC are not so spherical.

Summary of RVE size



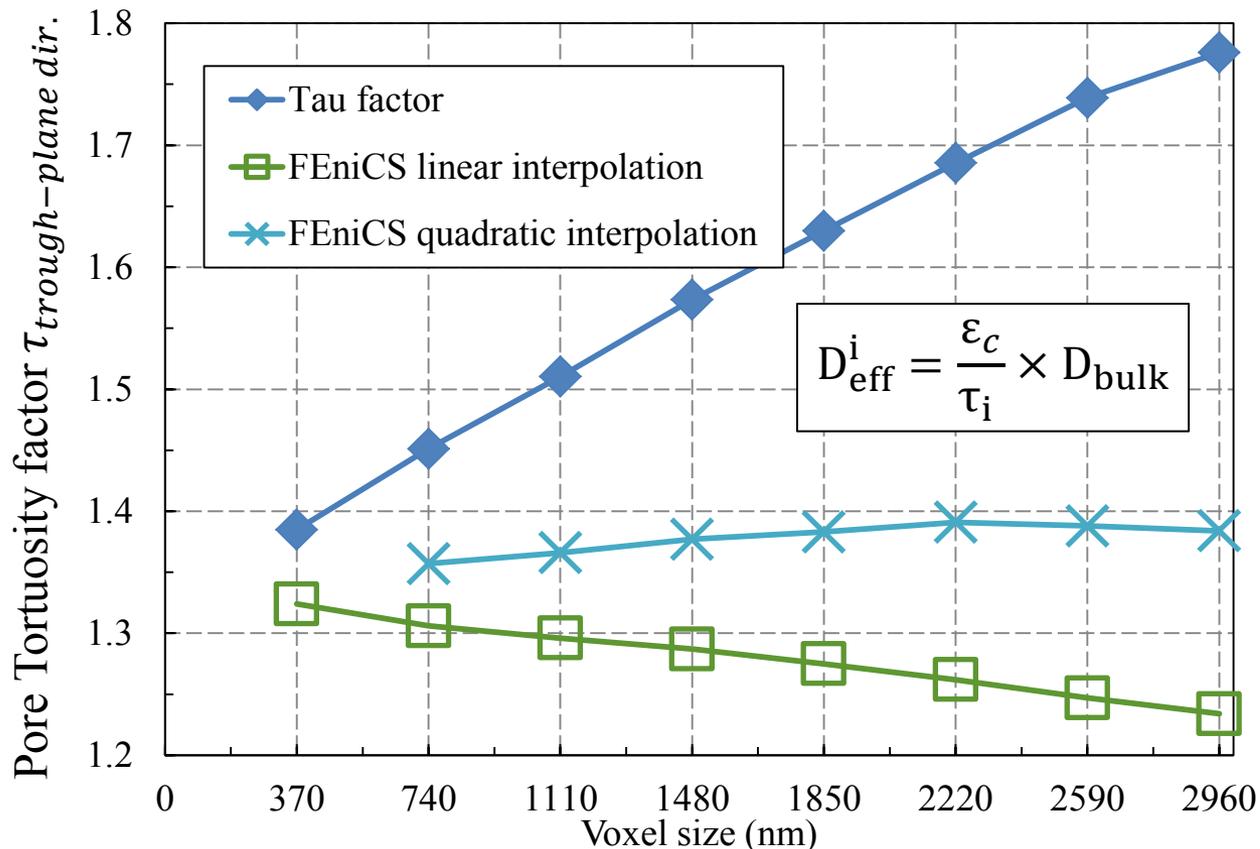
Quadratic polynomial surface fit on RVE size

| Pore RVE (μm) | Mean | Max | Std |
|-----------------------------|------|-------|------|
| Volume fraction ϵ | 63,9 | 97,1 | 13,7 |
| Connectivity δ | 38,9 | 44,3 | 3,4 |
| Mean particle size D_{50} | 73,2 | 123,1 | 20,3 |
| Specific surface area S_p | 79,5 | 123,3 | 20,9 |

| NMC RVE (μm) | Mean | Max | Std |
|-----------------------------|------|-------|------|
| Volume fraction ϵ | 62,1 | 88,4 | 16,6 |
| Connectivity δ | 50,9 | 90,6 | 17,6 |
| Mean particle size D_{50} | 69,6 | 105,8 | 13,4 |
| Specific surface area S_p | 78,3 | 123,7 | 19,3 |

RVE is property dependent

Factor of tortuosity: voxel size dependence analysis

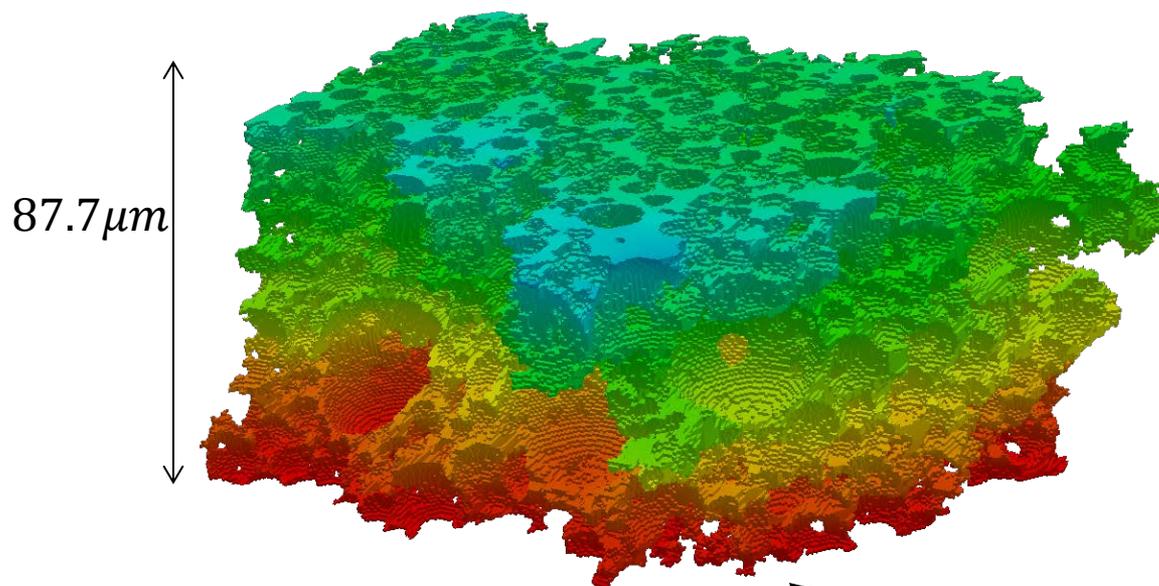


- Both methods (FEM & neighbors difference) are converging to the same value.
- FEniCS has been used since it allows applying different boundary conditions.
- Save CPU time and memory: FEniCS with a linear interpolation and a voxel size of 740 nm.

- **Tau factor** (open source) iteratively solves the Laplace equation, using a neighbors difference, with Dirichlet Boundary conditions and a great emphasis on speed convergence *S.J. Cooper et al., Software X 5 (2016) 203-210*
- **FEniCS** (open source) solves steady-state Laplace equation with the finite elements method. Dirichlet BC used in this figure.

Voxel size analyze performed on a pore subdomain ($\sim 185 \times 185 \times 50 \mu\text{m}^3$) of the 90 wt un-calendared electrode.

Factor of tortuosity: field of view and resolution achieved

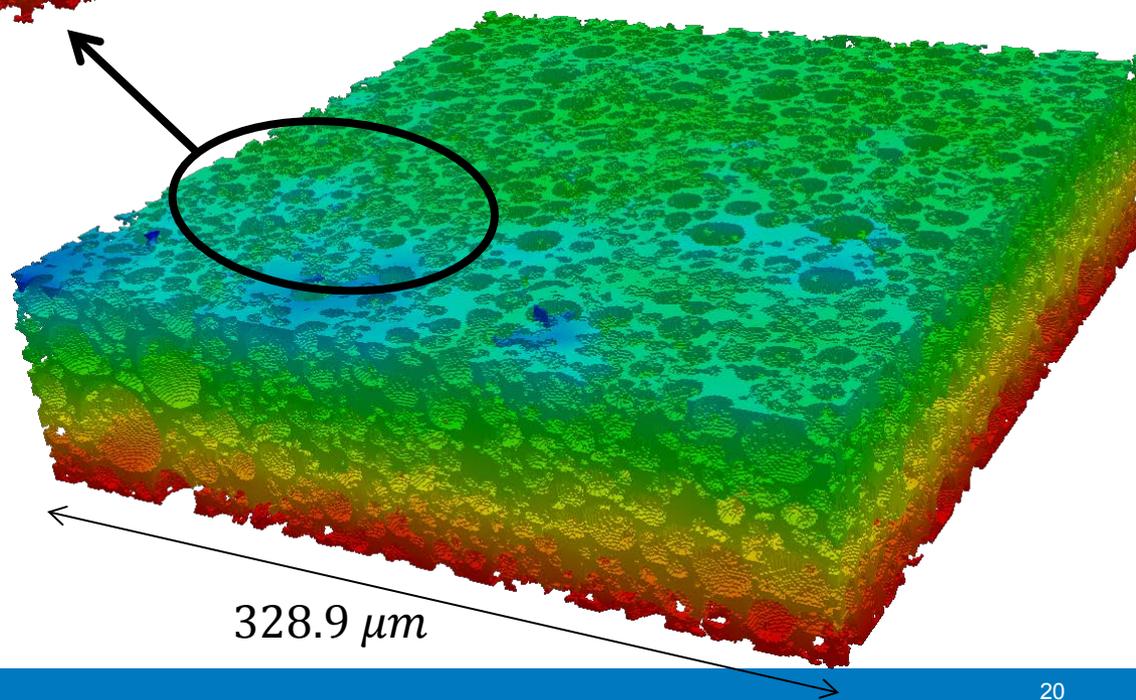


Concentration field
calculated on the 96 wt
calendared (2,000 bar)
electrode, within the pore
with mixed boundary
condition.

$$328.9 \times 328.9 \times 87.7 \mu\text{m}^3$$

Voxel size: 740 nm
8,909,443 voxels &
13,026,509 degree of freedom
for the pore.
CPU time: ~245 seconds (HPC)

Achieved with FEniCS open
source software (Finite element
method)

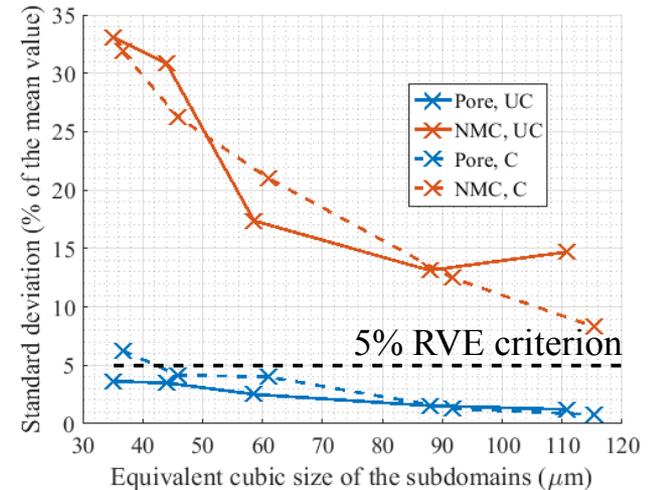
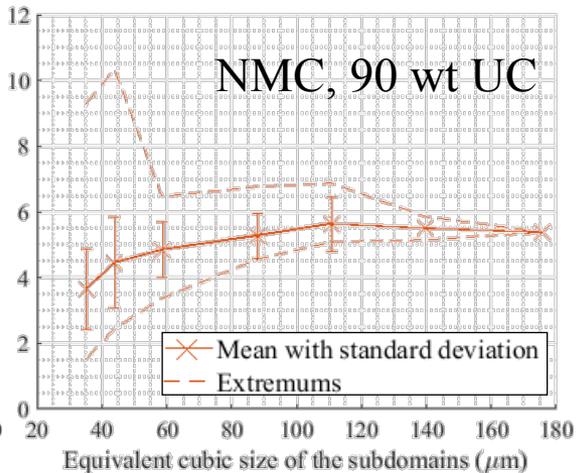
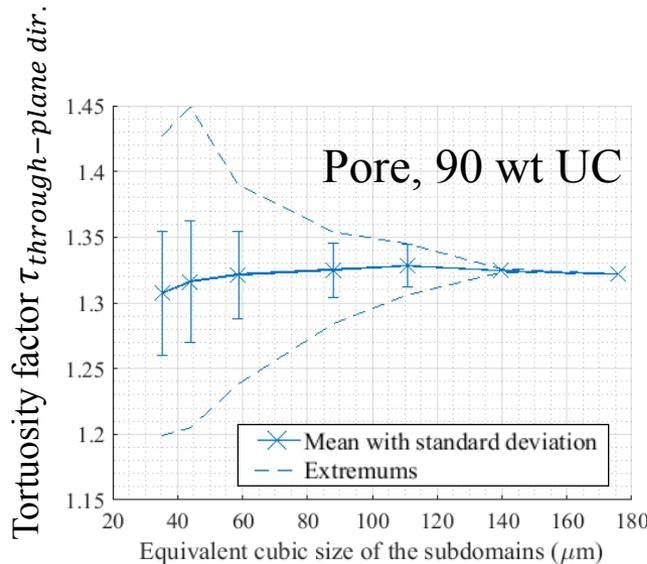


Factor of tortuosity: Representative volume element analysis

- **RVE analysis on $\tau_{through-plane dir.}$ with mixed BC (i.e. Dirichlet-Neumann)**

Illustrated on 90 wt, UC and C (2,000 bar) for both phases

For which domain's size $\tau_{through-plane dir.}$ is stable ?



