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A Comparison of Bulk Density Measurement Techniques for Carbon-Carbon Composites (CCCs)

by Jennifer M. Sietins, Ngon T. Tran, Faheem H. Muhammed, and Daniel B. Knorr Jr.

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14. ABSTRACT
Bulk density, or the mass of a material divided by its total volume including internal voids and space, is a simple yet highly consequential characterization of carbon-carbon composites (CCCs). Because the performance of CCCs is strongly correlated to their density, and the manufacture of CCCs is relatively time-consuming and expensive, bulk density is routinely measured and its accuracy is important. Interestingly, multiple methods are used to determine bulk density, but the methods' accuracy has not been thoroughly studied for carbon materials. This report discusses five common methods of determining bulk density on nine CCCs with the same 3-D architecture but different densities. These methods are geometric density, geopycnometry (GeoPyc), X-ray micro-computed tomography (xCT), mercury intrusion porosimetry (MIP), and Archimedes' principle. We demonstrate that the Archimedes' density tends to overestimate while geometric density tends to underestimate bulk density. In addition, GeoPyc and MIP yield similar density values to xCT, which may reflect the true bulk density of the materials tested.

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1. Introduction

Carbon-carbon composites (CCCs) are a material class of prime interest for many high-temperature applications due to their high-temperature resistance and high strength, stiffness, and toughness. As these properties may scale with the bulk density of the material, density is a widely used first-order metric for assessing the material's quality and production progress after subsequent densification cycles. As such, it is important to measure density in a consistent and accurate way, especially since the production of CCCs is often time-consuming, labor intensive, and infrastructure demanding. For solids like CCCs, the five main methods of measuring bulk density are geometric density, geopycnometry (GeoPyc), X-ray micro-computed tomography (xCT), mercury intrusion porosimetry (MIP), and Archimedes' principle. Typically, the Archimedes' method is used by most researchers and material developers due to its simplicity, sample generality (e.g., physical state and shape), and lack of specialized equipment.

All five density methods use the same technique (i.e., a balance) to measure mass, but they differ in how volume is determined, which affects accuracy and could cause limitations. Because the geometric method measures volume using calipers and known volume formulas, geometric density is often the simplest and most affordable method for bulk density measurements. However, inaccuracies can arise when the objects have rough surfaces and irregular shapes (e.g., not a perfect sphere or cylinder), which can also make volume calculations laborious. This is shown in Figure 1, where the red arrows indicate regions of air surrounding the CCC that, for more accurate bulk density measurements, should not be included in the volume measurement.

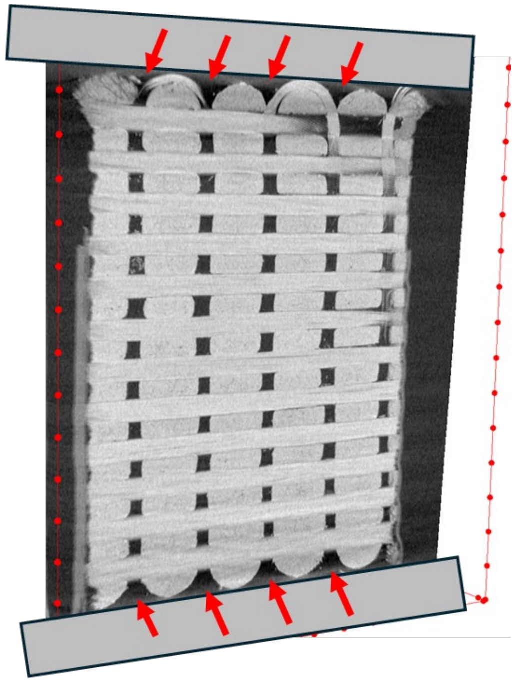

Figure 1. Image of the CCC surface roughness overestimating the volume with the inclusion of air at the locations of the red arrows when using calipers to measure the geometric volume.

