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Surface areas of fractally rough particles studied by scattering

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The small-angle scattering from fractally rough surfaces has the potential to give information on the surface area at a given resolution. By use of quantitative neutron and x-ray scattering, a direct comparison of surface areas of fractally rough powders was made between scattering and adsorption techniques. This study supports a recently proposed correction to the theory for scattering from fractal surfaces. In addition, the scattering data provide an independent calibration of molecular adsorbate areas.

Small-angle scattering has long been a valid way to determine the specific surface area of "smooth" porous and granular materials[1] whose surfaces are locally flat at the smallest resolved scale, which for a scattering experiment is the inverse of the largest scattering vector, $q=(4\pi/\lambda)\sin(\theta/2)$ (λ is the wavelength of the radiation in the scattering medium and θ is the scattering angle). The equivalence of scattering measurements with other surface-area measurements, such as gas adsorption, has been demonstrated for *smooth* surfaces many times.[2]

Although it has been realized recently that many materials can be described as fractally rough,[3,4] there have been no quantitative tests of scattering theories for such surfaces, partly for lack of a complete scattering theory for fractal surfaces and partly because of the difficulties in making absolute scattering intensity measurements. (Here the term "rough" describes irregular surfaces, not necessarily related to "roughening transitions.") Since acceptable calibration standards for neutron intensity have now been established,[5] it is possible to address a recent controversy over the fractal-surface scattering theory.[6,7] Here we compare quantitative small-angle x-ray-scattering (SAXS) and small-angle neutron-scattering (SANS) measurements on carbon and silica powders with independent gas adsorption measurements by the BET (Brunauer, Emmett, and Teller) method. Our data favor a recently proposed correction[6] to the scattering formulas[7] for fractal surfaces and provide an independent check on the much debated[8] adsorbate molecular areas (effective area of a molecule in an adsorbed monolayer).

The area S of a fractal surface, whether self-similar or self-affine,[3] depends on the size r of the probe used, $S(r)=S_x r^{2-D}$, where D is the surface fractal dimension and S_x is a sample-dependent prefactor. Smooth surfaces have $D=2$. For the specific surface area (area per unit mass)

$$\sigma(r)=\frac{S(r)}{V\rho_0}=\sigma_x r^{2-D}, \qquad (1)$$

we require the prefactor S_x, where $\sigma_x=S_x/(V\rho_0)$ and ρ_0 is the mass density of the sample. Our general approach is to measure σ_x and D by scattering, then to evaluate the area $\sigma(r)$ at a resolution r appropriate to a given molecular adsorbate in order to compare with adsorption measurements.

The density correlation function for small r of a material is[1]

$$\gamma(r)\xrightarrow[r\to 0]{}1-\frac{1}{4}\,\frac{1}{\phi(1-\phi)}\,\frac{V_b(r)}{V}, \qquad (2)$$

where ϕ is the volume fraction of material (assumed to have a sharp interface) and V is the volume under consideration. Equation (2) holds when r is much less than the characteristic particle or feature size in the material but not necessarily smaller than features on the surface. $V_b(r)$ is the volume of material within a distance r of the interface, i.e., the material inside "Minkowski" spheres of radius r centered at every point on the interface. Bale and Schmidt realized that $V_b(r)=rS(r)$, leading to the celebrated formula for the large-q asymptote of the scattered intensity[7]

$$\begin{aligned}I(q)&=I_0V(\Delta\rho)^2\phi(1-\phi)\int_0^\infty\gamma(r)\frac{\sin(qr)}{qr}r\pi r^2dr\\&\xrightarrow[q\to\infty]{}A(D)q^{D-6}+\cdots, \qquad (3)\end{aligned}$$

where I_0 is a constant determined by the incident intensity, usually so that I has the units cm^{-1}, $\Delta\rho$ is the electron (SAXS) or neutron scattering length (SANS) density difference between the two media, and the amplitude