Tortuosity table (the RVE are written in parentheses)

| | Pore | | NMC | |
|-----------------------------|------------------------------|-----------------------------|--|--|
| | UC | C (2000 bar) | UC | C (2000 bar) |
| $\tau_{through-plane dir.}$ | 1.322 (<35.2 μm) | 1.593 (42.2 μm) | 5.379 (>110.7 μm , std~15%) | 3.597 (>115.4 μm , std~10%) |

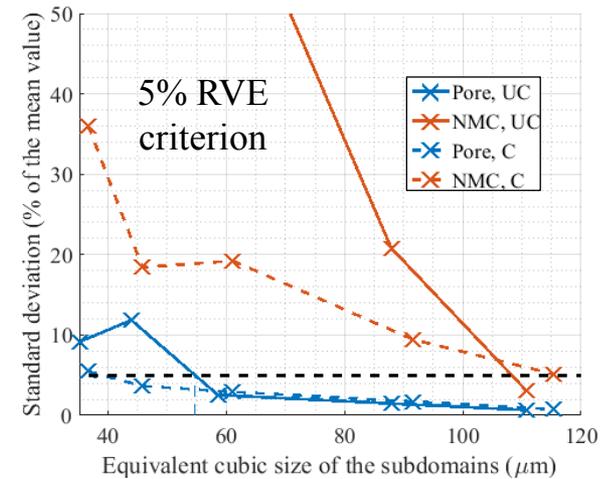
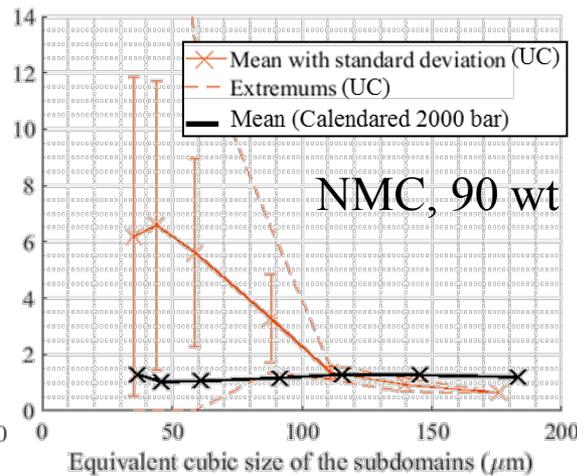
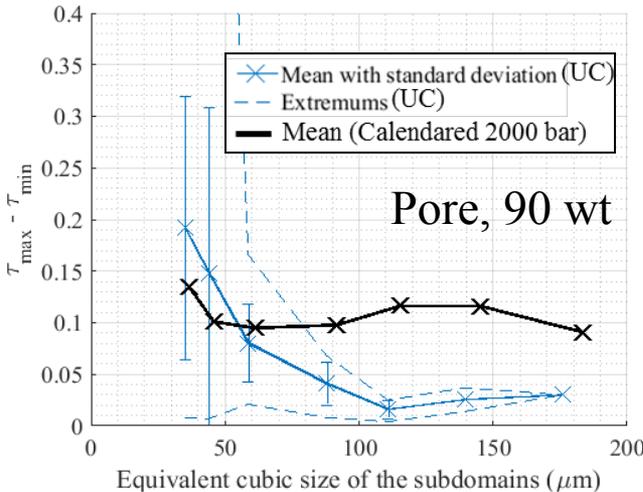
RVE pore < RVE solid & $\tau \uparrow \Rightarrow \text{RVE} \uparrow$

Mean value subdomains \neq value whole domain

Factor of tortuosity: Representative volume element analysis

- RVE analysis on τ anisotropy with mixed BC**
 Illustrated on 90 wt, UC and C (2,000 bar) for both phases

For which domain's size $\max\{abs(\tau_i - \tau_j)\}$ is stable?



Isotropy is expected since solid phase is made of quasi-spherical spheres with a random space distribution.

Tortuosity anisotropy table (the RVE are written in parentheses)

| | Pore | | | | NMC | | | |
|---------------------------|-------|-----------------------|--------------|-----------------------|------|------------------------|--------------|------------------------|
| | UC | | C (2000 bar) | | UC | | C (2000 bar) | |
| $\tau_{max} - \tau_{min}$ | 0.030 | (54.7 μm) | 0.091 | (39.0 μm) | 0.63 | (108.3 μm) | 1.194 | (115.4 μm) |

RVE $\tau_{anisotropy} \approx$ RVE $\tau_{through-plane dir}$
 (While being inferior for the NMC)

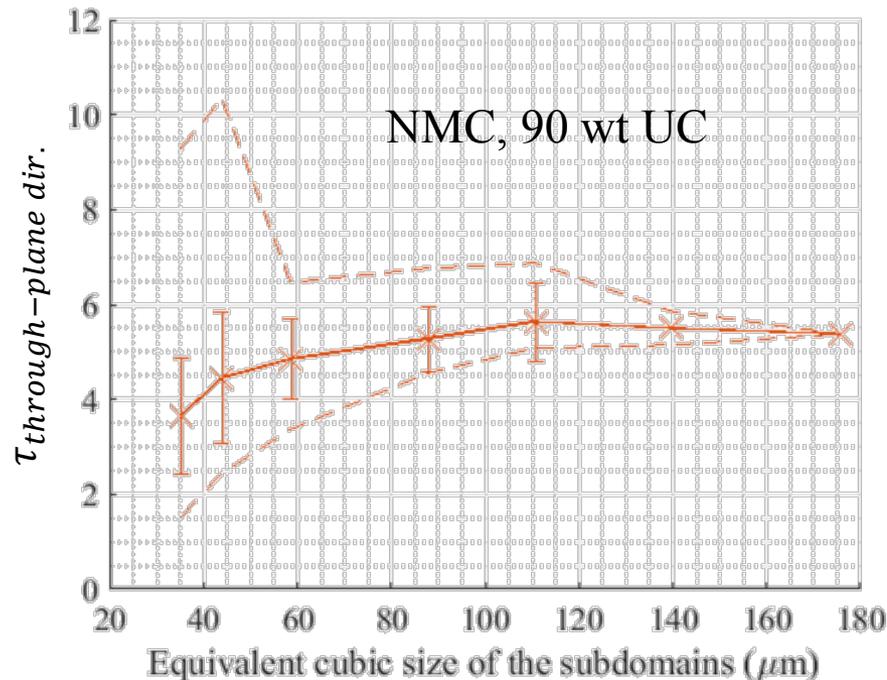
For the un-calendared electrode, subdomains are anisotropic while whole domain is isotropic: isotropy emerges only for large volume

Calendaring affects isotropy

RVE on boundary conditions has been also evaluated (back-up slides)

Factor of tortuosity: rule of mixture & percolation loss

Why factor of tortuosity obtained on subdomains differs from the whole domain?

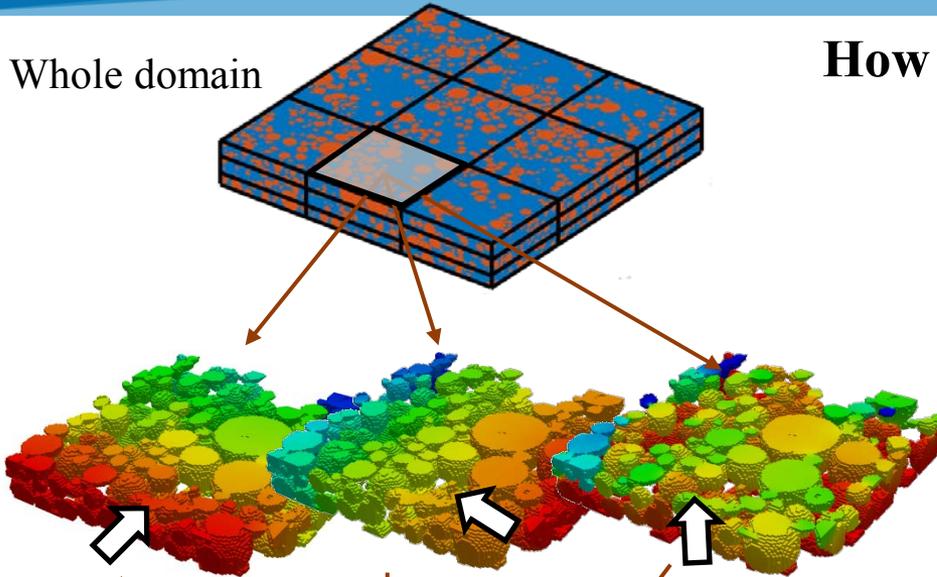


Loss of percolation on small subdomains should increase tortuosity by creating local bottleneck at the edges...but we see the opposite.

That's because taking the mean value (thus performed a **rule of mixture**) is a poor idea...it is **true only when the subdomains are assembled in parallel with the flux** (details in the annexes slides)

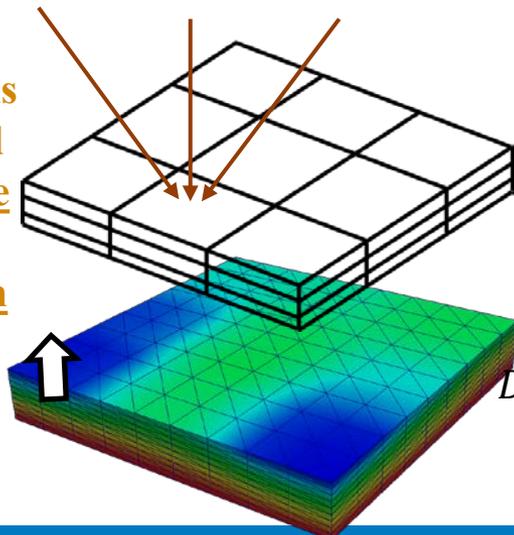
Factor of tortuosity: two-step homogenization numerical scheme

How to avoid using the mean value: two-step homogenization numerical scheme



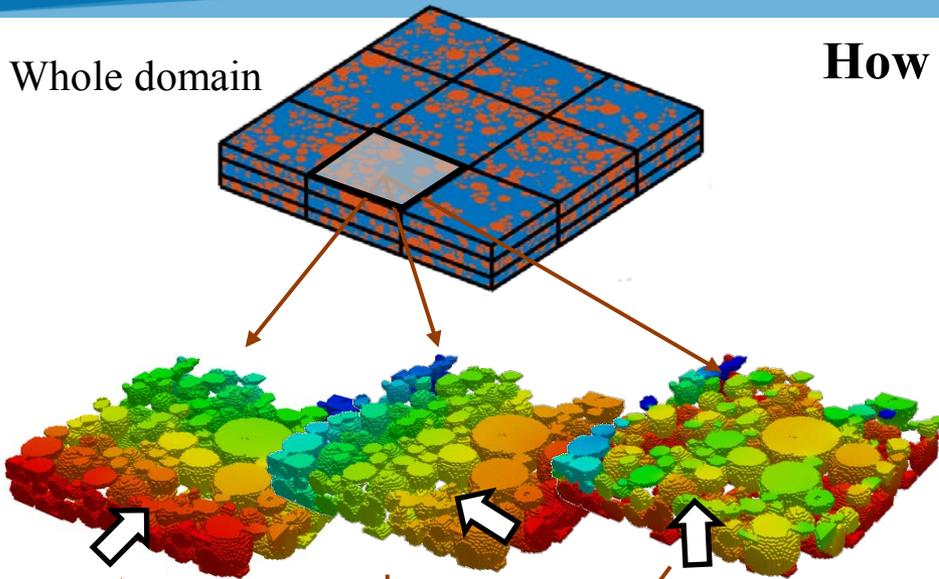
For each subdomain, D_x^{sub} , D_y^{sub} and D_z^{sub} are calculated (*1st homogenization calculation*)

