

Elasticity of a percolation system: silica smoke

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Cab-O-Sil powder is a cluster aggregate of silica spheres formed from silica smoke. The fractal dimension of clusters of 14 nm diameter spheres is determined to be $\bar{d} = 1.71 \pm 0.05$, in good agreement with that calculated for the cluster-aggregate model, $\bar{d} = 1.75$. Measurements of Young's modulus (Y) of packed 7 nm Cab-O-Sil powder, with an occupied volume fraction in the range $0.035 < f < 0.3$, are well described by the percolation threshold $f_c = 0.017 \pm 0.002$ and an elasticity exponent $\tau = 2.9 \pm 0.2$. The measured exponent is larger than the calculated scalar Born (balls and springs) result, $\tau = 2.0$, but smaller than the more realistic bond-bending result, $\tau > 3.55$. The measured result is attributed to bond bending within a complex percolation structure.

La poudre Cab-O-Sil est un agrégat d'amas de sphères de silice formé à partir de fumé de silice. La dimension fractale d'amas de sphères de 14 nm de diamètre a été déterminée comme étant $\bar{d} = 1,71 \pm 0,05$, en bon accord avec la valeur calculée pour le modèle d'agrégat d'amas, $\bar{d} = 1,75$. Des mesures du module de Young (Y) de poudre Cab-O-Sil de 7 nm compacte sont bien décrites par le seuil de percolation $f_c = 0,017 \pm 0,002$ et un exposant d'élasticité $\tau = 2,9 \pm 0,2$. La valeur mesurée de l'exposant est plus grande que le résultat Born scalaire (balles et ressorts) calculé, $\tau = 2,0$, mais plus petite que le résultat plus réaliste de flexion de liaison, $\tau > 3,55$. Le résultat mesuré est attribué à la flexion des liaisons à l'intérieur d'une structure de percolation complexe.

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1. Introduction

Aggregated small particles have been used to study percolation (1) and fractal structures (2). The aggregation can be formed from colloidal deposition (3), supercritical drying of colloids (aerogels) (4), condensed smoke (5), composite formation (6), or sintering of metal powder (7). Experimental techniques have included analysis of electron microscope pictures (5, 8), small-angle scattering of X-rays (3) and neutrons (9), light scattering (3), measurements of electrical (6) and thermal conductivity (4, 10), heat capacity (10), ultrasonic velocity and attenuation (4, 11), current noise (12), dielectric constant (6), optical properties (6), pore-size distribution (4), and time-resolved fluorescence decay (13).

These experiments have shown percolation behaviour with percolation thresholds in the range $0.01 < f_c < 0.26$, where f_c is the threshold value of the occupied volume fraction, f , and fractal dimensionalities for the aggregates in the range $1.55 < \bar{d} < 2.6$. These are to be compared with $f_c \sim 0.16$ for lattice-based site percolation models (1) and fractal dimensionalities of 1.75 and 2.5 for cluster aggregation (14) and diffusion-limited aggregation respectively (15).

One interesting question, concerning the universality of elasticity and conductivity of a percolation system above threshold (16), was addressed by measuring the two properties for a series of packed and sintered submicrometre silver-powder beams (7). The result, in agreement with an earlier experiment on a two-dimensional (2D) system (17), was that the elasticity exponent was significantly larger than the conductivity exponent. In detail, if the elasticity (Young's modulus) and conductivity are expressed as,

$$[1] \quad Y \propto (f - f_c)^\tau, \quad \sigma \propto (f - f_c)^t$$

then it was found that $f_c = 0.06$, $\tau = 3.8 \pm 0.5$, and $t = 2.15 \pm 0.25$. Subsequent experiments on copper-plastic and carbon-Teflon composites found $t = 2.15 \pm 0.25$ and

1.85 ± 0.25 (19) respectively. These conductivity exponents overlapped the best theoretical estimate for the exponent, $t = 2.0$ (1). The elasticity exponent is in agreement with the result predicted by the bond-bending model of elasticity of the three-dimensional (3D) lattice-based bond percolation model (20); that is, the elasticity is determined not by the stretching of the bonds but rather by the change of angle between neighbouring bonds at a lattice site.