$A(D)$ is

$$A(D)=\pi I_0(\Delta\rho)^2 S_x \Gamma(5-D)\sin[(3-D)\pi/2]\,. \qquad (4)$$

Wong and Bray[6] recently suggested that V_b must be found by integrating volume elements of the form $\partial V_b = S(r)\partial r$ to finite r, yielding a correction $A(D) \rightarrow A(D)/(3-D)$. Without the "$(3-D)$" correction in the denominator, the leading term in the scattered intensity vanishes in the limit $D \rightarrow 3$, in disagreement with published data.[9] However, Pfeifer and Schmidt[10] have argued that the scattered intensity can indeed vanish in cases where the space-filling limit $D \rightarrow 3$ involves vanishing pores.

In this paper, we test the Bale-Schmidt and Wong-Bray amplitudes by comparing scattering and adsorption surface areas. In adsorption studies, if $n(r)$ is the number of moles of adsorbed gas at monolayer coverage, with molecular area r^2, and the monolayer volume is $V_b = rS(r)$ (that is, without the $(3-D)$ correction[4]), then the specific surface area is $\sigma(r) = n(r)r^2$. Thus, a comparison of scattering and adsorption data from the same sample should test the validity of the $(3-D)$ correction as long as the sample has negligible closed porosity, which is inaccessible to adsorbates.

As an alternative to the absolute intensity formulas, or lacking an absolute calibration for the incident intensity, the scattering can be normalized to the total scattered intensity,[1] $Q=\int_0^\infty q^2 I(q)dq = 2\pi^2 I_0(\Delta\rho)^2 V\phi(1-\phi)$; thus, from Eqs. (3) and (4) we have[11] for σ_x,

$$\sigma_x = \frac{\lim(q^{6-D}I)}{\pi F(D)\Delta\rho^2\rho_0} = 2\pi\frac{\phi(1-\phi)}{\rho_0 F(D)}\,\frac{\lim(q^{6-D}I)}{Q}\,, \qquad (5)$$

where lim( ) denotes the largest-q limit, and $F(D) = \Gamma(5-D)\sin[(3-D)\pi/2]$ or $F(D)/(3-D)$ in the Bale-Schmidt or Wong-Bray formulas, respectively. In this study, we relied on absolute intensity calibration to determine $I(q)$. We used Q to check the material density ρ_m via $\Delta\rho$ when Q could be estimated to $\pm 20\%$ (requiring good representation of both high- and low-q regimes). From the known packing density of the sample, ϕ could then be found.

The fumed silica [Cab-O-Sil (Ref. 12)] samples, in various grades that differ in specific surface area, consist of primary particles ($\simeq 10^2$ Å) fused together into large aggregates ($\simeq 1$ μm).[13] Previous studies have suggested that the variation in surface area is due partly to surface roughness;[13,14] EH-5 is the roughest grade ($D \approx 2.6$) and the highest in area whereas L90D is smooth ($D = 2.0$) and lowest in area. Three other silica samples were derived from EH-5 by heat treatment at 950 ± 50 C for 180, 330, and 425 (± 5) min. With longer heat treatment, the surfaces are smoother,[11] satisfying $\sigma(r) = \sigma_0(r/r_0)^{D-2}$, where $r_0 = 18.4$ Å and $\sigma_0 = 170$ m^{2}g^{-1}, for $q > 0.05$ Å^{-1}.

Ten carbon samples[15] were also studied ranging in surface area from 10 (coal, graphite) to over 1000 m^{2}g^{-1} (carbon black) as determined by nitrogen BET. Carbon blacks consist of aggregated spherical particles[16] much like fumed silica, whereas the other carbon samples were angular chips of material.

For scattering studies, the dry powders were loosely packed at density ρ_0 in cells of known path length. X-ray scattering was performed at Oak Ridge National Laboratory using graphite as a (secondary) standard for intensity calibration. Neutron scattering was done at Argonne National Laboratory for the silica samples and at Oak Ridge National Laboratory for the carbon samples. The intensity was calibrated against (primary) standards of water and aluminum (Al-4).[5] Relative intensity SANS was done at Los Alamos National Laboratory on the L90D silica to establish that it has smooth surfaces for an adsorption standard.[14] The constants D and $\lim(q^{6-D}I)$ were determined by plotting $q^{6-D}I$ against q in the range $0.02 < q < 0.3$ Å^{-1}, then the prefactor σ_x was found using Eq. (5). Representative scattering data are shown in Fig. 1(a).