Each subdomain is represented with a dense anisotropic coarse mesh

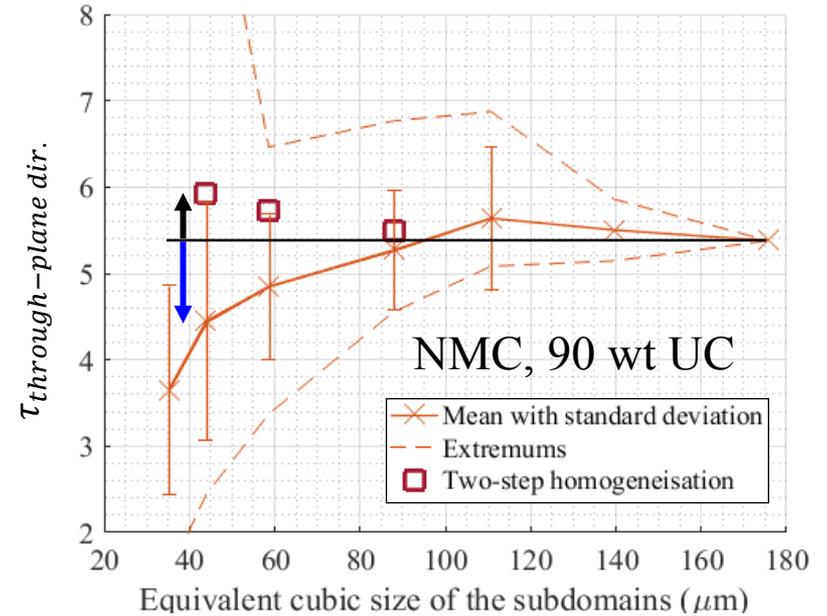


D_z^{eff} is calculated (*2nd homogenization calculation*)

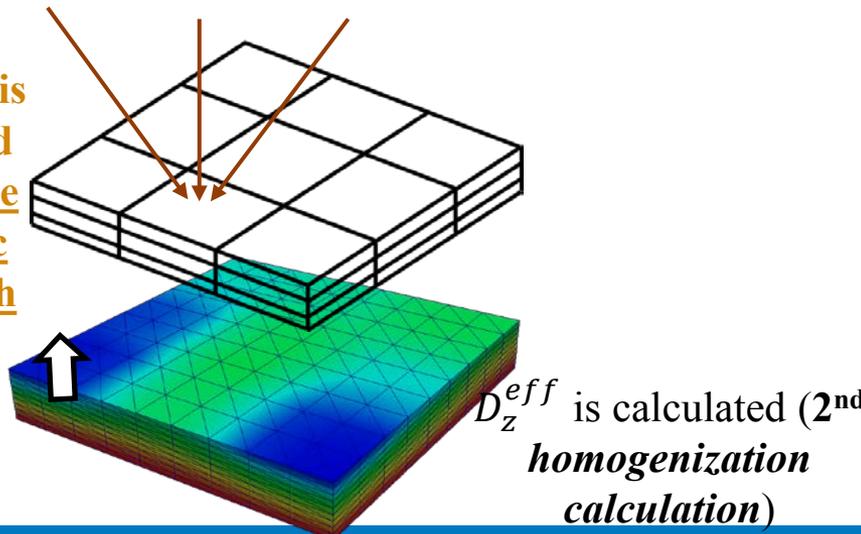
Factor of tortuosity: two-step homogenization numerical scheme



How to avoid using the mean value: two-step homogenization numerical scheme



Each subdomain is represented with a dense anisotropic coarse mesh

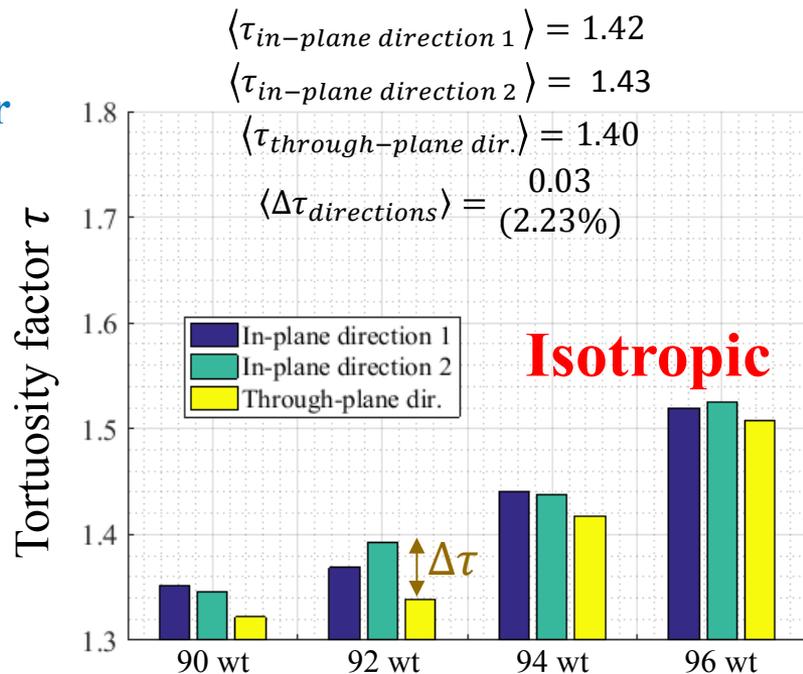


- ↑ Two-step homogenization: overestimation due to percolation loss
- ↓ Mean value: underestimation due to misuse of rule of mixture

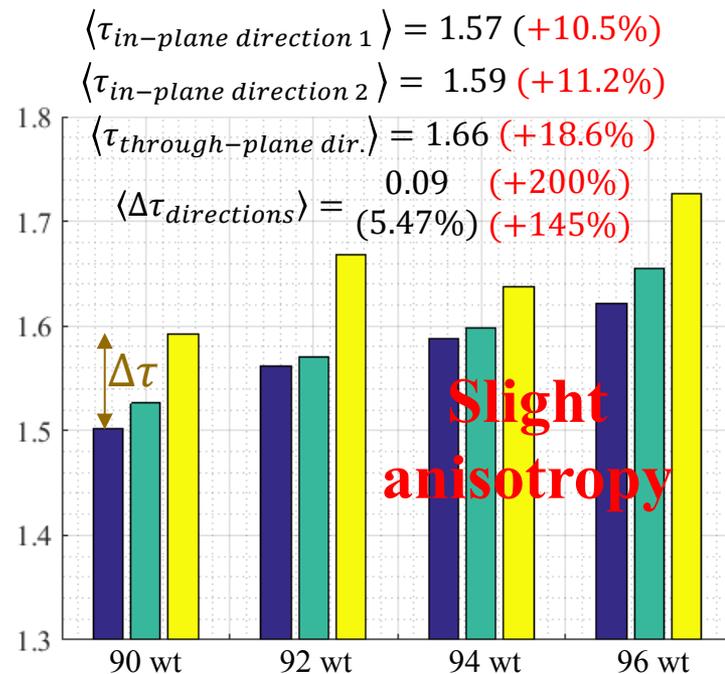
Even though this method suits better highly connected structure, it still gives a better estimation than the mean value.

Factor of tortuosity: calendaring effect

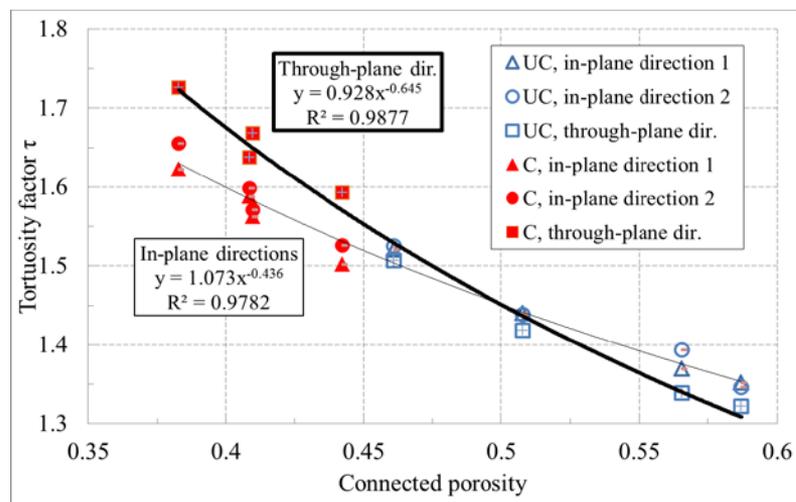
0 Bar



2,000 Bar

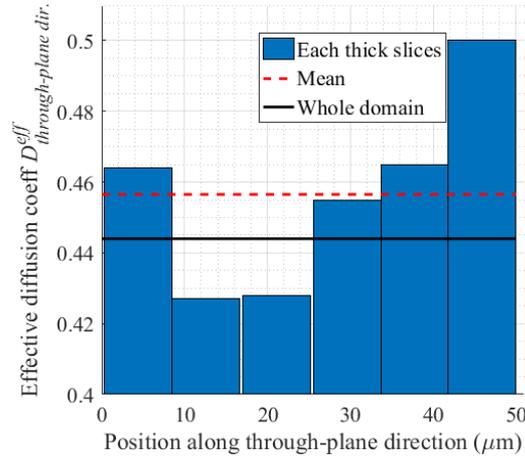
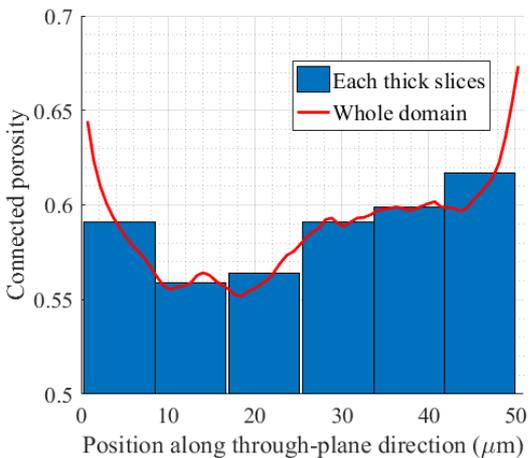


Calendaring induce a general increase of the tortuosity, due to the decrease of the connected porosity (Bruggeman exponent 0.65) & a slight anisotropy between in-plane directions and through-plane direction (could be induced by a change of NMC particle shape)



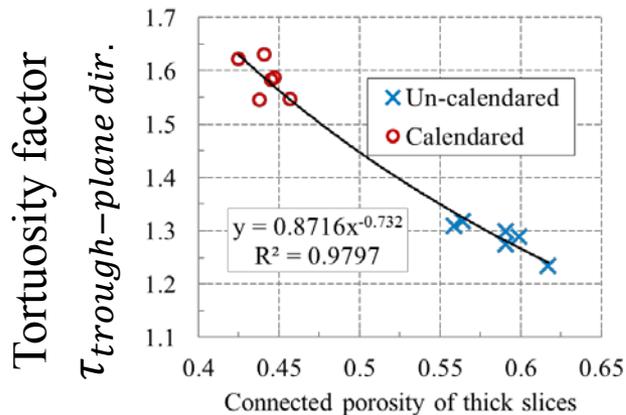
Factor of tortuosity: along electrode thickness