There are good reasons to study the elasticity and other properties of *insulating* aggregates near percolation. In particular, there is interest in the dynamical modes of an aggregate and their relation to the structure and elasticity. Specific-heat and thermal-conductivity measurements can probe these modes but only in an insulating aggregate. In a metallic system, the electrons determine these properties. Furthermore, far above the percolation threshold, Pohl and Tait have measured interesting specific-heat and thermal-conductivity anomalies in compressed silica and alumina powder (10). Therefore, this study is aimed at investigating the structure and elasticity of aggregated silica powder. The material chosen is Cab-O-Sil³ because of its properties and availability. After completion of this work, a report on similar measurements with silica aerogel was published (21).

2. Cab-O-Sil powder

Cab-O-Sil is formed by the hydrolysis of SiCl_4 in a hydrogen-oxygen flame. The molten spheres of silica that are formed collide and aggregate. The resultant material has a light, fluffy form with an occupied volume fraction, as received, of $f = 0.02$ or a density of $\sim 40 \text{ g} \cdot \text{L}^{-1}$. The size of the spheres can be varied by the production process, from 7 nm to 24 nm. Figure 1 is a scanning electron micrograph of a few Cab-O-Sil clusters showing the aggregated-spheres structure. Several years ago, Forrest and Witten (5) analyzed an electron micrograph of a large Cab-O-Sil cluster and determined a fractal dimension of $1.55 < \bar{d} < 1.85$. This measured

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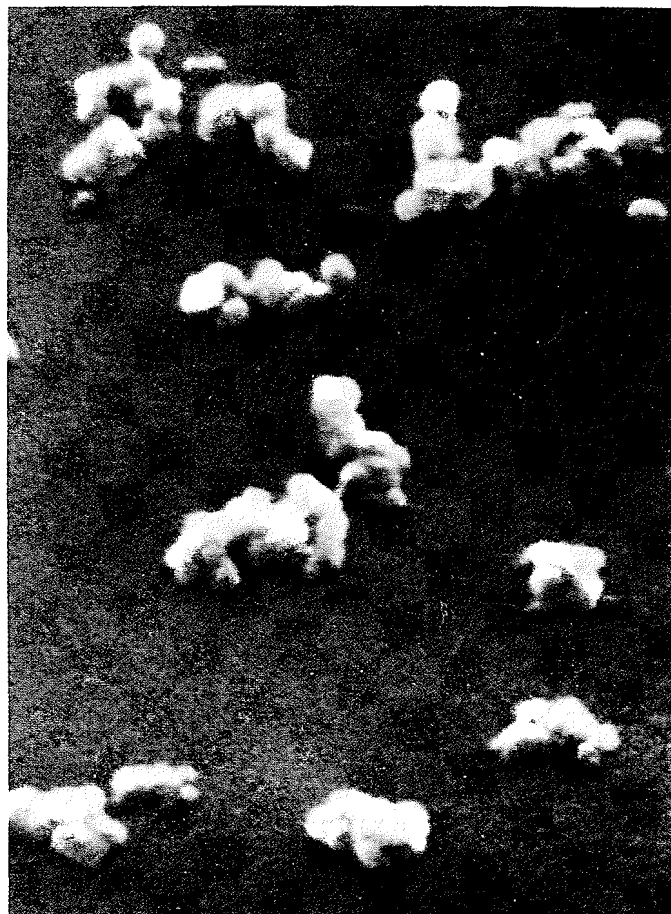


FIG. 1. Electron micrograph of gold-shadowed Cab-O-Sil powder showing the sphericity of the individual particles that have fused into the aggregates (from CAB-O-SIL® properties and functions, CAB-O-SIL Division, Cabot Corporation).

value is consistent with the theoretical cluster-aggregation result, $\bar{d} = 1.75$ (15).