GeoPyc density measures volume by a displacement measurement technique that uses a quasi-fluid called DryFlo, which consists of small, rigid spheres (diameter = 6 µm) that have a high degree of flowability. Specifically, the sample is placed on a bed of DryFlo and is followed by agitation, which allows DryFlo to gently consolidate around the sample. For reproducible accuracy, the instrument manufacturers recommend that the sample occupies no less than 20% by volume of the DryFlo bed. In addition, the sample should not be compressible (10–100 N) or brittle toward the DryFlo media.[1] For the samples analyzed, 40 N of force was applied. Compared with the geometric method, the GeoPyc method can handle irregular shapes and measure a more accurate volume for samples with rough surfaces. However, a source of error may arise if the surface roughness is smaller than the diameter of the DryFlo.

xCT is not commonly used as a density measurement technique for materials due to large upfront instrument costs and long scan times. The xCT procedure is similar to a medical scanner, collecting a series of projection images over the course of a 360° rotation and reconstructing those images into a 3-D volume. After reconstruction and image segmentation, a volumetric analysis can be performed to calculate the bulk density. This nondestructive evaluation technique is primarily used for obtaining other microstructural information such as the size, location, and distribution of defects or pores, so xCT can provide more detailed porosity information in conjunction with the bulk density measurements. And, like the GeoPyc method, xCT can handle irregular shapes.

Similar to GeoPyc, MIP uses a displacement measurement technique to measure volume. Specifically, a sample is placed inside a sample holder (i.e., penetrometer), vacuum is pulled, and then a nonwetting liquid (i.e., mercury) at 0.5 psia is allowed to undergo intrusion into the sample holder.[2] The nonwetting liquid surrounds the sample, but the pressure is not strong enough to infuse into the sample pores. Like the GeoPyc method, MIP can accommodate irregular shapes and has the following limitations: 1) the sample volume should be no less than 25% of the sample holder volume, 2) samples cannot be compressible, 3) samples cannot be brittle, and 4) the pores of the samples cannot be too large, such that the nonwetting ability of mercury would be overcome by its surface tension. The last three limitations can be more acute given the use of vacuum and pressure in MIP.

The Archimedes' principle method is also a displacement method to measure volume, comparable to the GeoPyc and MIP methods.[3] Specifically, a sample is placed in a solvent and the displaced solvent fluid, which would be equal to the volume of the sample if completely immersed, is measured. Like most of the other density methods, Archimedes can handle irregular shapes, but it has unique limitations due to its use of solvents. Inaccuracies in volume can arise from 1) buoyancy (if the sample floats, the displaced solvent volume would be less than the sample volume), 2) surface tension (arising when interfacial tension forces compete with buoyancy forces),[4] and 3) temperature fluctuations, which affect volume measurements.

Similar to the GeoPyc, MIP, and Archimedes' methods, helium pycnometry (HePyc) is also a displacement method. Specifically, the volume and density of a sample is determined by how much helium (He) gas can be displaced by it. The sample is placed in a chamber, and He gas is introduced. He atoms are small enough to penetrate even the tiniest pores in the material. By measuring the pressure change as the He fills the voids, the HePyc calculates the true or skeletal density of highly porous or irregularly shaped samples.

Based on Table 1, the "gold standard" for accurate bulk density measurements with the fewest number of experimental limitations is xCT. However, the cost of implementation and speed of xCT analysis is significant, and the CCC community typically uses Archimedes' method due to its simplicity and low cost. To our knowledge, no one has performed a direct comparison of these five density methods on the same CCC samples. This report compares and contrasts the five methods for bulk density measurements on nine CCC materials that were derived from a consistent carbon-fiber preform, but different matrix precursor materials and processing methods.

Table 1. General assessment of bulk density measurement techniques.

Experimental capability	Geometric	GeoPyc	xCT	MIP	Archimedes
Nondestructive	Yes	Yes	Yes	No	Yes
Ease of quantification	Easy[a]	Easy	Difficult	Easy	Easy
Cost of implementation	Low	Moderate	High	Moderate	Low
Speed of analysis	Quick	Quick	Slow	Slow	Quick
Surface roughness	No	Yes	Yes	Yes	Yes
Irregular shape	No	Yes	Yes	Yes	Yes
Compressible	Yes	No	Yes	No	Yes
Brittle	Yes	No	Yes	No	Yes
Large pore sizes (>300 µm)	Yes	Yes	Yes	No	Yes
Intolerant of buoyancy	. . .	. . .	. . .	. . .	No
Intolerant of temperature	. . .	. . .	. . .	. . .	No
Skeletal density	No	No	Yes	Yes	Yes
Pore size distribution	No	No	Yes	Yes	No

[a] This technique is by far the fastest and most convenient method with minimal instrumentation and analyses required.