After checking the material density ρ_m by calculating $\Delta\rho$ from Q, we found that many of the carbons appeared significantly less dense than crystalline graphite by both SAXS and SANS, probably due to microporosity;[16] for these, we used the densities derived from SANS listed in Table I.

Three sets of gas adsorption studies were conducted: The silica was studied at the University of New Mexico (set I), and the carbon was studied at both Sandia National Laboratories (set II) and Laboratoires de Mar-

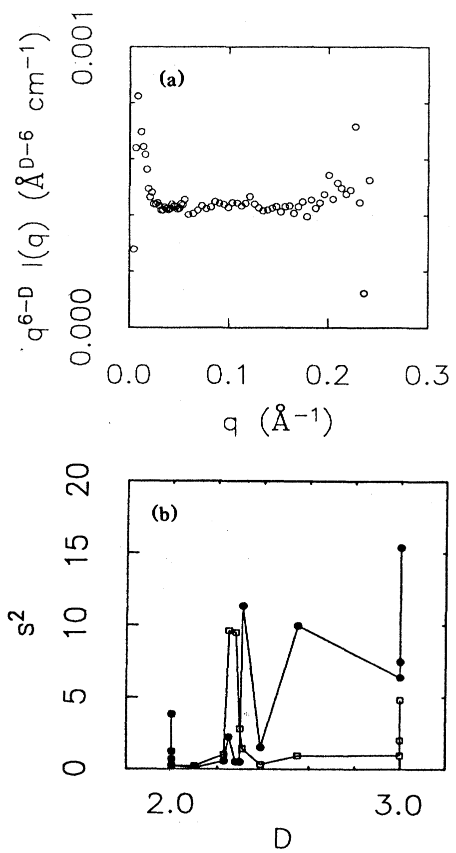

FIG. 1. (a) Neutron scattering data from YS carbon black ($D = 2.7$). (b) Comparison of Wong-Bray (open squares) and Bale-Schmidt (solid circles) scattering theories for surface areas using squared relative errors, $s^2 = (\sigma_{\text{SANS}} - \sigma_{\text{BET}})^2/(\delta\sigma)^2$.

TABLE I. Absolute intensity scattering data and specific surface areas. The carbon densities ρ_m were determined from total scattered neutron intensity where possible. Areas σ are given for nitrogen BET adsorption, SANS, and SAXS according to the Wong-Bray (WB) and Bale-Schmidt (BS) formulas.