Un-calendared electrode 90 wt, Pore, **cut in 6 slices**



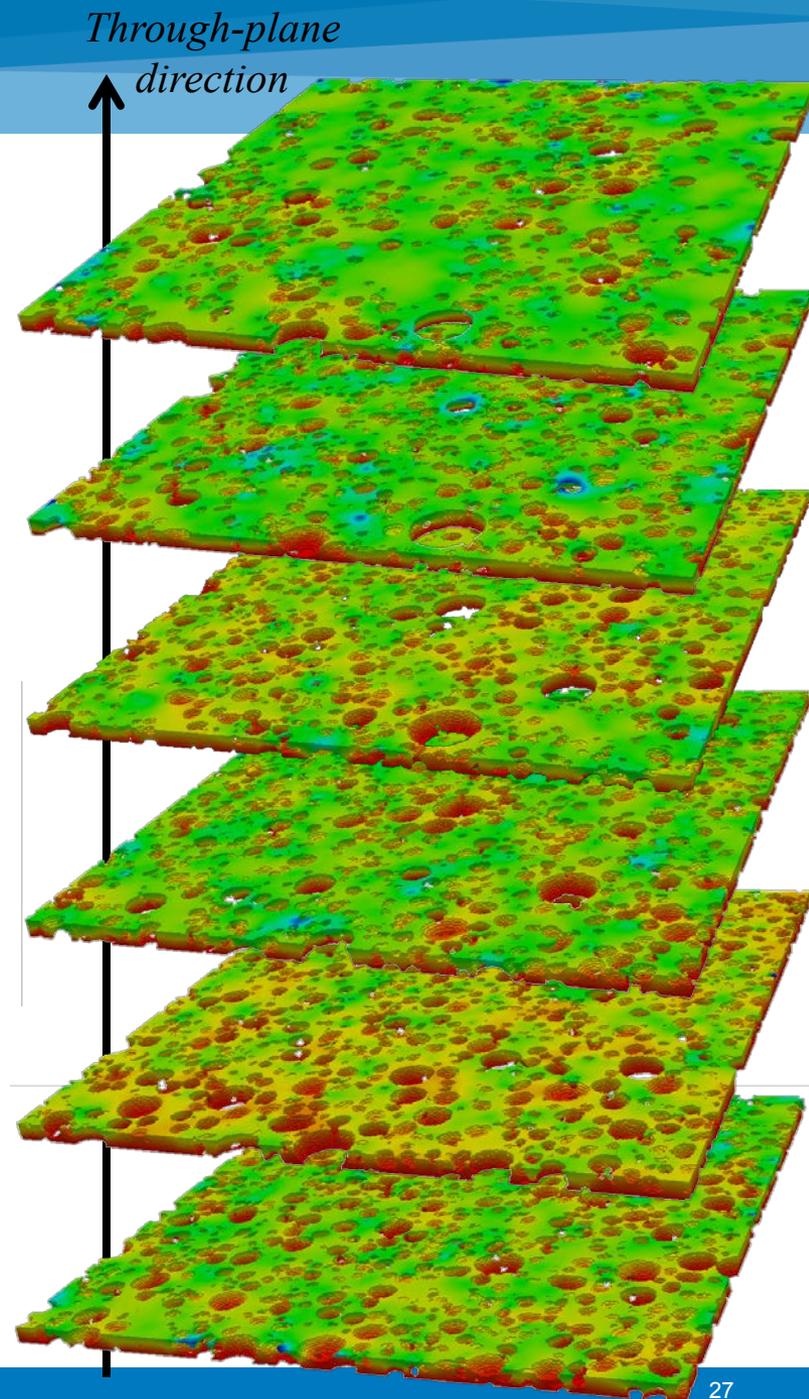
Each individual thick slice has conserved its connectivity (edge effect insignificant)

Effective diff coefficient ranges from ~ 0.42 to 0.5 .



Difference on tortuosity can be explained by porosity (Bruggeman exponent 0.73)

1D-macromodel could use such $\tau_z = f(z)$



Conclusions 1/2: numerical aspects

- **RVE**
 - Are property-dependent
 - Simple rule such as RVE size = x times mean particle size doesn't stand for structure with wide size distribution. RVE size increases with heterogeneity (i.e. standard deviation of parameters)
- **Particle size and surface area (annexes)**
 - Dependent on the voxel size.
 - The product $S_p \times d_{50}$ is less sensitive to the voxel size and exhibits more similar values compared with S_p and d_{50} taken individually: it is thus a better identifier of the microstructure.
- **Bias & assumption**
 - Connectivity suffers from a border effect. It should be monitored on small domains.
 - Particle size depends a lot on the chosen method. One should not rely on a unique approach.
 - Spherical assumption is incorrect both for Pore and NMC. Shown for particle size: pore are less spherical than NMC, which are themselves not really spherical. Results obtained on the product $S_p \times d_{50}$ goes to the same direction (annexes)

Conclusions 2/2: practical information

- **Microstructure observation**
 - Image quality of the segmented data set can be evaluated with the image level of detail parameters.
 - Consider standard deviation of the particle size when choosing your field of view.
- **Calendaring pressure**
 - Increases solid phase connectivity
 - Reduces the pore size
 - General increase of the tortuosity + slight anisotropy that hinder the diffusion in the through-plane direction (likely due to particle rearrangement and/or change of particle shape), something we would prefer to avoid.
- **Modeling**
 - 1D-model could take advantage of spatially varying parameter along the electrode thickness (as illustrated for tortuosity).
- **Tortuosity determination for large domain**
 - Consider using the two-step homogenization method to analyze if your domain is too big (or if you don't have access to an HPC). It's better than relying on a rule of mixture.

Thank you for your attention

Any questions?

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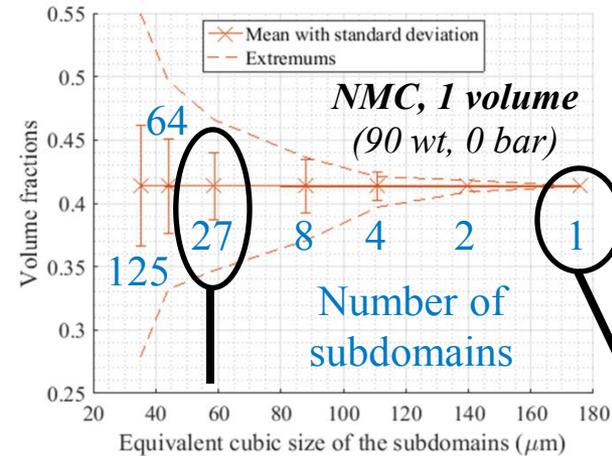
Annexes: RVE

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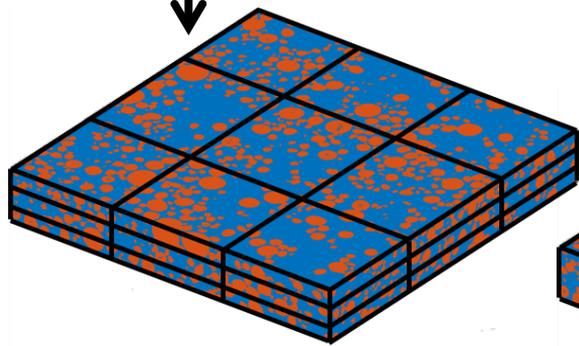
Determination of the RVE based upon subdomains

Representative volume element analysis illustrated on volume fractions ε

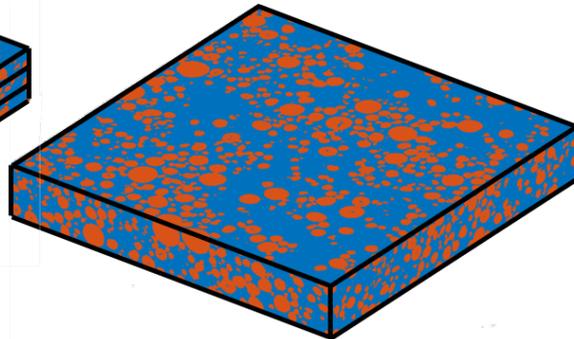


Property is calculated on independent subdomains

Step 1



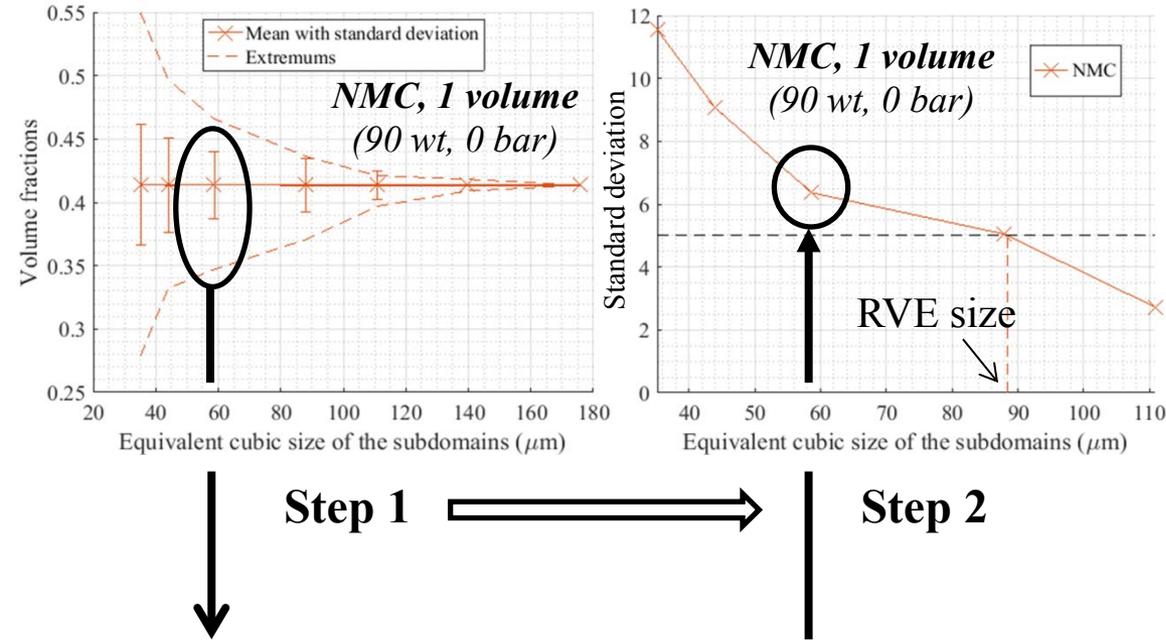
27 independent (i.e. non overlapping) subdomains



Whole domain

Determination of the RVE based upon subdomains

Representative volume element analysis illustrated on volume fractions ε

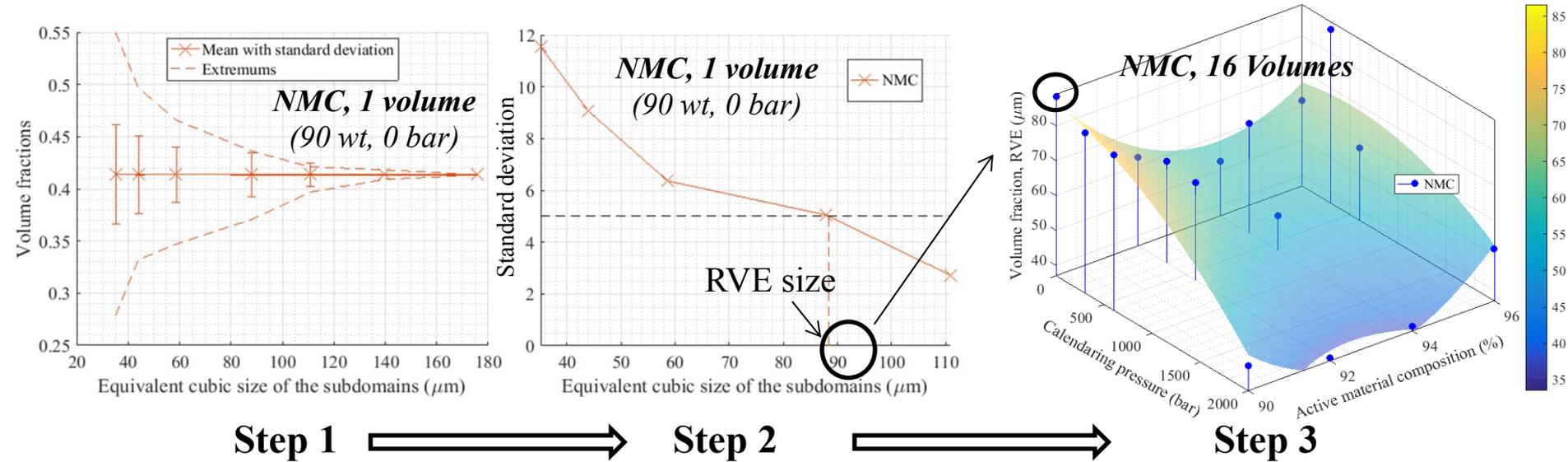


Standard deviation obtained on subdomains is expressed in % of the mean value

When the std is lower than a critical value (5%) then the volume is large enough to be representative: it is the RVE size

Determination of the RVE based upon subdomains

Representative volume element analysis illustrated on volume fractions ϵ



Step 1 \Rightarrow

Step 2 \Rightarrow

Step 3

Quadratic polynomial surface
fit on RVE size

The RVE size obtained on each
microstructure (16 volumes) are plotted
as a function of the calendaring pressure
and of the active material composition.