2. Materials and Processing

The CCC materials evaluated in this effort all included a common carbon-fiber preform. This preform was a 0.5-inch-thick, 3-D woven orthogonal preform woven by TEAM, Inc. The CCCs used in this effort were densified using two different processing approaches that included chemical vapor infiltration and resin infusion and pyrolysis methods. The details of the specific densification procedures are not included in this paper since processing details are irrelevant to the experimental methods for measuring the bulk density.

Upon completion of the densification stages, 0.5-inch-diameter cores were cut from the composite plates using a 0.5-inch diamond abrasive coring bit. Burrs, which commonly formed on the bottom edge of the cores, were gently sanded off. The specimens were then cleaned of machining dust and dried.

3. Density Measurement Procedures

3.1 Geometric Density Measurement

For geometric density measurements, the geometry of the specimen cores was measured using calipers. Core diameters were measured a total of nine times per specimen. Three measurements were taken near the top of the core, three near the center, and three near the bottom. At each location, the three measurements were taken at different rotations of the specimen around its axis to account for possible lack of circularity in the cross section. The nine diameter measurements were averaged together. Three thickness measurements were also taken and averaged, and a volume of the specimen was calculated. The specimen mass was measured on a standard laboratory scale to the nearest 0.0001 g, and the density was calculated from these measurements.

3.2 GeoPyc Density Measurement

A Micromeritics GeoPyc 1365 Envelope and Analyzer was also used to measure bulk density. This is accomplished by measuring the displacement of DryFlo, a solid medium designed for this application. DryFlo has small spheres and is flowable, which allows packing around objects of arbitrary shape without infiltrating into pores in the sample. The GeoPyc comes with a variety of chamber and plunger assemblies to accommodate specimens of different sizes. For the specimens of this effort, the 19.1-mm-diameter chamber was chosen. This size allows sufficient DryFlo medium to surround the specimen, while maintaining an adequate ratio of specimen volume to DryFlo medium volume. Larger-diameter chambers resulted in an excess of DryFlo volume compared with the specimen, which leads to signal-to-noise deficiencies in the measurement. Approximately 5.7 cc of DryFlo was loaded into the chamber for each test (corresponding to a depth of 2 cm on the scale on the side of the chamber). When subsequently loading the specimen into the chamber, the chamber was tilted on its side, and the specimen was allowed to gently slide down onto the bed of DryFlo. The chamber was then rotated around its axis multiple times while tilted to slowly surround the specimen in DryFlo and maintaining approximate alignment of the specimen axis with the chamber axis. This procedure resulted in more consistent results between tests compared with less careful loadings that resulted in random orientation of the specimen relative to the chamber. The GeoPyc was configured to take 12 consecutive measurements of each specimen per loading and report the average and standard deviation of these measurements.

3.3 Archimedes' Method

Archimedes' measurements of density were conducted according to ASTM D792,[3] using Method A. Samples with a thickness and diameter of 0.5 inches were first weighed on a Mettler Toledo AX205 DeltaRange balance, which has a precision of 0.00001 g. To ensure accurate measurements, a standard was weighed before each test to calibrate the balance, and the balance was routinely serviced for precision and reliability. The density determination involved submerging the samples in water and calculating the buoyant force, or the weight of the displaced water, based on the sample's wetted weight. The density was then computed by dividing the mass of the sample in air by the volume of the sample, which was derived from the volume of water displaced.

3.4 X-ray Computed Tomography

A Zeiss Xradia 520 xCT scanner was used for nondestructive evaluation and bulk density quantification. Samples were scanned with a voxel size of 15.74 µm to capture the entire sample within the field of view. Quantitative analysis was conducted in Bruker's CTAn (CT Analyzer) software. The top and bottom planes of the sample height were manually selected. The images were binarized with the automatic Otsu thresholding algorithm and a shrink-wrap function was used to virtually wrap the outside of the sample. 3-D analysis was conducted to compute the volumes for each sample and the densities were calculated with the simple equation dividing the mass over volume. To obtain upper and lower bound variability, erosion and dilation functions were used to shrink and grow the volume by 3 pixels. This value was chosen because it is a resolution limit for detectability based on the scan voxel size.[5]