	D		σ_x ($\mathrm{m}^D\mathrm{g}^{-1}$)			$\sigma \pm \delta\sigma$ ($\mathrm{m}^2\mathrm{g}^{-1}$)		
Sample	SAXS	SANS	SAXS	SANS	ρ_m ($\mathrm{g\ cm}^{-3}$)	BET	SANS (WB,BS)	SAXS (WB,BS)
M-5		2.10		2.45×10^{1}	2.20	200 ± 20	213, 192 ±15%	
HS-5[a]		2.23		2.78	2.20	350 ± 35	403, 310 ±15%	
EH-5-0		2.55		3.01×10^{-3}	2.20	385 ± 39	442, 199 ±15%	
EH-5-180		2.30		4.45×10^{-1}	2.20	231 ± 23	293, 205 ±15%	
EH-5-330		2.28		7.52×10^{-1}	2.20	204 ± 20	321, 231 ±15%	
EH-5-425		2.00		1.69×10^{2}	2.20	172 ± 17	169, 169 ±15%	
Monarch 1100	2.26	2.25	1.10	2.45	1.17	282 ± 60	546, 410 ±15%	245, 181 ±20%
Pittsburgh coal	3.00	3.00	1.71×10^{-7}	7.13×10^{-7}	0.615	537 ± 200	744, 0 ±15%	425, 0 ±59%
Super Carbovar	2.22	2.31	3.22	4.46×10^{-1}	1.65	426 ± 37	364, 251 ±16%	376, 293 ±27%
BRX	3.00	3.00	4.14×10^{-7}	6.75×10^{-7}	0.394	929 ± 300	1675, 0 ±13%	1030, 0 ±29%
Sterling MT	2.35	2.00	2.14×10^{-3}	1.50×10^{1}	2.20	8.4 ± 3.0	15, 15 ±25%	4.2, 2.7 ±40%
Vulcan 6	2.42	2.00	8.53×10^{-3}	1.45×10^{2}	1.76	126 ± 23	145, 145 ±12%	75, 44 ±27%
Graphite 2 μm	2.15	2.00	1.77×10^{-1}	1.63×10^{1}	2.20	11.6 ± 4.0	16.3, 16.3 ±19%	13, 11 ±26%
YS	2.70	3.00	4.91×10^{-5}	1.62×10^{-8}	2.15	63 ± 15	40.2, 0 ±38%	185, 52 ±43%
Black Pearls	2.43	2.39	1.55×10^{-2}	1.23×10^{-1}	2.20	498 ± 110	567, 346 ±36%	86, 49 ±43%
Vulcan 3		2.00		1.28×10^{2}	1.68	115 ± 23	128, 128 ±13%	
± (typical)	±0.15	±0.15			±0.10			

[a] Data taken from Ref. 11, relative intensity used.

coussis (set III). The silicas were outgassed at 373 K and 50 μm Hg for 1 h, and various gases were adsorbed at relative pressures up to 30%. Nitrogen, argon, and krypton were run at 77 K, and *n*-pentane, hexane, and heptane were run at 293 K. For each gas, the molecular cross-sectional area was measured on the *smooth* L90D standard, thereby avoiding misleading calibrations due to roughness. The nitrogen cross-sectional area[8] was taken as 0.162 nm^2, and the areas for all other gases were calculated[14] using the resulting standard area for L90D (Table II). The carbon samples in sets II and III were treated in similar manner, but only nitrogen was used. Agreement between sets was within 30% except for samples BRX and Pittsburgh Coal, owing apparently to a slow approach to full monolayer coverage because of microporosity. The uncertainties $\delta\sigma$ in average area (Table I) reflect variation between sets.

To compare the scattering and adsorption surface areas, we evaluated the scattering function $\sigma(r)$ in Eq. (1) at the resolution appropriate to the molecular adsorbate. The size for nitrogen, for instance, was taken to be $r^2 = 0.162$ nm^2. The agreement between scattering and adsorption is illustrated in Fig. 1(b), which shows the squared residuals divided by the squared uncertainties, $s^2 = (\sigma_{\mathrm{SANS}} - \sigma_{\mathrm{BET}})^2/(\delta\sigma)^2$, as a function of D. These uncertainties reflect *identifiable* errors in the data collection (such as counting statistics) and analysis (such as error in r). Clearly, not all sources of error have been identified since there remain significant disagreements between SAXS and SANS data. In two of the carbon blacks, for example, D differs by more than the typical error (±0.15), in spite of repeated experiments to resolve the conflict. Differences in σ_x are largely artificial due to its D-dependent units. Although these artificial differences are resolved after evaluating $\sigma(r)$, there remains experimental uncertainty not entirely accounted for, mainly in the SAXS.

The comparison of scattering theories is most rigorously tested by the samples with large fractal dimensions. To make a meaningful comparison, we used the standard[17] "F test" on ratios of $\chi^2 = \sum_i s_i^2$ calculated for the Bale-Schmidt (χ_1^2) and Wong-Bray (χ_2^2) formulas. For the roughest samples with $D > 2.3$, $F = \chi_1^2/\chi_2^2 = 11.6/1.75 = 6.6$ (SANS, 6 samples) indicating a 98% likelihood that the Wong-Bray formula is more appropriate for our samples. The comparison is less conclusive for the SAXS

TABLE II. Molecular areas determined by (1) calibration to a known smooth silica substrate (L90D Cab-O-Sil), (2) literature average (Ref. 8), and (3) SANS.

