Using NMR to Measure Fractal Dimensions

In a recent Letter [1], Stallmach *et al.* reported pulsed field gradient (PFG) NMR measurements of the time-dependent diffusion constant $D(t)$ in water saturated sands. According to theory [2], $D(t)$ decreases from the bulk water value D_0 with increasing observation time t:

$$D(t)/D_0 = 1 - 4Sr/9\sqrt{\pi}V + \text{higher order terms.} \quad (1)$$

Here S/V is the pore space surface-to-volume ratio and $r = \sqrt{D_0 t}$ is the diffusion length. The authors studied samples with different grain diameters d_g and found that the surface area per unit mass obeyed $S_m \propto d_g^{-0.8}$. They interpreted this as evidence that the surface was fractal with dimension D_S and identified the exponent as $D_S - 3$. However, micrographs of the sands do not appear fractal. In this Comment, we point out several serious problems with their analysis and suggest a better one.

First, the authors neglected the fact that each sample has unknown upper and lower cutoff length scales of fractality, L and ℓ, respectively. The full scaling behavior is $S_m \propto (d_g/L)^2(L/\ell)^{D_S}\ell^2/d_g^3$ [3]. Their assertion that $S_m \propto d_g^{D_S-3}$ is true only if (i) $L \propto d_g$ for the different samples and (ii) ℓ is identical for all the samples. Additionally, the use of Eq. (1) requires a third assumption (iii) $\ell > r$ for all the samples, where r spans the range 2–10 μm in Ref. [1]. Since sands and rocks are known to have fractal pore surfaces below about 1 μm [4] and the claimed region of fractality in Ref. [1] is 100–1000 μm, assumption (iii) requires a window of smoothness that fortuitously coincides with the range of r. This picture of the pore geometry is both unnatural and unjustified.

The key point is that Eq. (1) was derived for *nonfractal* surfaces but it requires a modification for *fractal* surfaces. Physically, the term $4Sr/9\sqrt{\pi}V$ arises because molecules within a boundary layer of volume $V_B \approx Sr$ can, on average, reach the pore surface within time t; hence, their diffusion is impeded. For smooth surfaces, S/V is constant and so $V_B \propto r$. For fractal surfaces, it is easy to see that $V_B \propto (d_g/L)^2(L/r)^{D_S}r^3/(3 - D_S)$ [3] and Eq. (1) can be expressed as $1 - D(t)/D_0 \propto V_B/V$. Hence, independent of d_g and L, we have at short times

$$1 - D(t)/D_0 \propto r^{3-D_S} \propto t^{(3-D_S)/2}. \quad (2)$$

How L and ℓ compare to r will emerge from the analysis.

To illustrate how this works, we show in Fig. 1 PFG NMR data on Indiana limestone and a packing of plastic beads; experimental details are given in Ref. [5]. According to Eq. (2), a log-log plot of $1 - D(t)/D_0$ vs r should give a straight line with slope $3 - D_S$. As can be seen, the data for plastic beads are consistent with $D_s = 2$, but the limestone data give $D_S = 2.58 \pm 0.14$. It is evident that $\ell < r < L$ for the limestone, consistent with the multiscale pore features (> 1 μm) that are seen in typical optical micrographs. In this analysis, it is essential to measure D_0 directly with bulk fluid under the same conditions and to a precision that is much smaller than the change in $D(t)$. In Fig. 1, D_0 was determined to a precision of $\pm 0.5\%$ and the *minimum* change in $D(t)$ is over 5%. In contrast, Stallmach *et al.* *forced* $D_s = 2$ in Eq. (2) and let D_0 be a fitting parameter, resulting in $D_0 = 2.3(1) \times 10^{-9}$ m^2/s for four samples. The $\pm 4\%$ variation in D_0 is significant compared to the *entire* 10%–20% change in $D(t)$ they analyzed. Our method will test their assumptions (ii) and (iii), but assumption (i) will remain questionable.

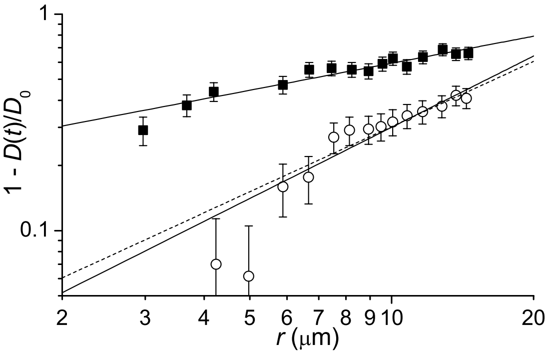

FIG. 1. Time-dependent diffusion data for water-saturated samples of Indiana limestone (squares) and unconsolidated 15 μm diam polystyrene beads (circles). The solid lines show least-squares fits to Eq. (2), yielding $D_S = 2.58 \pm 0.14$ for the limestone and 2.2 ± 0.4 for the beads. In the latter case, we also show a dashed line with D_S fixed at 2.

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