Micro-CT investigation of spatial heterogeneity

Doctoral (Ph.D.) Thesis

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1. Introduction and aims

Materials science is a widely researched field today. To understand the properties and behavior of materials and to create new, specific materials and systems, it is essential to have a thorough understanding of their internal microstructure. Determining the spatial position of defects, pores, cracks and different material components is of particular importance, as they can have a major influence on the physical properties of materials.

The porosity of materials is one of their most important and most studied characteristics. Not only the number, size, and shape of the pores are important, but also their spatial distribution. High-resolution computed tomography (micro-CT) is a 3D X-ray imaging technique based on the different X-ray attenuation of materials. It is particularly suited for the investigation of porous materials and the mapping of the pore structure, but the quantitative characterization of the spatial distribution of pores is not a trivial task. Lacunarity is a quantitative measure of spatial heterogeneity. Lacunarity could play an important role in many fields from medicine to earth science and materials science, but its widespread adoption is hampered by the huge computational requirements of the classical computational method (the gliding box method). This is particularly significant for real 3D micro-CT datasets, as the computational demand cubically scales with the size of the volume of interest.

To solve this problem, I have set two main goals in my research: to create a widely applicable, easy-to-use computational method for determining lacunarity and to demonstrate the importance of lacunarity in various systems relevant to materials science. To do this, we first present a method for calculating lacunarity, prove its applicability, and analyze in detail the accuracy and computational time of our method in comparison with the gliding box method. We prove that the new calculation method can be reliably applied to real 3D micro-CT datasets. We then demonstrate the significance of lacunarity calculations on two systems relevant to materials science.

To compare systems with different porosities, two concrete samples prepared in different ways (by the conventional method and by adding a superplasticizer) are used as model systems, and the effect of pore size on the spatial distribution in different regions of the samples is investigated. We also investigate the applicability of lacunarity to describe the mixing of granular materials.

2. Experimental methods

Our high-resolution computed tomography measurements were performed with a Bruker Skyscan 2211 micro-CT device. The 3D structural reconstruction of the tested samples was performed using NRecon® software (Skyscan, Bruker, Belgium). During the reconstruction, we corrected the most common imaging errors, and most frequently occurring artifacts (ring artifacts, beam hardening, misalignment), performed X-Y correction based on reference images, and masked the defective pixels. After the reconstruction, volume-rendered 3D micro-CT images were generated using CTVox® (Skyscan, Bruker, Belgium) software. For 4D or *in situ* studies, images acquired in different conditions were rotated and registered (the 3D images were spatially superimposed) using DataViewer® (Skyscan, Bruker, Belgium) software.

We calculated the lacunarity curves for the samples from segmented (binary) images generated by CTAn® (Skyscan, Bruker, Belgium) software using our self-developed software (Lac3D). After selecting the volume of interest (VOI) size to be investigated and the box sizes to be used for the calculations, the 3D lacunarity values were calculated for the selected box sizes using the gliding box and/or fixed-grid method. One normal-performance computer (Intel® Core™ i3-2348 M @ 2.3 GHz processor) and one high-performance computer (Intel® Xeon® E5-2640 v4 @ 2.4 GHz processor) were used for the calculations.

Ten concrete cubes, each with a volume of $3 \times 3 \times 3$ cm^3, were prepared to compare samples of different porosities. For the traditional concrete samples (TC), Portland composite cement (EN 197-1 CEM II/B-M (V-LL) 32.5 N, DDC Beremend) and sand with a particle size $d < 1$ mm were used. For samples prepared with the addition of superplasticizer (SPC), VIP-Rex SF additive (Vip-Rex Ltd., Kisújszállás, viprex.hu) was used. From both sample types 5-5 pieces were prepared, left to solidify in the mold for 2 days, and then stored under water for another 26 days of curing time. Before the micro-CT investigations, the samples were dried at room temperature until mass stability was reached. Concrete cubes were fracture tested using a Zwick Roell Zmart Pro tensile testing machine with a preload of 50 N, a preload speed of 100 mm/min, and a measuring speed of 0.5 MPa/s. The samples were wrapped in Parafilm® M universal sealing film to prevent specimen disintegration during fracture and to allow micro-CT testing of the fractured samples. The rotation and registration of the images taken at different stages (before and after the fracture test) were performed using DataViewer® software. Detailed 3D porosity analysis of the concrete samples was also performed using

CTAn® software. For the lacunarity calculations, the largest volume of interest (VOI) had a side length (M) of 800 voxels, while for the smaller volume, $M = 400$ voxels.