$\sim 40 \mu\text{m} < \text{RVE } \epsilon \text{ NMC} < \sim 90 \mu\text{m}$
Calendaring pressure \nearrow RVE ϵ NMC \searrow

Similar analysis have been performed for
the other properties

$\sim 50 \mu\text{m} < \text{RVE } \epsilon \text{ Pore} < \sim 100 \mu\text{m}$

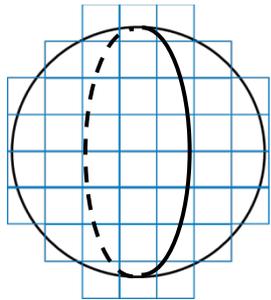
Annexes: Surface area

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Specific surface area

- Based upon a **direct counting method** (over-estimation corrected with a 2/3 factor that use a spherical assumption)



$$S_{discretized} \approx 6 \times \pi \times R^2$$

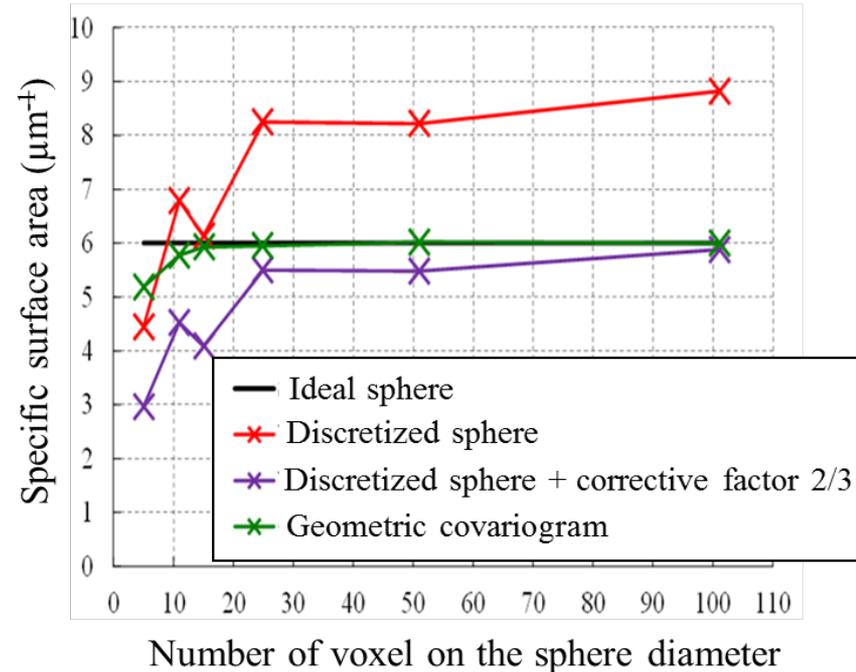
$$S_{ideal\ sphere} = 4 \times \pi \times R^2$$

- Alternative method based upon the **geometrical covariogram** K that gives the exact value without overestimation, but requires an isotropic assumption.

$$K(V, \bar{h}) = \text{Mes}(V \cap V_{\bar{h}})$$

$$\text{Surface area} = -4 \times \left. \frac{d(K(V, h))}{dh} \right|_{h=0}$$

A. Haas et al., *Annales des mines* **XI**, 736–753 (1967).



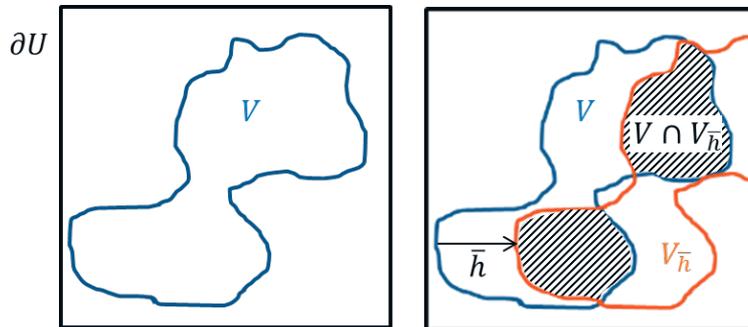
Less voxel per sphere diameter are required to get the actual specific surface area with the geometric covariogram method.

Specific surface area, geometric covariogram

$$K(V, \bar{h}) = \text{Mes}(V \cap V_{\bar{h}}) = \iiint_{V(\bar{h})} k(x, y, z) \times k(x + h_1, y + h_2, z + h_3) \times dV$$

$$A = -4 \times \left. \frac{d(K(V, h))}{dh} \right|_{h=0} \quad \text{if } V \text{ isotropic}$$

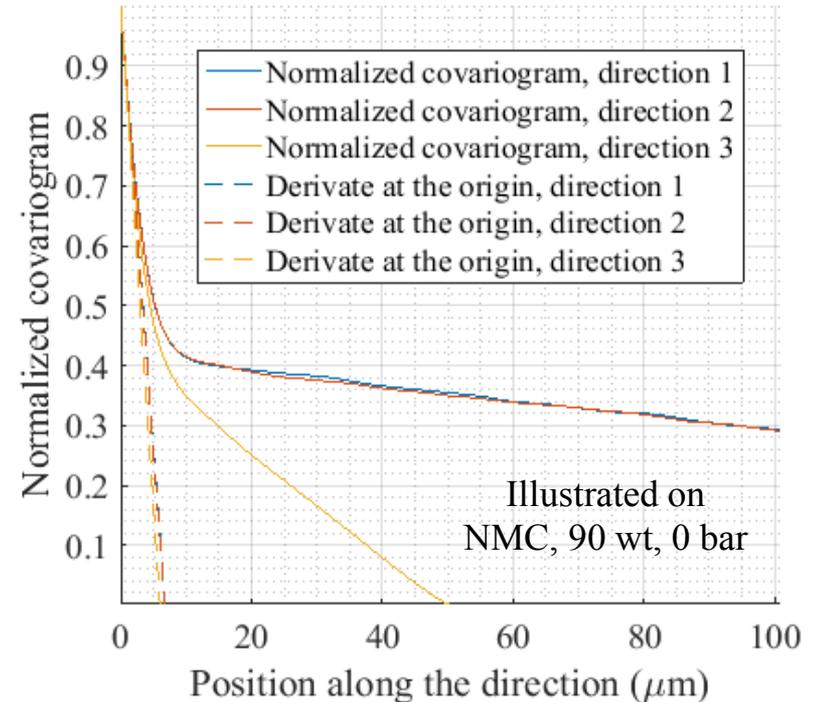
$$\text{with } \begin{cases} k(x, y, z) = \begin{cases} 1 & \text{if } (x, y, z) \in V \\ 0 & \text{if } (x, y, z) \notin V \end{cases} \\ \bar{h} = h_1 \bar{e}_x + h_2 \bar{e}_y + h_3 \bar{e}_z \end{cases}$$



$$S_p(V) = \frac{\delta V}{\text{mes}(V)} = \frac{-4 \times \left. \frac{dK(V, h, \alpha)}{dh} \right|_{h=0}}{\text{mes}(V)} \quad \text{if } V \text{ isotropic}$$

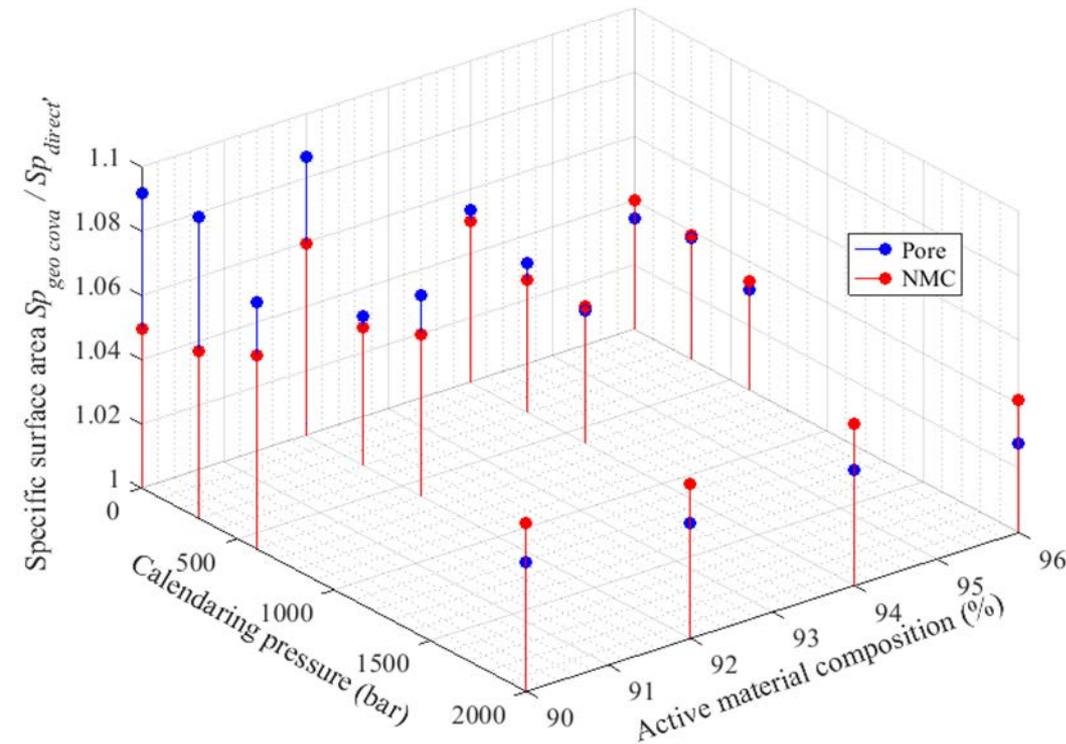
No overestimation since the function is based upon a volume calculation. Volume does not depend on the medium discretization

Covariogram, NMC, Superimposed curves



In the case the volume analyzed is a cube, this function can be used to evaluate the medium isotropy.

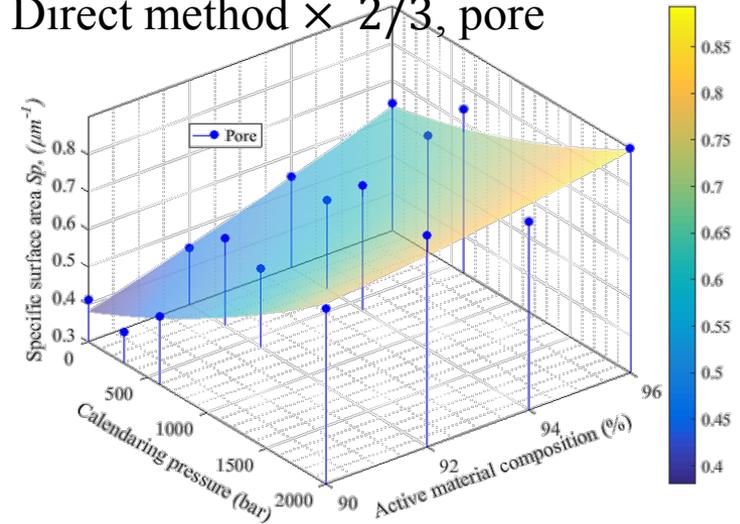
Specific surface area, results compared between methods



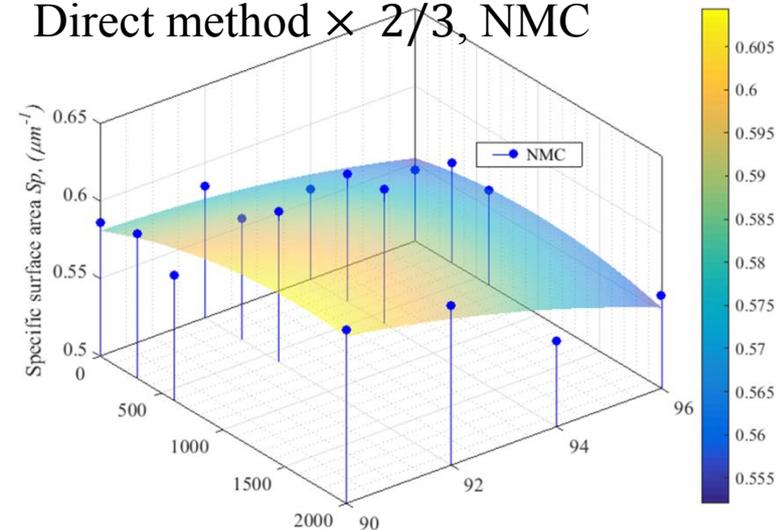
$$1.028 \leq \frac{S_p \text{ Geometric covariogram}}{S_p \text{ direct method} \times 2/3} \leq 1.094$$