3. Experimental method and results

For this study, we reinvestigated, with a different method, the fractal structure of Cab-O-Sil clusters and then measured the elasticity of beams of packed Cab-O-Sil powder.

3.1 Fractal dimension

The determination of the fractal nature of Cab-O-Sil clusters was made relatively simple by the inclusion of an electron micrograph of about 30 clusters in the brochure accompanying the powder, and by the publication of a paper describing a method for determining fractal dimensionality of 3D clusters from 2D images (8). The method is based upon a theorem, due to Mandelbrot (2), that the fractal dimension of a 3D cluster remains unchanged upon projection onto a 2D plane provided $\bar{d} \leq 2$. Therefore, $M \propto L^{\bar{d}}$ is replaced by $A \propto L^{\bar{d}}$, where L is the linear dimension of the cluster, M is the mass and A is the projected area. The linear dimension of the cluster was taken as the geometric mean of the largest linear dimension and the perpendicular linear dimension. The projected area was measured with a mechanical planimeter. Figure 2 is the electron micrograph of the ~ 30 clusters of 14 nm silica spheres. Figure 3 is a graph of projected area versus mean linear dimension for all of the clusters shown in Fig. 2. Very good scaling behaviour was obtained for almost two orders of magnitude

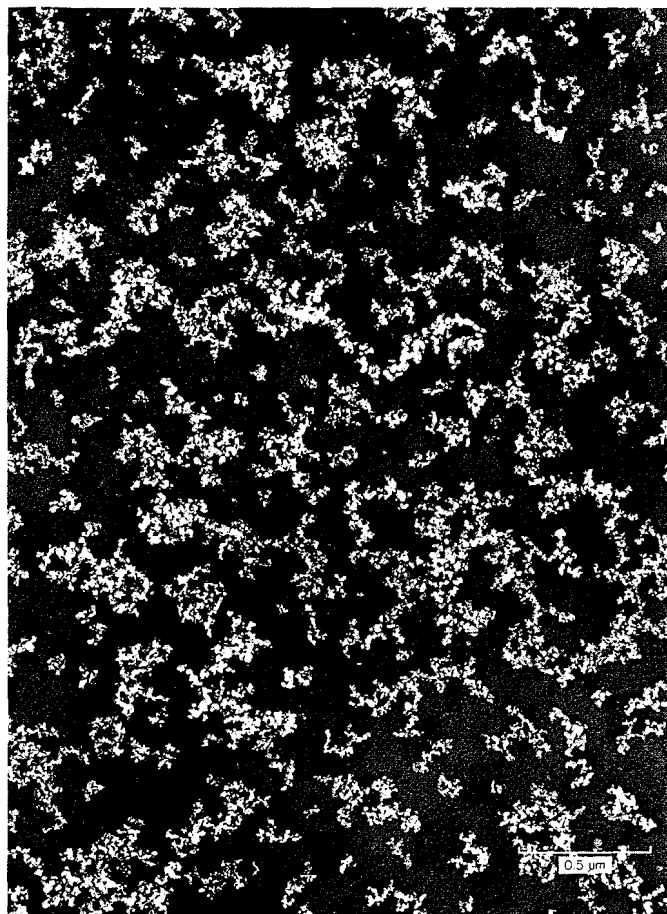


FIG. 2. Electron micrograph of the M-5 Cab-O-Sil (14 nm diameter) aggregates that were used for the analysis of the fractal dimensionality (from CAB-O-SIL® properties and functions, CAB-O-SIL Division, Cabot Corporation).

variation in the linear dimension. A least squares fit to the data gave $\bar{d} = 1.71 \pm 0.05$, in good agreement with the cluster-aggregation model (15) and with the earlier Forrest and Witten result. However, the result differs from that found for silica aerogel, where fractal structure over only a decade in linear dimension ($\sim 1-10$ nm) and $\bar{d} \sim 2$ were observed (22). Differences in growth behaviour could account for the different results (23).

