

Pfeifer and Schmidt Reply: Wong and Bray¹ (WB) address the issue of whether in scattering from a surface with fractal dimension D , the leading-order scattered intensity vanishes or not in the space-filling limit $D \rightarrow 3$. The question, of interest for D -diagnostic purposes, is not new.²⁻⁵ For surface fractals, it is equivalent² to convergence or divergence for $D \rightarrow 3$ of the prefactor B in

$$V_b = Br^{3-D}, \quad (1)$$

where V_b is the volume of a boundary layer of thickness r at the surface. We show that the two different scattering laws correspond to two different scenarios for the limit $D \rightarrow 3$. In the first case (Bale and Schmidt²), the system size remains finite and the pore space shrinks essentially to zero. In the second case, envisaged by WB, we show that the system size goes to infinity so as to maintain a nonvanishing pore-size distribution. While realizations of the first scenario abound, it is not clear from WB how their case may be realized. We also answer that question. The details are as follows.

I. *The prefactor B is not unknown as claimed by WB.* We denote the scatterer by Σ (continuum representation, set of occupied points) and its surface by $\partial\Sigma$. The correct expression for V_b [so that Eq. (5) of WB gives the correct intensity] is given by⁵

$$V_b = (2/r) \int_0^r v(r') dr', \quad (2)$$

where $v(r')$ is the volume of the set of points in Σ whose distance from $\partial\Sigma$ is $\leq r'$. From (1) and (2) it follows⁶ that

$$B = \pi^{(3-D)/2} [(4-D)\Gamma((5-D)/2)]^{-1} \mu_D(\partial\Sigma), \quad (3)$$

where Γ is the gamma function and μ_D is D -dimensional Hausdorff measure. Recall⁶ that μ_D measures the content of a fractal object (generalization of length/area/volume). For $D=2$, Eq. (3) reduces to $B = \text{area of } \partial\Sigma$. In a lattice representation of Σ (lattice constant a , $a \ll$ cutoff length b of the D -dimensional behavior), one has, within a factor of order unity,

$$\mu_D(\partial\Sigma) \approx (\text{No. of surface sites}) a^D. \quad (4)$$

II. Equation (3) and the elementary bound⁶

$$\mu_D(\partial\Sigma) \leq L^D \quad (L \equiv \text{diam of } \Sigma) \quad (5)$$

imply that for fixed system size L and $D \rightarrow 3$, the factor B approaches a finite value which² makes the scattered intensity vanish for $D=3$. Thus, *Bale and Schmidt have not overlooked a subtle prefactor as claimed in Ref. 1.* They have given the correct scattering law for the physically interesting case where the system size remains finite. The finite L pushes the outer cutoff b (approximately the largest hole in Σ) to zero for $D \rightarrow 3$. So if we let $D \rightarrow 3$ and keep the lattice constant in (4) fixed [e.g., $a = \text{atomic length}$], there is a point where $b \sim a$, i.e., where the largest holes are of the order a . At this $D \approx 3$,

surface sites become indistinguishable, within resolution a , from bulk sites, and pore sites are gone [this is why in a rigorous limit $D \rightarrow 3$, one has to use (5) instead of (4)]. Beyond this D value, no density fluctuations and, thus, no scattering contributions from internal surface exist any more. All nonporous solids, but also zeolites and silicas⁴ ($D \approx 3$ with $b \sim 10 \text{ \AA}$), qualify for this scenario. The zero-intensity result for $D=3$ for mass fractals³ has the same origin.

III. In their discussion of the prefactor B , WB write $B = C/(3-D)$ where C is the prefactor in $S_r \equiv dV_b/dr = Cr^{2-D} \approx$ surface area measured with tiles of diameter r , and arbitrarily assume that C (rather than B) takes a finite, nonzero value for $D \rightarrow 3$. *This fails to answer under what conditions, if any, this assumption might hold; and why finiteness of C ($\neq 0$) should be any better than finiteness of B .* The answer is the following. Equations (3) and (5) give the bound $C \leq 2(3-D)L^D$. So if C is to remain nonzero for $D \rightarrow 3$, the system size L must grow as $(3-D)^{-1/D}$. This is a very different scenario than the one for the Bale-Schmidt result. The growing L for $D \rightarrow 3$ keeps the outer cutoff b and holes of sizes $\gg a$ from going to zero, whence nonzero scattering for $D=3$. Thus the two scattering laws are different sides of the same coin. To declare one of them as superior¹ misses the whole point of the $D \rightarrow 3$ limit: The limit is inherently path dependent because of $\lim \partial\Sigma \neq \partial(\lim \Sigma)$. A recent study of this dependence for pore-size distributions⁷ suggests that the $D=3$ result envisaged by WB can be obtained by keeping the total pore volume (equal to the volume of the convex hull of Σ minus the volume of Σ) fixed and may be realized by random processes whose rms displacement grows with time t as $t^{1/3}$.

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²H. D. Bale and P. W. Schmidt, Phys. Rev. Lett. **53**, 596 (1984).

³E.g., J. K. Kjems and T. Freltoft, in *Scaling Phenomena in Disordered Systems*, edited by R. Pynn and A. Skjeltorp (Plenum, New York, 1985), p. 133.

⁴D. Rojanski *et al.*, Phys. Rev. Lett. **56**, 2505 (1986).

⁵P. Pfeifer, unpublished.

⁶B. B. Mandelbrot, *The Fractal Geometry of Nature* (Freeman, San Francisco, 1983), pp. 358 and 363.

⁷P. Pfeifer, in *Characterization of Porous Solids*, edited by K. K. Unger, D. Behrens, and H. Kral (Elsevier, Amsterdam, to be published).