THE SIXTEEN-PERCENT SOLUTION:
CRITICAL VOLUME FRACTION FOR PERCOLATION

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INTRODUCTION

The English call it "value for money" (vfm). The American equivalent is "bang for the buck". The idea is simple: to provide a rough measure of the ratio of benefit to cost. For an author of scientific papers, one possibility for a vfm-type measure of "benefit" (impact) to "cost" (time and effort) is this:

vfm = (number of citations)/(paper's length in printed pages).

In my case, the vfm winner is clear. It is a two-page paper by Harvey Scher and myself, published quietly as a note in J. Chem. Phys. [1], which has been cited over 350 times. Later work related to the central idea of that paper has also been widely cited [2, 3]. That idea is the concept of a critical volume fraction for site-percolation processes.

NOSTALGIA

One afternoon in mid-May of 1970, at my desk in the research building of the Xerox complex near Rochester, NY, I was poring over experimental Raman spectra, searching for significant peaks with my "spectroscopist's eye" [4]. I was not having much luck, and I needed a break. So I left my office, walked down the hall, and went into the office of a colleague, Harvey Scher. Harvey was, as usual, good-natured and patient about the interruption of his own work, and he took the opportunity to describe an interesting problem that he was working on. A very approachable resident theorist, Harvey had been consulted by a technology group working on photosensitive layers in which photoconductor particles were dispersed in a resin. Their measurements had shown a dramatic threshold in the dependence of photosensitivity on photoconductor concentration. Elliott Montroll, then a frequent visitor to Xerox, had suggested to Harvey that he look at the literature on percolation theory. Harvey had assimilated that literature and made use of it, and he introduced me to percolation theory that afternoon. I was fascinated by this stuff, and when I got back to my office I did not return to the strip-chart recordings (no PC's in 1970). Instead, I worked on some geometry problems related to ideas that we had kicked around, and I became enthusiastic about writing up a short paper reporting what we had found.

Ten days later the paper was circulated internally within Xerox, and it was submitted for publication in mid-June. This speed was then, and is now, uncharacteristic of both authors. The reason for the choice of J. Chem. Phys. is somewhat obscure. We did not want to send it to a math or math-phys journal, and we had seen a short paper in J. Chem. Phys. that mentioned percolation. It turns out that the referee for our paper was almost certainly a mathematician! He (or she) chided us for the empirical and approximate nature of our critical density. (We knew it was approximate, and we were proud of "empirical"!) But he (or she) nevertheless pointed out to us an additional result for p_c (an exact value for the two-dimensional Kagomé lattice) which fit our ideas very well. We added it to the Table in our paper.

The anecdote described above, dealing with the fruitfulness of an afternoon schmooze session at the Xerox lab in Webster, NY, was characteristic of a period now remembered by some as a "golden age" of industrial research [5]. The scientific issue arose in the context of a technological setting, which is of course a familiar tradition in condensed-matter physics [6]. The atmosphere was one in which it was OK to spend time on scientific issues as well as on product-development and engineering ones. In the year 2000, that era is history and opportunities to do science are rare in present-day corporations. Globalization is sometimes given as the reason (or excuse) for this, but human herd-instinct considerations also enter: Everybody did it then (corporations supported research) because everybody else did it; nobody does it now because nobody else does it. This is a cooperative phenomenon, so perhaps we can hope that a phase transition can happen again.

CRITICAL VOLUME FRACTION

In three dimensions, the percolation threshold p_c for site-percolation processes varies from lattice to lattice by more than a factor of two [7]. For two-dimensional lattices, p_c varies by more than a factor of 1.5 [7, 8]. The Scher-Zallen construction for the critical volume fraction ϕ_c associates with each site a sphere (or circle, in 2d) of diameter equal to the nearest-neighbor separation. Spheres surrounding filled sites are taken to be filled. At p_c, the critical value of the site-occupation probability p, the fraction of space occupied by the filled spheres is taken to be the critical volume fraction ϕ_c. The key point is this: From lattice to lattice (in a given dimensionality), ϕ_c is nearly constant, varying by just a few percent. It is an approximate dimensional invariant. In three dimensions, ϕ_c is close to 0.16; in two dimensions, ϕ_c is close to 0.45 [1, 3].

