



## Less is more: A holey grail of materials science

We have known for a long time that it is possible to make something out of the right kind of nothing. I should note right off the bat that I am not discussing nothingness in the sense of the recent Isaac Asimov Memorial Debate on “The Existence of Nothing”<sup>1</sup> or the street-fight surrounding that debate.<sup>2</sup> I will leave that for another day along with discussions of the Casimir effect,<sup>3</sup> other vacuum engineering effects, and effects that might lead to discussions of less than nothingness.<sup>4</sup>

Instead, I am discussing the nothingness (from the atomic scale to the macroscale) that vacancies,<sup>5</sup> clusters of vacancies, voids, porosity, structured holes, aerogels,<sup>6</sup> and nanofoams<sup>7</sup> are made of that are more familiar to materials researchers.

We know that gases, liquids, and solids are mostly empty space—atoms floating in nothing. Additionally, solid crystals contain defects. Statistical mechanics informs us that, at temperatures above absolute zero, crystalline lattices will deviate from perfection and contain vacancies and interstitial atoms.<sup>8</sup> Other space-emptying (holey) defects include di-vacancies, vacancies next to impurity atoms, vacancy clusters, voids, and so on. Existence of these defects in materials and devices can alter their performance, reduce their reliability, and shorten their lifetime. However, defects including vacancies and other forms of nothingness can have beneficial properties.

Some vacancies are known to produce color centers in materials, including the alkali halides.<sup>9</sup> The simplest color centers are electrons trapped at a vacancy site, and their properties can be modeled reasonably well using a particle-in-a-box approach. The changing color of glass (glass bottles, panes in stained-glass windows) over many years of exposure to UV light from solar exposure is attributed to the formation of color centers. Color centers have been used for broadly tunable laser media, radiation dosimeters, and have been proposed for high-density memory devices. More recently, the nitrogen-vacancy center in diamond is being explored as a useful medium for quantum information applications.<sup>10</sup> Given the almost metaphysical sense in which quantum information is viewed by many these days, I am tempted to relate this to the *deus ex machina*, but I do not want to offend anyone’s beliefs.

At a much more macroscopic scale, porosity<sup>11</sup> plays an important role in the properties of a wide variety of materials, including concrete, brick, wood, and other structural materials, sieves and membranes, filters, paper, fabrics, and various other materials. The integration of controlled quantities of nothing at random into these materials can optimize their utility, while too much of nothing can cause them to fail (concrete, brick, wood) and too little of nothing can limit their performance (sieves, membranes, filters).

Photonic bandgap structures (PBGs)<sup>12</sup> are based upon geometric volumes of optical materials into which the controlled integration of nothing alters the optical frequency response of the material, up to and including opening forbidden bands that prevent the transmission of light of selected wavelengths through the material. Without the nothingness, the optical material may have significant transmittance in the spectrally forbidden region of the PBG structure.

Microstructured optical fibers (holey fibers) date back to ideas relating to air-core fibers that were generated in 1974.<sup>13</sup> Two-dimensional patterns of holes have now been generated in optical fiber cores so that waveguiding of light through the fiber is based upon the effective index of the holey core compared to the index of the cladding. Substantial arrays of submicron-sized holes have been fabricated over extended lengths in optical fibers, with applications in optical communications, fiber-optic gas sensors, optical-fiber lasers, and other areas. The integration of controlled quantities



of nothing with periodicity and order can enhance the properties of optical fibers for applications. Furthermore, recently, microstructured optical fibers with tailored, nonperiodic formulations of nothingness integrated into the core have been demonstrated to produce better Fresnel lensing and for other applications.

Aerogels<sup>6</sup> are another class of holey material that benefit from the incorporation of nothing. These extremely lightweight materials, known since the 1930s, have been made from silica, alumina, chromia, chalcogens, and carbon by using special processing to remove the liquid component, leaving only the solid matrix surrounding the very important nothing. Aerogels are good thermal and electrical insulators as well as good convective insulators.

The logical extension of aerogels are nanofoams.<sup>7</sup> In 2011, a team involving HRL Laboratories, the University of California–Irvine, and the California Institute of Technology produced an extremely lightweight nanofoam.<sup>14</sup> The nanofoam, consisting of a mesh of nickel nanotubes, was fabricated by first constructing a polymer mesh, then coating it with NiP using an electroless coating technique, then etching away the polymer. The authors of the work stated that the nanomesh was 99.99% nothing with a density of 0.9 mg/cm<sup>3</sup> compared to Styrofoam (20 mg/cm<sup>3</sup>) or a feather (2.5 mg/cm<sup>3</sup>). A group of researchers at Zhejiang University in Hangzhou, China, has developed a carbon nanofoam that has a density of 0.16 mg/cm<sup>3</sup>.<sup>15</sup> One is tempted to call this much ado about nothing, but I do not believe that that is what Shakespeare had in mind.<sup>16</sup> Lennon and McCartney<sup>17</sup> also wrote, “Nothing’s gonna change my world,” but I do not believe they had this in mind.

It is not yet possible to make something completely from nothing, although those of us that love science fiction look forward to the day when we can exploit the quantum vacuum. But even though we cannot yet work that miracle, it is possible to improve some materials or alter their properties in a beneficial way by adding nothing to them in a controlled fashion. Or to paraphrase Michael Faraday, “Nothing is too wonderful to be true.”<sup>18</sup>

Steve Moss

## References

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