For the mixing experiments, 3D-printed mixing containers made of polylactic acid were used. Approximately 500 calcium-alginate beads (average density of 1.2 g/cm^3 and average diameter of 1.75 mm) were mixed with approximately 5000 polystyrene beads (average density of 1.05 g/cm^3 and average diameter of 1.1 mm). Three mixing containers of different sizes were used in the experiments: a 20 × 20 × 25 mm^3, a 20 × 20 × 35 mm^{3,} and a 20 × 20 × 40 mm^3 volume. The shape of the mixing container is a square-based prism, which is the most suitable for the lacunarity calculation method we used. To ensure accurate repeatability, the mixing container was rotated during the experiments using a stepper motor. One mixing cycle corresponds to a 360° rotation of the container along a given axis. Ten mixing cycles were performed and micro-CT images of the systems were taken at baseline and after 1, 2, 3, 5, 7 and 10 cycles. For the mixing experiments, the lacunarity calculations were performed based on binary images of the calcium-alginate bead positions.

The discrete element method (DEM) simulations were performed using the general grain simulation software LIGGGHTS. The interaction force between two contacting particles was calculated using the Hertz model. This scheme allows the estimation of the following elastic and damping interaction parameters: Young's modulus (Y_m), Poisson's ratio (ν) of the material, restitution coefficient (e), and friction coefficient (μ). In our simulations, we used the following values: $Y_m = 5\times10^6$ Pa, $\nu = 0.45$, $e = 0.2$, $\mu = 0.5$. We used cells with closed boundaries of 20 × 20 × 35 mm^3 and 20 × 20 × 40 mm^3 filled with a two-component mixture of spherical particles. The mixture consisted of 5000 particles with a diameter of 1.1 mm and a density of 1.05 g/cm^3 and 500 particles with a diameter of 1.75 mm and a density of 1.2 g/cm^3. To mimic the mixing process, the container was rotated using a given rotation axis and period of rotation.

3. Novel scientific results

T1 **We developed an algorithm based on the fixed-grid method to compute 3D lacunarity and proved that it provides nearly identical results compared to the commonly used gliding box method, but orders of magnitude faster (computational time is measured in seconds instead of weeks).** The gliding box method uses overlapping boxes for the lacunarity calculation, hence for large 3D datasets, it is very computationally demanding, as the computational time scales with the sixth power of the side length of the volume of interest. In contrast, our algorithm works with non-overlapping boxes, reducing the required computational resources to a fraction. The lacunarity values computed by the two methods may differ significantly for very small datasets, due to the statistical nature of lacunarity, but they are practically the same ($R^2 = 0.999$) for large datasets (larger than $M = 200$ voxels side length, corresponding to 8 million data points), thus the algorithm we present can be used with high confidence for real micro-CT images.

T2 **We were the first to monitor the mixing of a closed, two-component granular system using computed tomography and to apply lacunarity to describe the change over time.** We have investigated the mixing due to axial rotation for granular materials of similar size and shape, but with widely different X-ray attenuation, and described the change over time by lacunarity curves. It was determined that 7 rotation cycles are required to reach the most homogeneous state in our system. We investigated the effect of the size of the mixing container on the mixing process and found that homogenization increased with increasing container size.

T3 **We have demonstrated that lacunarity can be used as a measure of mixing efficiency.** The variation of the lacunarity curves over time during mixing gives a good characterization of the mixing efficiency. As the number of mixing cycles increased, the mixture became more homogeneous and this change was followed by an increase in the slope of the lacunarity curve and a continuous numerical decrease in the lacunarity values for each box size. For the normalized lacunarity curves, the value corresponding to the most homogeneous state is 0 and to the most heterogeneous state is 1.