Once the corrective factor 2/3 is applied to the direct method, both methods provides very similar results. (difference <10%)

Direct method $\times 2/3$, pore



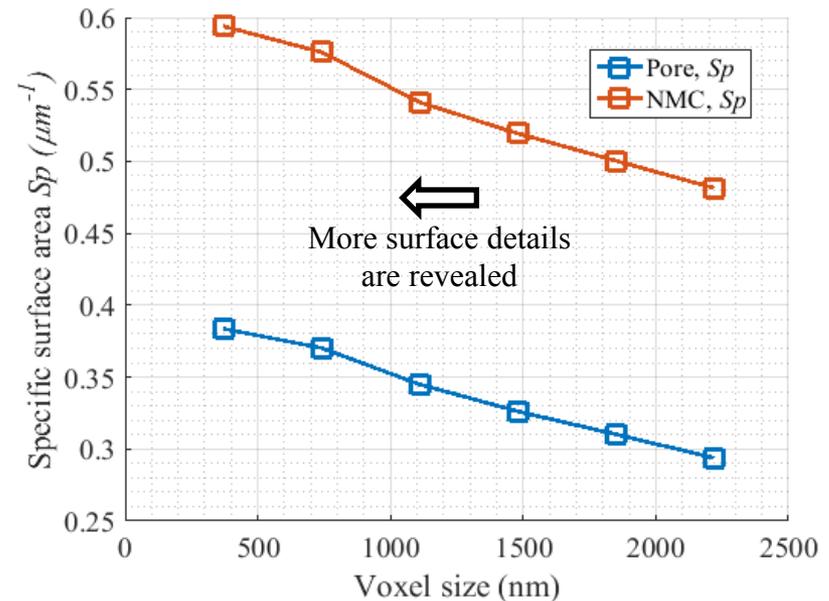
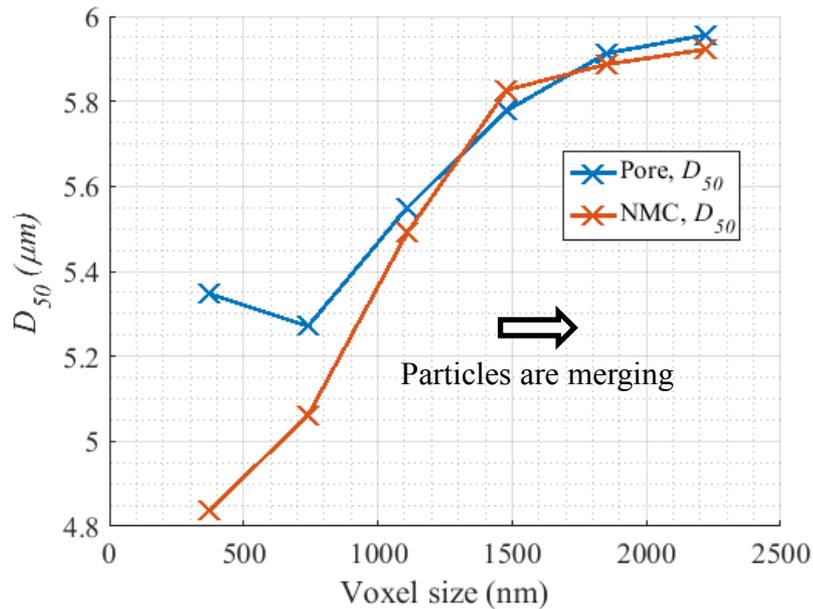
Direct method $\times 2/3$, NMC



$S_p \text{ Pore} \nearrow$ with calendaring pressure. NMC stays quasi constant (from 0.55 to 0.61 μm^{-1})

$$S_p = \frac{6}{d_{50}} \text{ Ideal spheres}$$

Voxel size dependence illustrated on 90 wt 300 bar

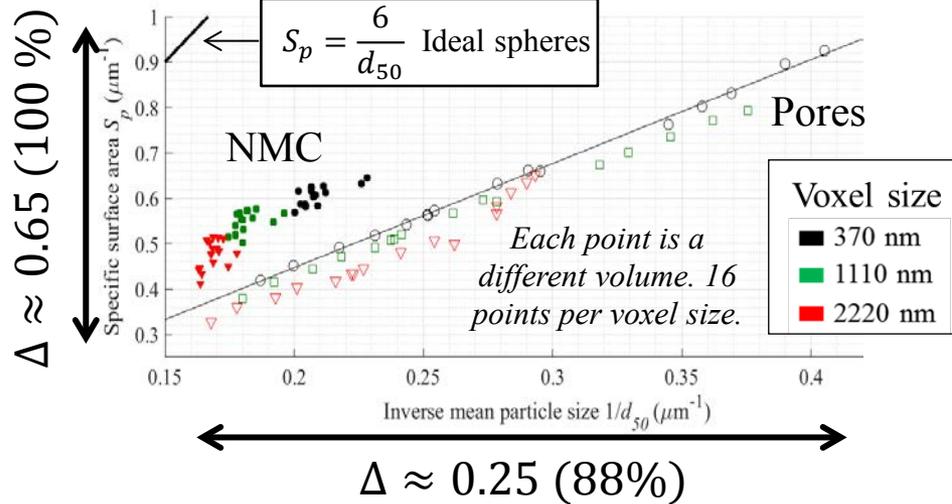


- Both properties exhibit opposite voxel size dependence trend.
 - Ideally, particle & pore size will converge but surface area will keep increasing (fractal property)

How to correlate them?

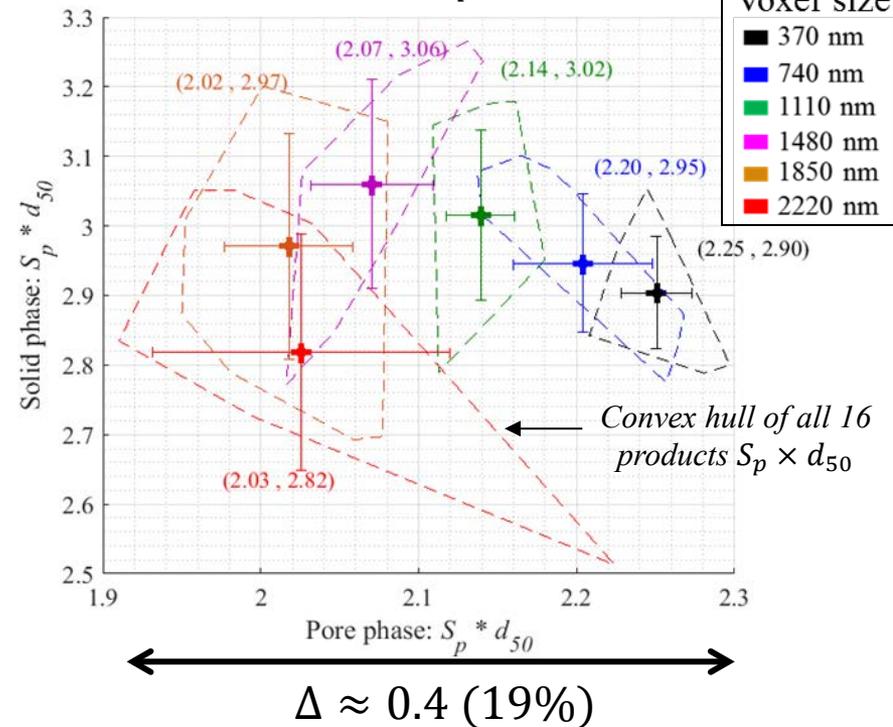
Particle size & specific surface area correlation

Specific surface area as a function of $1/d_{50}$



- The range of value for the pore is very large, both for S_p and d_{50} while it's basically the same microstructure.
- Linear correlation between S_p and $1/d_{50}$. Besides, the slope seems fairly constant with the image resolution.
- Let's consider the slope $S_p \times d_{50}$ as a better identifier of the microstructure, instead of S_p or d_{50} alone.

Product $S_p \times d_{50}$



Product $S_p \times d_{50}$ voxel is less dependent with voxel size than S_p or d_{50} alone. Thus, the product better identifies a specific microstructure

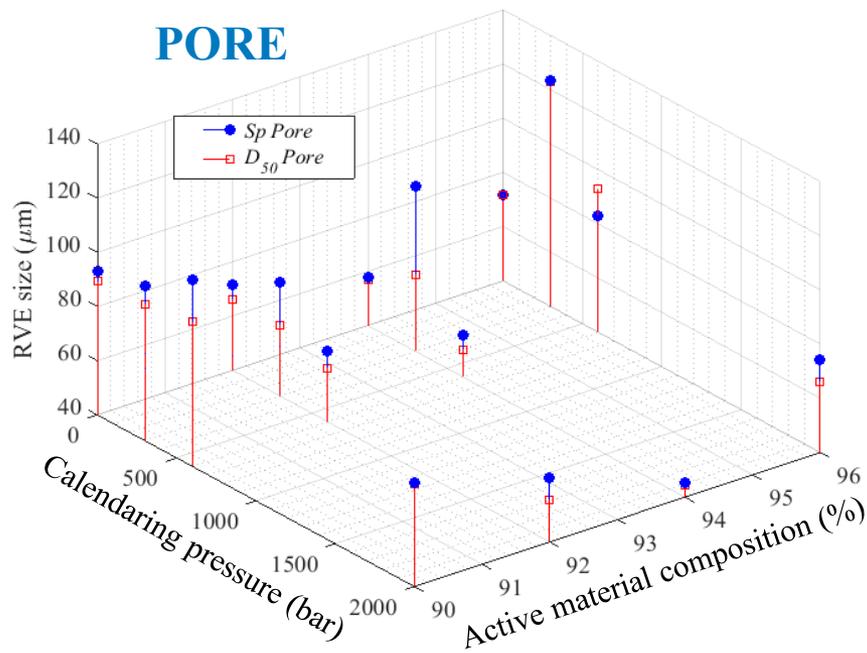
$$\begin{matrix} (S_p \times d_{50}) & (S_p \times d_{50}) & (S_p \times d_{50}) \\ \text{pore} & < & \text{NMC} < & \text{Spheres} \\ 2.02 - 2.25 & & 2.82 - 3.06 & & 6 \end{matrix}$$

Pore are less spherical than NMC particles.
NMC are not so spherical.