3.2. Young's modulus

Young's modulus of elasticity was measured by a beam-bending technique (7, 24). The Cab-O-Sil beams, 35 mm long \times 5 mm wide, were formed by pressing the Cab-O-Sil powder into demountable molds. Only one pressing per beam was used to avoid any layering effect or variable density across the height of the beam. Beams in the range $0.035 < f < 0.3$ were produced. The beam thickness varied from 2 mm for large values of f to 5 mm for small values of f . No sintering was required to achieve well-formed beams, although it was necessary to disassemble the mold from around the beam to prevent breakage. In fact, sintering at 900°C had almost no effect on the strength of the beams, except for cracking if the temperature was increased too quickly.

The beams were supported a few millimetres from each end and loaded in the centre by adding weights with a small manipulator. Plots of deformation of the centre of the beam versus load for loading and unloading were made. It was necessary to

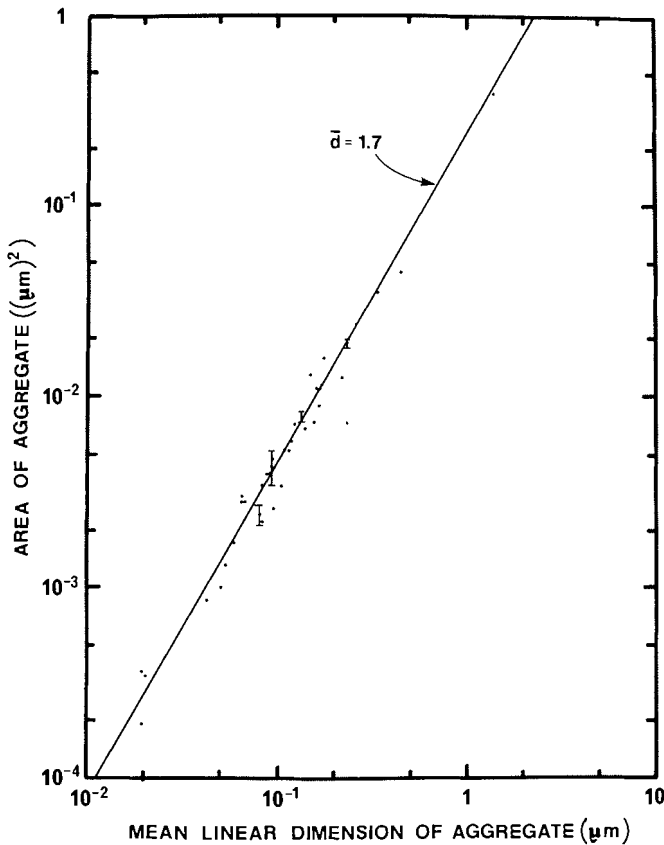


FIG. 3. Plot of area of a Cab-O-Sil aggregate as a function of the mean length of the aggregate for each of the aggregates shown in Fig. 2. The mean length (L) was defined as the geometric mean of the longest length and the length perpendicular to it. The best fit was given by $A \propto L^{\bar{d}}$ with $\bar{d} = 1.71 \pm 0.05$.

keep the load within the load limit, which corresponded to a deformation of about 10% of the beam height or a longitudinal strain of $\sim 1\%$. The slope of each plot was converted to Young's modulus (24). The uncertainty of each measurement of Young's modulus ($\sim \pm 10\%$) reflected the scatter in the deformation-load plots and the difference in the slopes for loading and unloading.