T4 **We were the first to use lacunarity to compare experimental and discrete element method (DEM) modeled/simulated results.** Given that the DEM method gives the trajectory of each particle, lacunarity calculations can be performed in any desired state of the system. We demonstrated that the shape and slope of the lacunarity curves for the experimental and simulated data are similar and they follow an identical trend and that the differences between the results are due to the imperfections in the real system.

T5 **We were the first to apply lacunarity to characterize the spatial distribution of the pore structure of concrete quantitatively. A method was developed to characterize the porosity of fragments separated during fracture experiments.** Computed tomography and lacunarity calculations were used to quantify the 3D homogeneity of the pore distribution. The spatial and size distributions of pores were compared for two different types of concrete with different porosities. We determined that the superplasticizer additive decreased the porosity, the average pore size, and the spatial heterogeneity of the pores, while the number of pores increased. For both sample types, large pores (d > 1 mm) showed a more heterogeneous distribution than small pores (d < 1 mm). In fracture tests, samples prepared with superplasticizer additives showed a more regular fracture pattern. To investigate the porosity of the broken-off and the remaining hourglass-shaped parts, the samples were wrapped with Parafilm before the fracture tests. In both cases, the porosity of the broken-off parts is approximately 20% higher than the remaining hourglass-shaped parts, and large pores are typically found in the broken-off parts or situated on the fracture surface.

4. Publications related to the present thesis

1. **Fast and accurate lacunarity calculation for large 3D micro-CT datasets**
   D. Sebők, **L. Vásárhelyi**, I. Szenti, R. Vajtai, Z. Kónya, Á. Kukovecz
   Acta Materialia, 2021, (214) 116970
   IF: 8,203

2. **Lacunarity as a quantitative measure of mixing – a micro-CT analysis-based case study on granular materials**
   L. Vásárhelyi, D. Sebők, I. Szenti, Á. Tóth, S. Lévay, R. Vajtai, Z. Kónya, Á. Kukovecz
   Oxford Open Materials Science, 2023, 3 (1), itad014
   IF: -

3. **Quantitative insight into the fracture behavior of concrete based on micro-CT derived three-dimensional pore heterogeneity data**
   L. Vásárhelyi, D. Sebők, I. Szenti, O. Szép, Z. Kónya, Á. Kukovecz
   Composite Structures, 2024, *submitted for publication*

5. Oral presentations related to the present thesis

1. **Pórusos és többkomponensű anyagok vizsgálata mikro-CT technikával**
   L. Vásárhelyi, D. Sebők, I. Szenti, Á. Kukovecz, Z. Kónya
   MMT 2019, Hungary/Siófok, 2019 (presentation)

2. **Pórusos rendszerek vizsgálata mikro-CT technikával**
   D. Sebők, **L. Vásárhelyi**, I. Szenti, Á. Kukovecz, Z. Kónya
   XII. OATK, Hungary/Balatonkenese, 2019 (presentation)

3. **Térbeli heterogenitás jellemzése mikro-CT technikával**
   L. Vásárhelyi, D. Sebők, I. Szenti, Á. Kukovecz, Z. Kónya
   MMT 2021, online, 2021 (presentation)

4. **Szemcsés anyagok keveredésének jellemzése mikro-CT technikával és DEM szimulációkkal**
   L. Vásárhelyi, D. Sebők, I. Szenti, Á. Kukovecz, Z. Kónya
   MMT 2022, Hungary/Siófok, 2022 (presentation)

5. **Térbeli heterogenitás vizsgálata mikro-CT technikával**
   Á. Kukovecz, Z. Kónya, D. Sebők, I. Szenti, **L. Vásárhelyi**
   IV. ORF, Hungary/Veszprém, 2023 (presentation)

6. Other publications

1. **Co_4N/nitrogen-doped graphene: a non-noble metal oxygen reduction electrocatalyst for alkaline fuel cells**
   T. Varga, G. Ballai, **L. Vásárhelyi**, H. Haspel, Á. Kukovecz, Z. Kónya
   Applied Catalysis B: Environmental, 2018, (237) 826-834
   IF: 14,229