3.5 Mercury Intrusion Porosimetry

A Micrometrics AutoPore V 9600 was used to determine percent porosity and porosity size of open pores as well as to calculate bulk and skeletal densities. The penetrometer was initially evacuated to a pressure of 0.0003 MPa (0.05 psia) and then filled with mercury to 216.7229 MPa (31,433 psia) over 231 logarithmically spaced intrusion pressures (i.e., from 0.01 psia at the beginning to 600–1200 psia at the end). For each pressure, the maximum intrusion was 0.010 mL/g and the sample was allowed to equilibrate for 30 s. The penetrometer was transferred from a low-pressure chamber to a high-pressure chamber at 40 psia, and care was taken to minimize any pressure generated while tightening the high-pressure chamber. The input for current "atmospheric pressure" was measured by the low-pressure transducer when the low-pressure port was opened immediately after the low-pressure analysis. Both the advanced and receding contact angles were 155°.[6]

3.6 Helium Pycnometry

A gas displacement pycnometer using ultra-high purity He gas (Micromeritics AccuPyc II) was used to determine the skeletal density of the samples. Prior to analysis, samples were heat-treated in an oven at 100 °C for 30 min to remove moisture and then weighed on a Mettler Toledo Analytical Balance model MS304TS/00. The sample holder (volume = 1 cm^3) was calibrated using a steel ball (0.718 cm^3) to ensure accurate volume measurements. The analysis included six purge and analysis cycles, during which the hydrostatic pressure was ramped from 0.05 to 15 psia. The skeletal density was then determined by dividing the measured mass of the sample by the volume of He gas displaced.

4. Results and Discussion

Results of the five different density measurement techniques are shown in Figures 2 and 3. The Archimedes' method is consistently about 0.05 g/cc higher than the xCT, MIP, and GeoPyc methods and always measured the highest compared with the other techniques. The geometric density measured the lowest of all the methods except for one instance. Surface roughness, similar to that shown previously in Figure 1, may cause the geometric density method to overestimate volume and, consequently, underestimate bulk density. Conversely, surface tension effects cause the Archimedes' method to underestimate volume (and overestimate density) because the Archimedes' principle assumes the buoyant force acting on a submerged object in a fluid is equal to the weight of the fluid displaced by the object without any consideration of influence of surface tension. This may be due to the presence of some surface-connected porosity that may absorb water, resulting in higher mass after immersion.[7] This higher mass will give an artificially high density result.

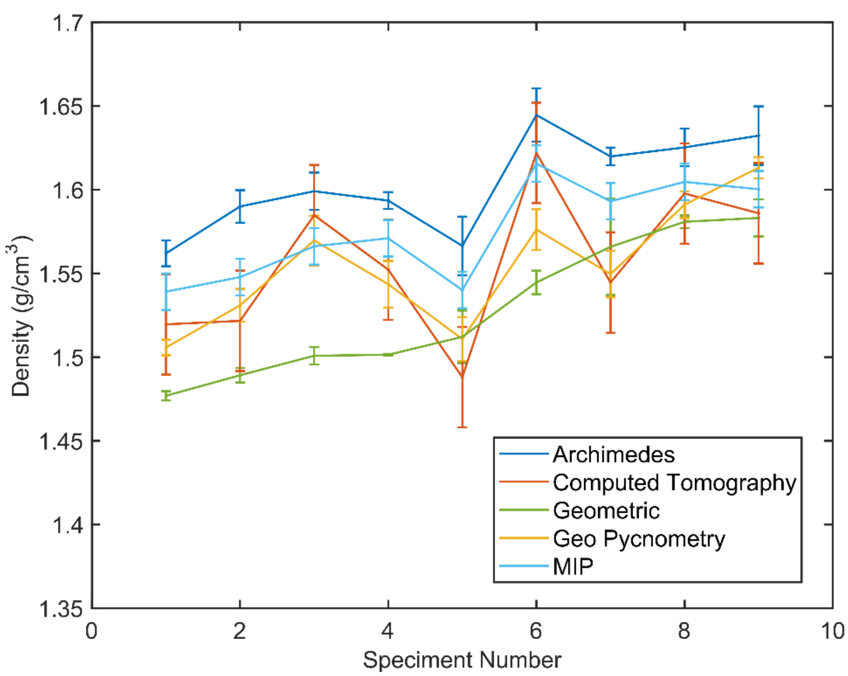

Figure 2. Density measurements taken by GeoPyc, geometric, xCT, MIP, and Archimedes' methods.