Young's modulus was fitted to the expression

$$Y = a(f - f_c)^\tau$$

by least squares fitting of the equation

$$\ln Y = \ln a + \tau \ln(f - f_c)$$

for a series of trial values of f_c . Figure 4 shows the values of χ^2 and τ as a function of the trial value of f_c . The best fit was for $f_c = 0.017$, and the χ^2 value of 0.994 was close to the value of 1 expected for a good fit. The exponent τ for this f_c value was 2.9. The assignment of uncertainty was not easy for this process, but we took $f_c = 0.017 \pm 0.002$ and $\tau = 2.9 \pm 0.2$. Figure 5 is a log-log plot of Y as a function of $(f - f_c)$ with $f_c = 0.017$, and the line through the data has a slope of 2.9.

The large surface area and hydrophilic character of the surface cause moisture adsorption by Cab-O-Sil. For instance, at 50% relative humidity, the equilibrium moisture pickup is about 8% by weight. Therefore, for each measurement of Young's modulus, the beam was made and measured on the same day and the relative humidity was recorded. There was no correlation of the deviations of the measured Young's modulus

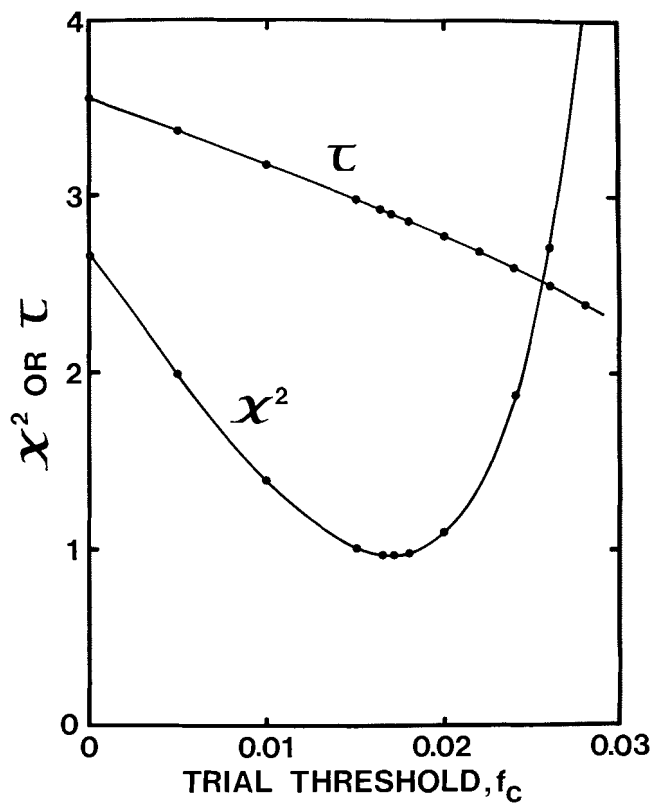


FIG. 4. The result of fitting the measured Young's modulus to the equation $\log Y = \text{constant} + \log(f - f_c)$, where f_c was a variable trial parameter. The upper curve shows the variation of τ with the parameter f_c . The lower curve is the result of the χ^2 test and shows a clear minimum (~ 1 as expected) for $f_c = 0.017$.

from the fitted curve with the relative humidity.

Cab-O-Sil starts to sinter at 800°C . Several samples were sintered at 900°C . This caused the beams to shrink about 2% in the linear dimension and to lose about 4% by weight, presumably due to the loss of moisture. On average, Young's modulus increased by about 10%, while the exponent τ remained unchanged. There was, however, significantly more scatter in the results.

4. Discussion

Figure 3 shows that the Cab-O-Sil clusters are fractal structures with a density that decreases with increases in cluster size. The fractal dimension $\bar{d} = 1.71 \pm 0.05$ is in good agreement with the theoretical value $\bar{d} = 1.75$ for cluster aggregation. This is perhaps no surprise, because the clusters are formed by just such a cluster-aggregation process from the condensation of the fumed silica. However, the Cab-O-Sil beams are not fractal structures, because above the percolation threshold, the percolation clusters scale with the Euclidian dimension rather than a fractal dimension.⁴

The value of the percolation threshold, $f_c = 0.017$, of the Cab-O-Sil beams supports this. Lattice-based site percolation models give a percolation threshold value of occupied volume fraction of ~ 0.16 . We can consider the beams as being made of a random packing of Cab-O-Sil clusters. Then, the percolation threshold occurs when the cluster packing reaches ~ 0.16 by volume. However, because the occupied volume fraction of

⁴See Chap. 3 of ref. 1.