2. **Noble-metal-free iron nitride/nitrogen-doped graphene composite for the oxygen reduction reaction**
   T. Varga, **L. Vásárhelyi**, G. Ballai, H. Haspel, A. Oszkó, Á. Kukovecz, Z. Kónya
   ACS omega, 2019, 4 (1) 130-139
   IF: 2,584

3. **Fast optical method for characterizing plasmonic nanoparticle adhesion on functionalized surfaces**
   L. Mérai, L. Janovák, D.S. Kovács, I. Szenti, **L. Vásárhelyi**, Á. Kukovecz, I. Dékány, Z. Kónya, D. Sebők
   Analytical and Bioanalytical Chemistry, 2020, (412) 3395-3404
   IF: 3,286

4. **Microcomputed tomography–based characterization of advanced materials: a review**
   L. Vásárhelyi, Z. Kónya, Á. Kukovecz, R. Vajtai
   Materials Today Advances, 2020 (8) 100084
   IF: -

5. **Binder-Free Construction of a Methanol Tolerant Pt/TiO2/Carbon Paper Anode by Atomic Layer Deposition**
   G. Ballai, T. Gyenes, H. Haspel, **L. Vásárhelyi**, I. Szenti, D. Sebők, Z. Kónya, Á. Kukovecz
   Catalysts, 2021, 11 (2) 154
   IF: 3,45

6. **Specific ion effects on aggregation and charging properties of boron nitride nanospheres**
   T. Hegedűs, D. Takács, **L. Vásárhelyi**, I. Szilágyi, Z. Kónya
   Langmuir, 2021, 37 (7) 2466-2475
   IF: 3,557

7. **Stability of Boron Nitride Nanosphere Dispersions in the Presence of Polyelectrolytes**
   L. Vásárhelyi, T. Hegedűs, S. Sáringer, G. Ballai, I. Szilágyi, Z. Kónya

Langmuir, 2021, 37 (17) 5399-5407
IF: 3,557

8. **Metastable wetting model of electrospun mats with wrinkled fibers**
A. Rawal, S. Shukla, S. Sharma, D. Singh, Y.M. Lin, J. Hao, G.C. Rutledge, **L. Vásárhelyi**, G. Kozma, Á. Kukovecz, L. Janovák
Applied Surface Science, 2021, (551) 149147
IF: 6,182

9. **Damage-tolerant 3D-printed ceramics via conformal coating**
S.M. Sajadi, **L. Vásárhelyi**, R. Mousavi, A.H. Rahmati, Z. Kónya, Á. Kukovecz, T. Arif, T. Filleter, R. Vajtai, P. Boul, Z. Pang, T. Li, C.S. Tiwary, M.M. Rahman, P.M. Ajayan
Science Advances, 2021, 7 (28) eabc5028
IF: 13,98

10. **Three-dimensional printing of complex graphite structures**
S.M. Sajadi, S. Enayat, **L. Vásárhelyi**, A. Alabastri, M. Lou, L.M. Sassi, A. Kutana, S. Bhowmick, C. Durante, Á. Kukovecz, A.B. Puthirath, Z. Kónya, R. Vajtai, P. Boul, C.S. Tiwary, M.M. Rahman, P.M. Ajayan
Carbon, 2021, (181) 260-269
IF: 11,307

11. **Superhydrophobic self-similar nonwoven-titanate nanostructured materials**
S. Sharma, A. Rawal, I.Y. Tóth, **L. Vásárhelyi**, G. Kozma, Á. Kukovecz, S. Jee, F. Ayaydin
Journal of Colloid and Interface Science, 2021, (598) 93-103
IF: 7,489

12. **Structural health monitoring of nonwoven materials via self-similar arrays of carbon nanotubes**
B. Singh, A. Gupta, D. Singh, S. Shukla, **L. Vásárhelyi**, I. Szenti, Á. Kukovecz, A. Rawal
Composites Communications, 2022, (32) 101155
IF: 7,568