Particle size & specific surface area correlation

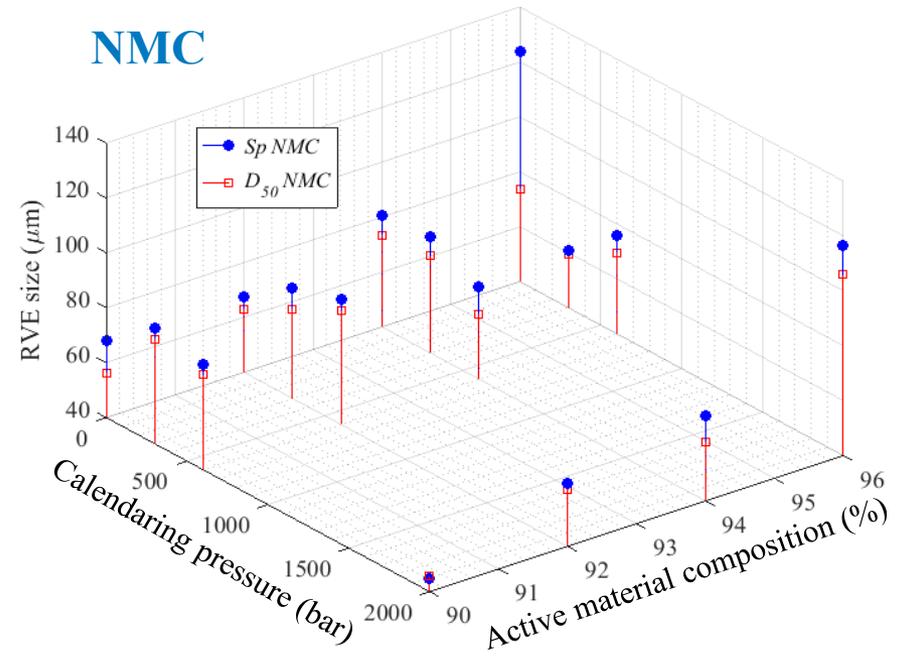
If they are intrinsically correlated, then they should share the same RVE size

RVE size of all 16 volumes, for S_p and D_{50}



$$\langle RVE S_p \rangle = 79.5 \mu\text{m}$$

$$\langle RVE D_{50} \rangle = 73.2 \mu\text{m}$$



$$\langle RVE S_p \rangle = 78.3 \mu\text{m}$$

$$\langle RVE D_{50} \rangle = 69.6 \mu\text{m}$$

As expected, Representative Volume Element sizes are very similar between S_p and D_{50}

$$\text{NMC: } \langle RVE S_p \rangle \sim 1.12 \times \langle RVE D_{50} \rangle$$

$$\text{Pore: } \langle RVE S_p \rangle \sim 1.09 \times \langle RVE D_{50} \rangle$$

Annexes: Particle size

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Particle size: statistical approach

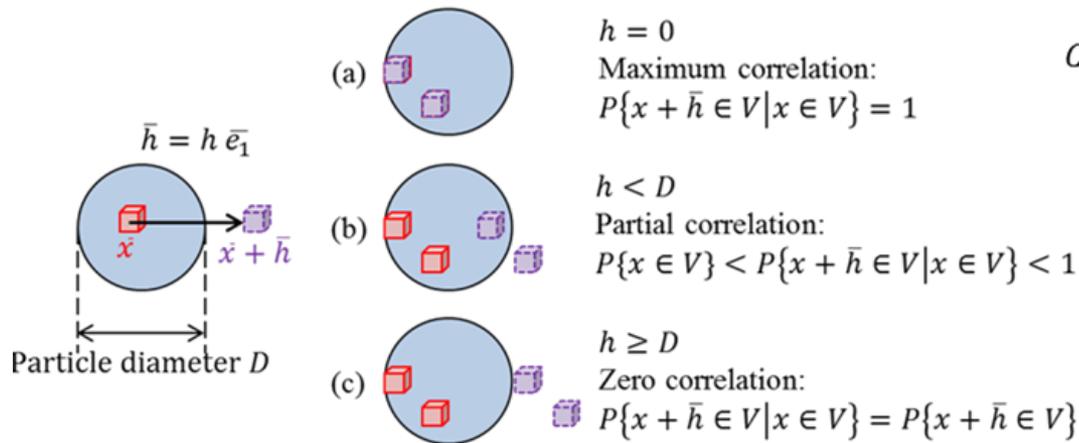
T. Kanit et al., *International Journal of Solids and Structures* 40 (2003) 3647–3679

$$C(V, \bar{h}) \begin{cases} = P\{(x, y, z) \in V \cap (x + h_1, y + h_2, z + h_3) \in V\} \\ = \frac{1}{N} \times \sum_{i=1}^N k(x, y, z) \times k(x + h_1, y + h_2, z + h_3) \end{cases}$$

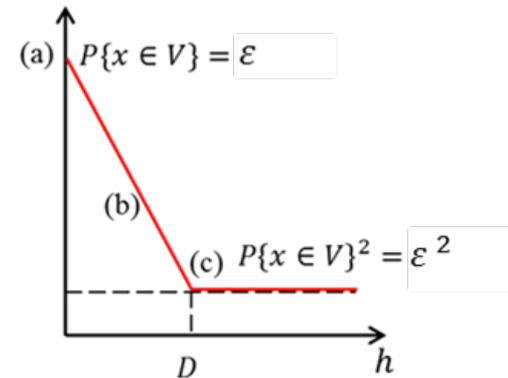
with $\begin{cases} k(x, y, z) = \begin{cases} 1 & \text{if } (x, y, z) \in V \\ 0 & \text{if } (x, y, z) \notin V \end{cases} \\ \bar{h} = h_1 \bar{e}_x + h_2 \bar{e}_y + h_3 \bar{e}_z \end{cases}$

Using the conditional probability:

$$C(V, \bar{h}) = P\{\bar{x} + \bar{h} \in V | \bar{x} \in V\} \times P\{\bar{x} \in V\}$$



$$C(V, \bar{h}) = P\{\bar{x} + \bar{h} \in V | \bar{x} \in V\} \times P\{\bar{x} \in V\}$$



The zero correlation (stage c in the figure) is reached for different value of h for particles of different size. The total loss of correlation (and thus the asymptotic value ε^2) is only achieved when all voxels have lost their correlation from their initial position: **thus it indicates the largest particle size and not the mean particle size.**

Particle size: statistical approach

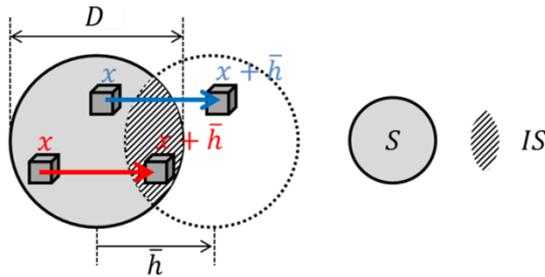
Original addition to the method

Using the conditional probability:

$$C(V, \bar{h}) = P\{\bar{x} + \bar{h} \in V | \bar{x} \in V\} \times P\{\bar{x} \in V\}$$

$$P\{x + \bar{h} \in V | x \in V\} = P\{A\} + P\{B\}$$

with $\begin{cases} \{A\} = \{x + \bar{h} \text{ belongs to the initial sphere on which } x \text{ belongs}\} \\ \{B\} = \{x + \bar{h} \text{ belongs to another sphere of same diameter}\} \end{cases}$



$$V_S = \frac{\pi}{6} \times D^3$$

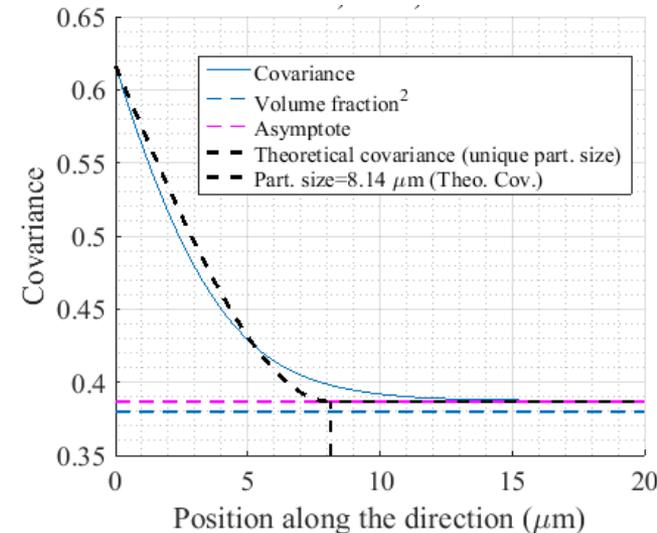
$$V_{IS} = \begin{cases} \frac{1}{12} \times \pi \times (2 \times D + h) \times (D - h)^2 & \text{if } h < d \\ 0 & \text{otherwise} \end{cases}$$

Events A and B are contained within the volume V_S of a sphere of diameter D . The ratio of voxels $x + \bar{h}$ that will be tested for the event A is V_{IS}/V_S , and it is sure they all belong to the phase V (since they are still in the initial particle). The ratio of voxels $x + \bar{h}$ that will be tested for the event B is $(V_S - V_{IS})/V_S$ and the probability they belong to the phase V is the volume fraction of V (since they are outside the initial particle). Then:

$$P\{A\} = \frac{V_{IS}}{V_S} \times 1$$

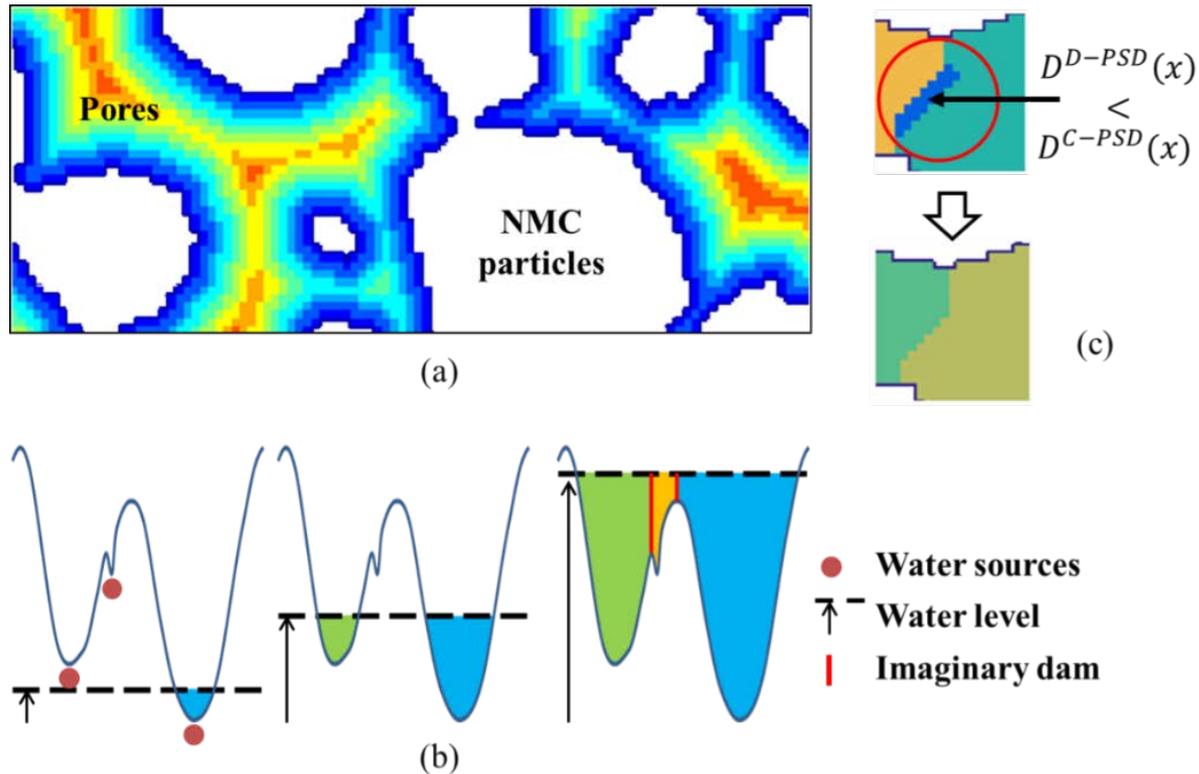
$$P\{B\} = \left(\frac{V_S - V_{IS}}{V_S} \right) \times \varepsilon$$