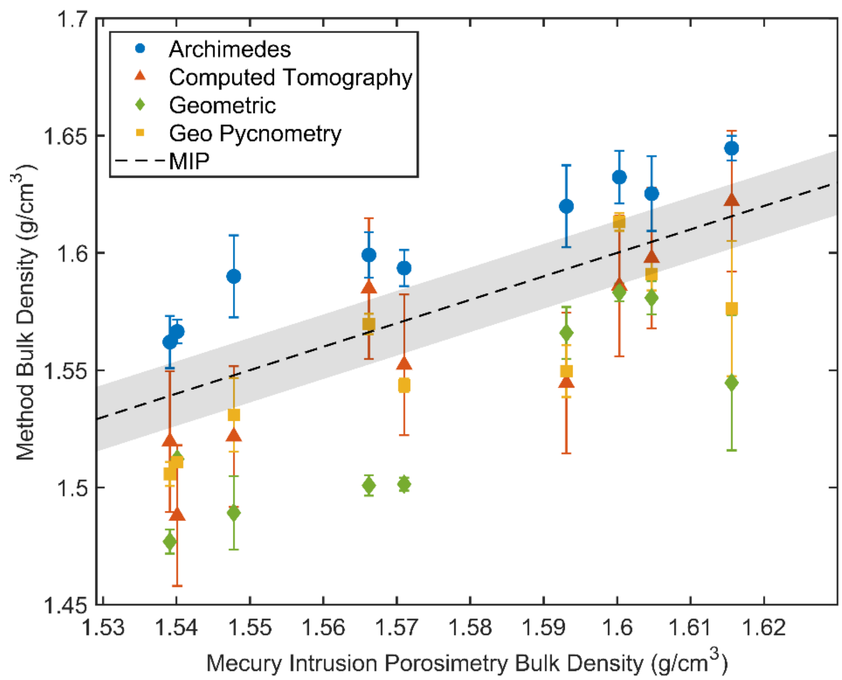

Figure 3. Average bulk densities of all measurement techniques plotted against MIP data. The shaded region represents the standard deviation of the bulk densities determined from two triplicate MIP datasets.

Figure 2 shows the average densities and standard deviations of the nine samples and their relationship to the bulk density measured by the MIP. The shaded region, representing the upper and lower bounds of a typical MIP measurement, was determined from two sample triplicates. Two samples were used with consideration to the amount of waste mercury produced each run and experimentation time. By visualizing the data in this way, it becomes clear that the experimental error in determining bulk density using the geometric and Archimedes' methods is unacceptably high, due to significant over- and underestimation of values.

Given that there are three methods for accurate bulk density measurements, other factors should be considered for routine bulk density collection (Table 1). These factors include ease of quantification, cost of implementation, and analysis speed. An important factor to consider is whether the technique is nondestructive in nature. Table 1 summarizes these attributes for the various measurement techniques. All the methods are nondestructive except for MIP, which also generates hazardous waste that can be difficult and expensive to properly dispose of. Ease of quantification generally correlates well with the speed of analysis with GeoPyc, geometric techniques being the simplest and fastest methods, and xCT being the most difficult and time-consuming. It is also important to consider the value of additional characterizations that the density methods provide. Both MIP and xCT can provide skeletal density and distribution of pore sizes. Unlike other methods, xCT also provides valuable information on the 3-D location of porosity within the sample. Overall, GeoPyc seemed to provide the best combination of speed, ease of use, cost, and measurement accuracy. However, MIP or xCT would be more desirable when skeletal density or pore size distribution information is needed.