The relationship between ϕ_c and p_c is $\phi_c = f\,p_c$, where f is the filling factor of the lattice when viewed as a sphere packing. The p_c values forming the basis of the 1970 paper correspond to familiar crystal structures. A structure that is not crystalline but is experimentally well defined is random close packing (rcp). The rcp structure corresponds to the atomic-scale structure of simple amorphous metals [3]. Since f is known for the rcp structure, $\phi_c = 0.16$ predicts the p_c value for this structure. Experiments carried out to determine the conductivity threshold (insulator-to-metal transition) of rcp mixtures of insulating and metallic spheres are in good agreement with this prediction [9, 10, 11].

One way to view $\phi_c = f\,p_c$ is as an expression connecting the ease-of-percolation with the connectivity of the underlying structure. For bond percolation, such an (approximate) connection had been found earlier, in 1960 [12, 13]. A reasonable measure for the ease-of-percolation for a given structure is $(1/p_c)$, the reciprocal of the percolation threshold. For bond percolation, $(1/p_c)$ is very close to (2/3)z in three dimensions and (1/2)z in two dimensions. Here z is the average coordination number of the lattice. The proportionality between ease-of-percolation and coordination number shows that, for bond-percolation processes, the coordination number is the appropriate measure of the connectivity of the lattice. This, of course, makes sense. But for site-percolation processes, z does not work. Instead, $\phi_c = f p_c$ shows that $(1/p_c)$ is proportional to f. This reveals that, for site-percolation processes, the sphere-packing filling factor is the appropriate measure of the connectivity of the underlying structure. This insight is a byproduct of the work on the critical volume fraction.

LIMITATIONS

Thanks to the piece of information provided by the unknown referee, we knew immediately that ϕ_c is only approximately invariant. The site-percolation threshold is known exactly for two two-dimensional lattices, the triangular lattice (2d close packing) and the Kagomé lattice, so that ϕ_c is exactly determined for each. The two values differ by 2%. A few people in the critical-phenomena community took an instant dislike to ϕ_c. It wasn't exact. It wasn't rigorous. It wasn't even an exponent, so why care about it? [One can imagine one of them having the following reaction to the experimental discovery of a new superconductor: "So T_c is 450 K, so what? What are the exponents?" But maybe that's unfair.]

The value of ϕ_c can be estimated from a plot of $(1/p_c)$ versus f [3]; the slope is $(1/\phi_c)$. Here a question arises at the low end of the plot, where the proportionality between the ease-of-percolation and the filling factor has to eventually fail because $(1/p_c)$ cannot be less than 1. This consideration is unimportant in three dimensions in which $(1/p_c)$ does not closely approach unity; the values cluster in the region from about 2.3 to 5.0. In two dimensions, typical $(1/p_c)$ values are closer to 1.0, lying between 1.4 and 2.0. Within this region, the proportionality of $(1/p_c)$ to f holds very well [1]. However, Suding and Ziff [8] have recently considered very-low-connectivity two-dimensional lattices with $(1/p_c)$ values down to 1.24. Their results show that at these very low connectivities, the deviation from $(1/p_c) = (1/\phi_c) f$ becomes appreciable. Suding and Ziff offer a revised, nonlinear relation between p_c and f that improves the fit in the very-low-connectivity region. Most structures of physical interest are far from this region.

APPLICATIONS

The notion of a critical volume fraction insensitive to the details of local structure, as suggested in the 1970 paper, is an attractive one. But it is heuristic, empirical, approximate. It had been my original plan for this paper to review its success (or failure) in relation to experimental literature on metal/insulator composites. This has turned out to be too mammoth an undertaking for the presently available space and time, and will have to be deferred. The experimental literature is vast; one extensive compilation can be found in a 1993 article by Ce-Wen Nan [14]. The experimental studies span an enormous variety of systems and differ greatly in depth and quality.