Fitting the diameter h of the theoretical covariance



Particle size: watershed method

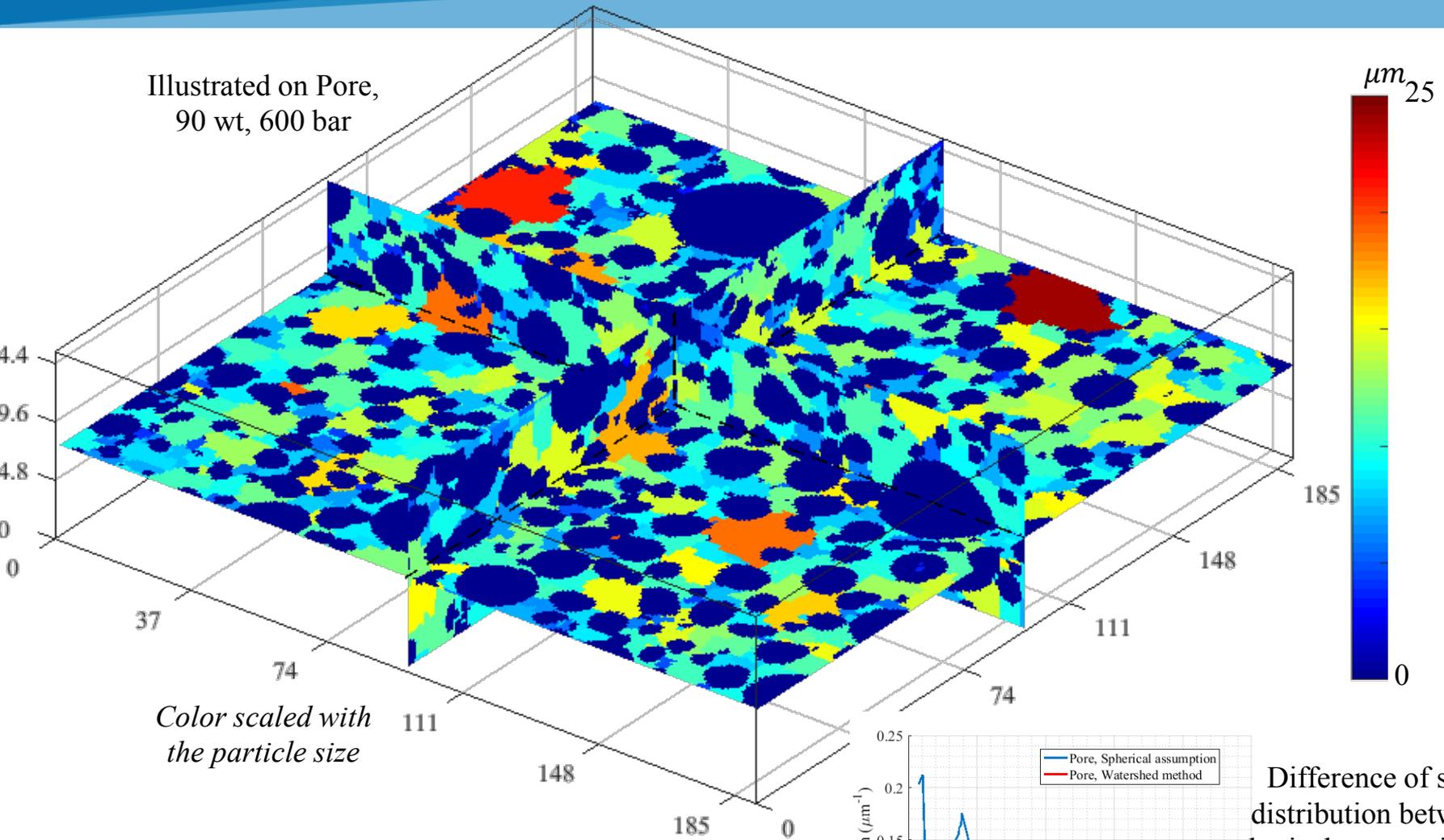
Luc Vincent and Pierre Soille, *IEEE Transactions on pattern analysis and machine intelligence*, Vol 13, No 6, 1991



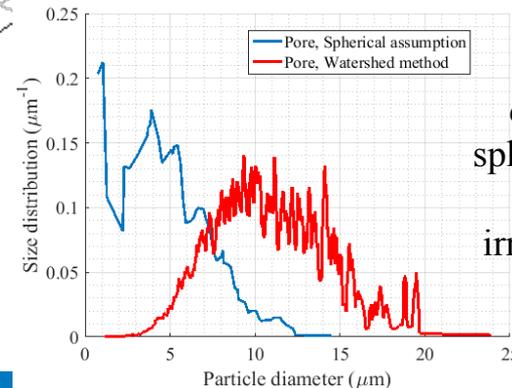
(a) Euclidean distance transform (EDT) of the pores calculated on a two-dimensional subset of a positive electrode. Values are scaled with the color: from dark blue to red (maximum distance). **(b) One-dimensional schematic of the immersion watershed process**, from left to right. Three catchment basins (i.e. distinct particles) have been identified. The smallest one appears to be an artifact due to the local noise gradient. **(c) Original addition to the algorithm: Voxels in the smallest distinct particle are considered to be irrelevant since their local size verifies $D^{D-PSD}(x) < D^{C-PSD}(x)$.** The red circle illustrates $D^{C-PSD}(x)$ while one unique color is attributed to $D^{D-PSD}(x)$.

Particle size: watershed method

Illustrated on Pore,
90 wt, 600 bar



*Color scaled with
the particle size*



Difference of size
distribution between
spherical assumption and
watershed. Small
irrelevant particles
have been removed.

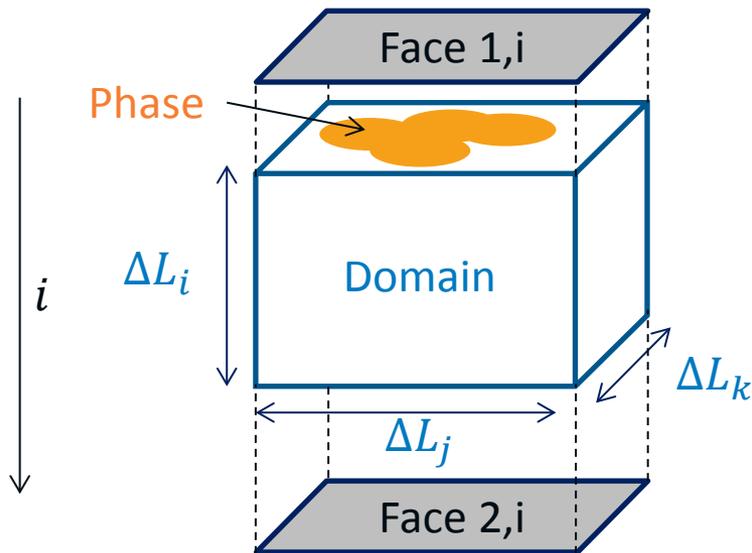
Annexes: Tortuosity

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Factor of tortuosity

- Factor of tortuosity (homogenization method)



Effective section area normal to direction i :

$$S_i^{eff} = \Delta L_j \times \Delta L_k$$

Actual section area normal to direction i at

face 1: $S_{i,face\ 1}^{actual} = \iint_{F_{1,i}} 1\ ds(\text{phase})$

Step 1: Mean concentration at the face F_1

$$c_{i,1} = \iint_{F_{1,i}} c\ ds / S_{i,face\ 1}^{actual}$$

Step 2: Effective surface density flux at the face F_1

$$\varphi_{i,1} = \iint_{F_{i,1}} -k_{bulk} \times \overline{\text{grad}(c)} \cdot \bar{n}\ ds / S_i^{eff}$$

Step 3: Deduce the effective diffusion coefficient (1D diffusion law)

$$k_i^{eff} = -\varphi_{i,1} \times \frac{\Delta L_i}{c_{i,2} - c_{i,1}}$$

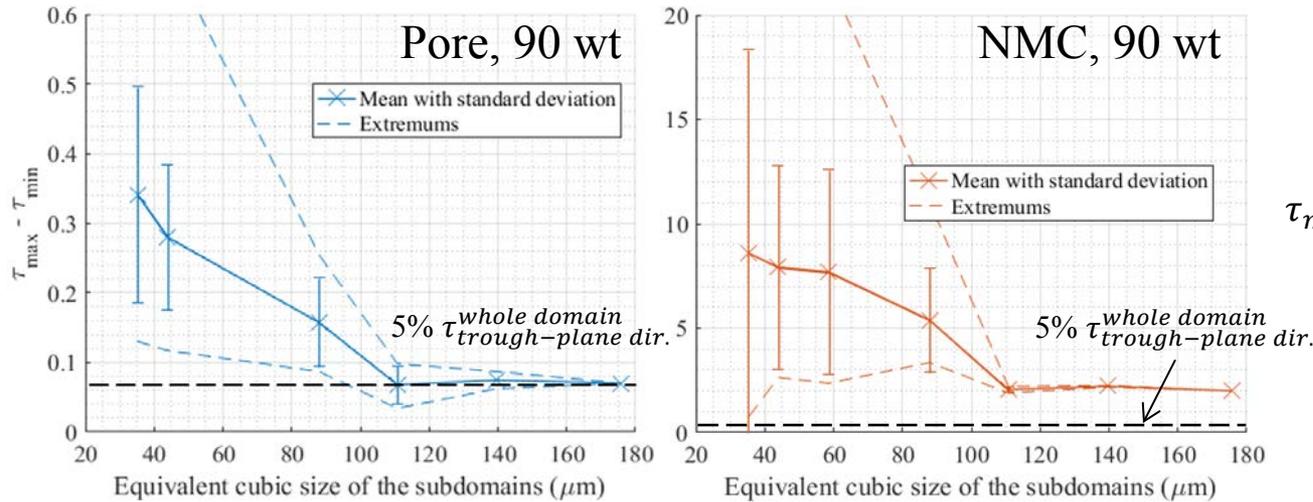
Step 4: Deduce the factor of tortuosity

$$\tau_i = \varepsilon \times k_{bulk} / k_i^{eff} \geq 1$$

Factor of tortuosity: Representative volume element analysis

- **RVE analysis on $\tau_{through-plane dir.}$ with different boundary conditions**

For which domain's size $\tau_{through-plane dir.}$ does not depend on the chosen BC?



RVE criterion is different:
 Instead of std must $\rightarrow 0$:
 $\tau_{max} - \tau_{min}$ **must $\rightarrow 0$**
 $\tau_{max} - \tau_{min} \leq 5\%$ of $\tau_{through-plane dir.}^{whole domain}$

To remove the boundary conditions dependence, a larger domain is required.

The plateau obtained for large domains indicates a convergence issue. It could be solved with a quadratic interpolation (better convergence is expected).

Tortuosity Boundary conditions table (written in brackets are the RVE)

| | Pore | | NMC | |
|---------------------------|------------------|------------------|------------------|-----------------|
| | UC | C (2000 bar) | UC | C (2000 bar) |
| $\tau_{max} - \tau_{min}$ | (110.8 μm) | (115.5 μm) | (> 175 μm) | (>183 μm) |

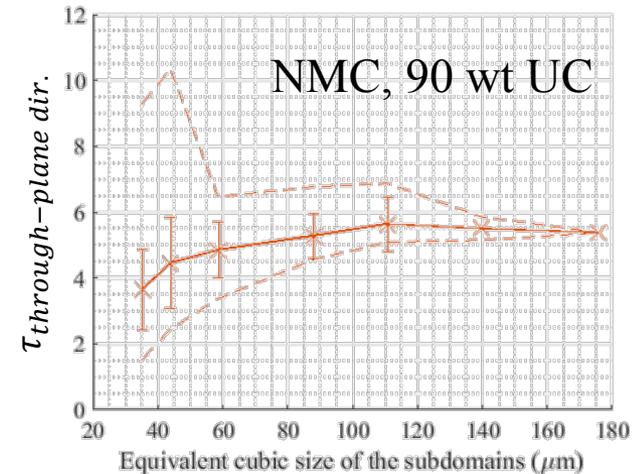
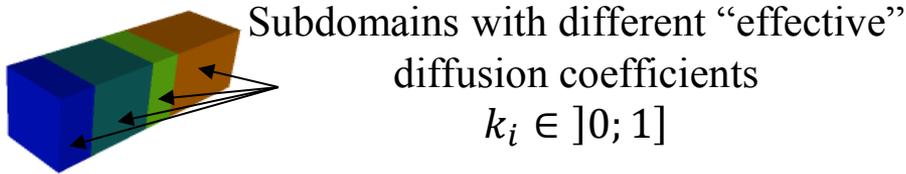
$$RVE \tau_{Boundary conditions} > RVE \tau_{Dirichlet-Neumann}^{Through-plane dir.}$$

*T. Kanit et al., Inter. J. of Solids and Structures, 40 (2003) 3647-3679
 J. Laurencin et al., JPS, 198 (2012) 182-189*

Factor of tortuosity: rule of mixture & percolation loss

Why factor of tortuosity obtained on subdomains differs from the whole domain?

Loss of percolation on small subdomains should increase tortuosity by creating local bottleneck at the edges...but we see the opposite.



| | Concentrations field | Density flux | Theoretical effective diffusion coefficient | Numerical one (FEniCS) | |
|-----------------------------------|----------------------|--------------|--|------------------------|--|
| Flux in series along subdomains | | | $\frac{1}{k_{series}^{eff}} = \frac{\sum_i w_i}{\sum_i w_i k_i} = 0.441$ | 0.440 | Using a rule of mixture consists of assuming flux of all the subdomains are in parallel...which is not necessary true. |
| Flux in parallel along subdomains | | | $k_{parallel}^{eff} = \frac{\sum_i w_i \times k_i}{\sum_i w_i} = 0.543$ | 0.543 | |

Rule of mixture