	Molecular cross-sectional area (nm^2)					
	N_2	Ar	Kr	Pentane	Hexane	Heptane
(1)	0.162	0.134	0.211	0.501	0.607	0.709
(2)	0.162	0.142	0.202	0.492	0.562	0.639
(3)	0.188	0.178	0.209	0.432	0.568	0.861
	±0.034	0.030	±0.023	±0.072	±0.076	±0.144

data, $F = 5.0/1.9 = 2.6$ (9 carbon samples) or 90% likelihood in favor of the Wong-Bray correction.

Closed porosity is evident as systematically smaller BET areas than the Wong-Bray SANS areas, as seen in Table I and Fig. 2. The SAXS values show no such trend; however, since these rely on a secondary intensity standard unlike the primary standard of the SANS, we expect larger, and possibly systematic, errors. On the whole, the basic scattering theory equation (3) works gratifyingly well if the "$3-D$" correction is applied.

Another way of interpreting our data is to compare the molecular cross-sectional areas r^2 derived from scattering and adsorption (Table II). From Eq. (1) and $\sigma = nr^2$, the scattering molecular area is $r^2 = (\sigma_x/n)^{2/D}$. We used σ_x from SANS on the silica samples. The largest deviation in the scattering values is for heptane, which is also the largest and most linear molecule. The scattering values from rougher samples gave larger areas for the linear molecules, indicative of an alignment effect on smooth surfaces.

In summary, we have shown that scattering measurements from fractally rough powders agree well with adsorption measurements when the Wong and Bray[6] correction is used with the Bale and Schmidt[7] formula. Pfeifer[18] has pointed out that the $3-D$ correction accounts for the difference in the surface neighborhood volume V_b measured by scattering, which probes many lengths at once, and the adsorbed monolayer volume $rS(r)$, the difference being small pores not accessible to the adsorbate molecules. It is possible[10] to realize the $D=3$ limit by the proliferation of these small pores either at the expense of large ones (total area fixed) or not (total area increasing). Since the former limit implies zero scattering intensity as in the Bale-Schmidt formula, we conclude that our samples fall into the latter category. Finally, the success of Eq. (1) to describe the scaling of the surface area down to $r \simeq 4$ Å is not *a priori* justified by the scattering data, even though power-law scattering holds in all samples to $q \simeq 1/(4\ \text{Å})$, because the data are typically noisy in this regime. Indeed, the asymptotic behavior, Eq. (3), and all related measured scattering quantities were usually established by wave vectors corresponding to $r \simeq 20$ Å. The final justification of Eq. (1) for both scattering and adsorption is that it appears to work; this is well known, of course, for smooth, Porod scatterers[2] and we have demonstrated it for fractal surfaces as well.

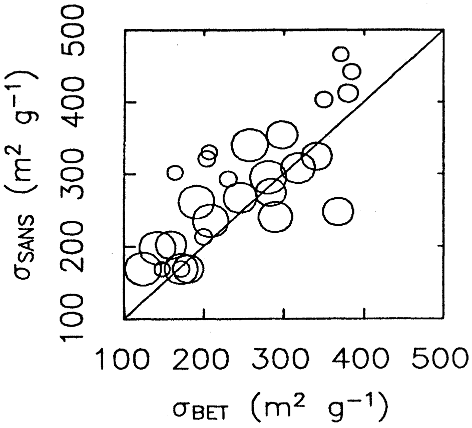

FIG. 2. Correlation of surface areas by scattering and adsorption for six different adsorbates. The area of the circle is proportional to the molecular area from L90D calibration (Table II). The $3-D$ correction was applied to the SANS, yielding a correlation coefficient of 0.8 (1.0 is perfect correlation).

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