Like GeoPyc, HePyc offers a convenient and nondestructive method for quantifying and characterizing the skeletal density of a sample. In this report, HePyc was used as a secondary check to evaluate the effectiveness of the MIP through comparative analysis, as shown in Figure 4. The HePyc method, which uses He gas to provide a value that most accurately represents the material's true skeletal density, showed a strong correlation with the MIP method. This correlation serves as experimental validation for the protocol described in the MIP methods section. Moreover, Figure 3 further supports the conclusion of previous work that the MIP can fully characterize a composite sample as it relates to void distribution and density characteristics.[8]

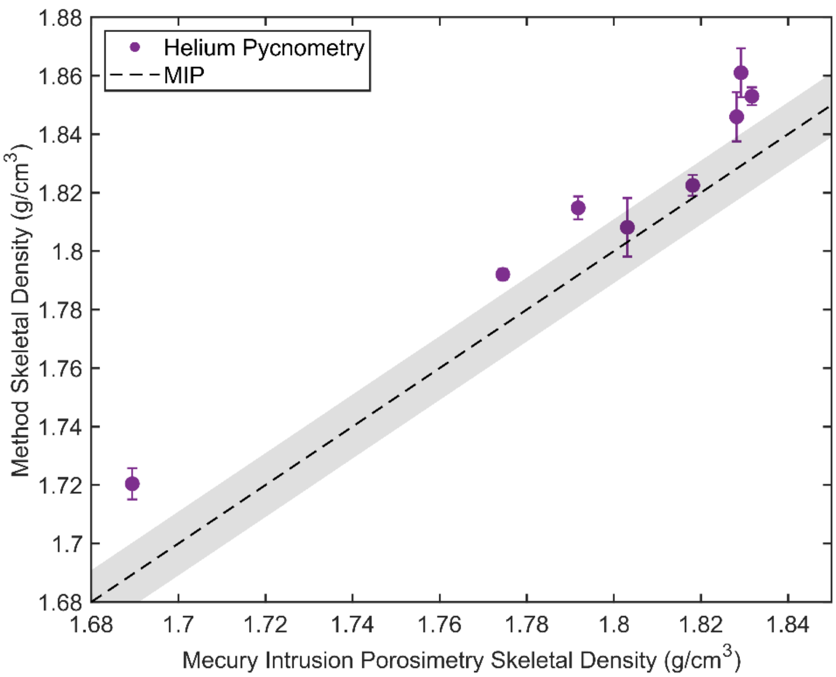

Figure 4. Comparison of skeletal values determined from HePyc plotted against MIP data. The shaded region represents the standard deviation of the skeletal densities determined from two triplicate MIP datasets.

5. Conclusions and Recommendations

Our study compares five of the common measurement techniques used in determining bulk density to evaluate the accuracy of each technique for carbon materials. Interestingly, the Archimedes' method that uses water as the solvent, which is the most common method used in industry and reported in literature, seems to give biased high results by a small but significant amount. Conversely, geometric measurements are almost always yielding lower bulk density values than other measurements, providing a low bound, and GeoPyc, MIP, and xCT measure similar density values to one another. Given that xCT has the fewest sample limitations and sources of inaccuracies, one can infer that xCT provides the most accurate bulk density. The main sources of error in bulk density are derived from the volume measurements of each technique. For geometric density, surface roughness is the likely culprit because surfaces of the CCC samples were textured. For the Archimedes' method that uses water as the solvent, surface tension is likely the culprit.

Accurate bulk density can be measured from all five methods as long as the sample limitations are considered and the sources of errors are minimized. In practice, however, it is desirable to choose a method that is operationally simple and applicable (in terms of accuracy) to the widest arrays of sample sizes, textures, compressibility, brittleness, processing history, etc. Hence, we recommend the following for accurate bulk density measurements:

1) Avoid using the geometric method.
2) Avoid using the Archimedes' method with water as the solvent. Use a solvent (e.g., toluene) with lower surface tension and higher wettability with hydrophobics, such as CCCs.
3) Use GeoPyc, MIP, or xCT for accurate bulk density measurements. For compressible or brittle samples, MIP and GeoPyc should be used with caution.
4) Use MIP or xCT if additional information (i.e., skeletal density or pore size distribution) is desirable.

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List of Symbols, Abbreviations, and Acronyms

3-D	three-dimensional
CCC	carbon-carbon composite
GeoPyc	geopycnometry
HePyc	helium pycnometry
MIP	mercury intrusion porosimetry
xCT	X-ray micro-computed tomography

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