13. **Exploration of Li-Ion Batteries during a Long-Term Heat Endurance Test Using 3D Temporal Microcomputed Tomography Investigation**
G. Ballai, M.A. Sőrés, **L. Vásárhelyi**, I. Szenti, R. Kun, B. Hartmann, D. Sebők, F. Farkas, A. Zahoor, G. Mao, A. Sápi, Á. Kukovecz, Z. Kónya
Energy Technology, 2023, 11 (8) 2300207
IF: 4,149

14. **An Exploratory In Vitro Microcomputed Tomographic Investigation of the Efficacy of Semicircular Apicoectomy Performed with Trephine Bur**
E. Nagy, B. Vőneki, **L. Vásárhelyi**, I. Szenti, M. Fráter, Á. Kukovecz, M.Á. Antal
Applied Sciences, 2023, 13 (16) 9431
IF: 2,838

15. **Nature-inspired self-similar carbon nanotubes-nonwoven nanostructured materials for fog harvesting applications**
S. Shukla, S. Sharma, K. Koul, H. Saraswat, **L. Vásárhelyi**, A. Rawal, Á. Kukovecz
Composites Communications, 2023, (43) 101694
IF: 8

16. **Droplet navigation on metastable hydrophobic and superhydrophobic nonwoven materials**
S. Sharma, S. Shukla, A. Rawal, S. Jee, F. Ayaydin, **L. Vásárhelyi**, Á. Kukovecz, V. Kumar, N. Kadi
Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2024, (683) 132993
IF: 5,518

7. Other presentations, posters, and conference attendances

1. **Vas-nitrid/nitrogénnel adalékolt grafén kompozitok oxigén redukciós aktivitása**
L. Vásárhelyi, T. Varga, Z. Kónya
OFKD, Hungary/Budapest, 2018 (presentation)

2. **Iron-nitride/nitrogen-doped graphene composite: a non-noble metal catalyst for the oxygen reduction reaction**
L. Vásárhelyi, T. Varga, G. Ballai, H. Haspel, A. Oszkó, Á. Kukovecz, Z. Kónya
SIWAN8, Hungary/Szeged, 2018 (poster)

3. **Electrocatalytic activity of Co4N/nitrogen-doped graphene composites in the oxygen reduction reaction**
G. Ballai, T. Varga, **L. Vásárhelyi**, H. Haspel, Á. Kukovecz, Z. Kónya
SIWAN8, Hungary/Szeged, 2018 (poster)

4. **In situ investigation of crack propagation in ceramics by micro-CT technique**
L. Vásárhelyi, I. Szenti, D. Sebők, Á. Kukovecz, Z. Kónya
CYSC-2019, Serbia/Novi Sad, 2019 (presentation)

5. **Belső szerkezeti változások in situ vizsgálata mikro-CT technikával**

L. Vásárhelyi, D. Sebők, I. Szenti, Á. Kukovecz, Z. Kónya
PhD Hallgatók Anyagtudományi Napja, Hungary/Veszprém, 2019 (presentation)

6. **Bór-nitrid nanorészecskék kolloid stabilizálása polielektrolitokkal**
   L. Vásárhelyi, T. Hegedűs, Sz. Sáringer, I. Szilágyi, Z. Kónya
   XLIII. KEN, online, 2020 (presentation)

7. **Mikro-CT technika orvosi, biológiai és anyagtudományi alkalmazásai a Szegedi Tudományegyetemen**
   Á. Kukovecz, Z. Kónya, D. Sebők, **L. Vásárhelyi**, I. Szenti
   II. ORF, online, 2021 (presentation)

8. **CT és mikro-CT infrastruktúra a Szegedi Tudományegyetemen**
   Á. Kukovecz, D. Sebők, I. Szenti, **L. Vásárhelyi**
   III. ORF, Hungary/Veszprém, 2022 (presentation)

8. Scientometrics

Peer-reviewed papers total: 18	out of this, related to the topic of this thesis: 2
Cumulative impact factor: 105.6	out of this, related to the topic of this thesis: 8.2
Independent cites total: 249	out of this, related to the topic of this thesis: 9