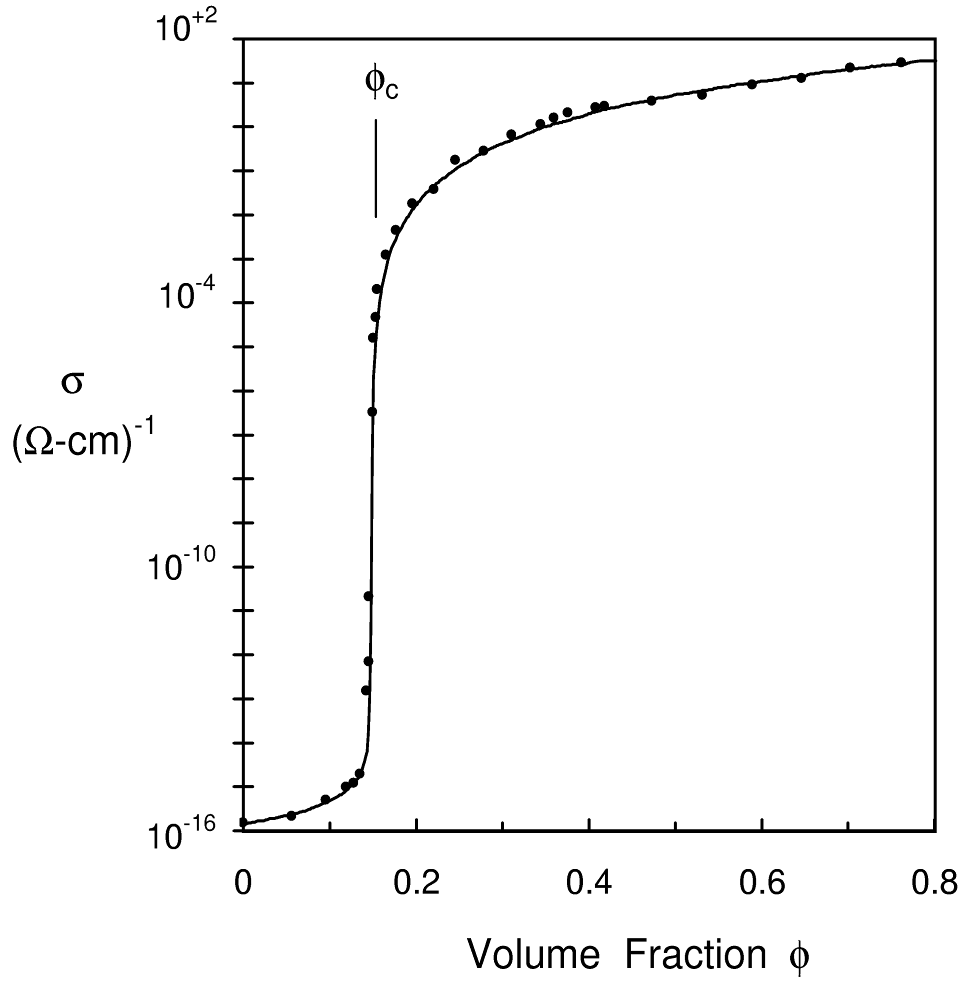

Figure 1. The conductivity threshold in graphite/boron-nitride composites [19].

At a later time I may attempt a plot of frequency-of-occurrence versus ϕ_c value, but here only some less-than-satisfactory observations will be offered. For three-dimensional composites a value close to 0.16 is very often encountered, and it is interesting that this occurs for some of the most carefully studied systems. Examples are the carbon-black/polymer composites studied by Heaney and co-workers [15, 16, 17] and the graphite/boron-nitride composites studied by Wu and McLachlan [18, 19]. Figure 1 displays the very clean experimental results of Wu and McLachlan, showing a conductivity threshold spanning many orders of magnitude. Graphite and boron nitride are structural and mechanical isomorphs, but differ in conductivity by a factor of 10^{18}. The points are measured values; the curves are scaling-law fits that closely determine ϕ_c (0.15 for this system).

But there are many systems for which ϕ_c is quite different from 0.16; this value is not universal. The reason is unclear, though different classes of topology have been suggested. One of these is the “Swiss-cheese” void-percolation topology analyzed by Halperin and co-workers [20] and studied experimentally by Lee et al. [11]

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5. In the seventies, the Xerox lab in Palo Alto was the site of some now-famous computer-science examples: Hiltzik, M.A. (1999) *Dealers of Lighting*, Harper, New York.
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