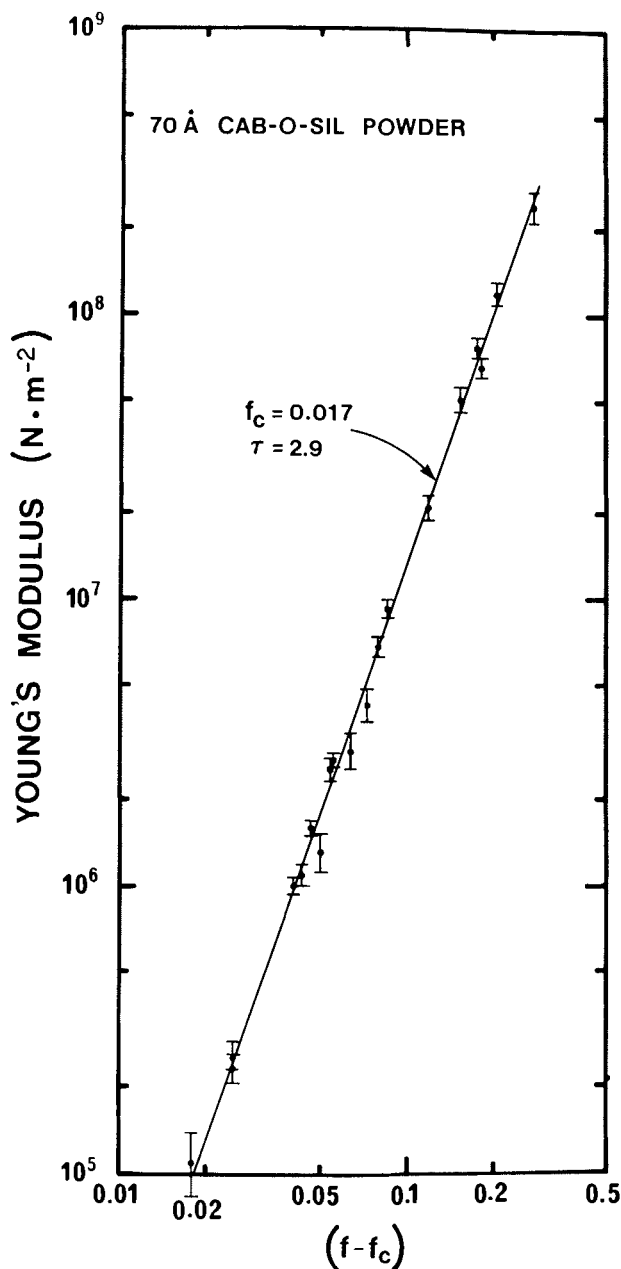


FIG. 5. A log-log plot of the measured Young's modulus as a function of $(f - f_c)$ with $f_c = 0.017$. The solid line has a slope of $\tau = 2.9$ and corresponds to the best fit illustrated in Fig. 4.

each cluster is low, the threshold occurs when the Cab-O-Sil packing is much less than 0.16 by volume. The ratio of measured to theoretical thresholds is a measure of the occupied volume fraction of the average Cab-O-Sil clusters, ~ 0.1 in this case. The occupied volume fraction of a fractal structure varies with the size of the structure as

$$\frac{M/M_0}{V/V_0} \sim \frac{(L/L_0)^{\bar{d}}}{(L/L_0)^3} \sim \left(\frac{L}{L_0}\right)^{\bar{d}-3}$$

where M , V , and L are the mass, total volume, and size of the structure, and M_0 , V_0 , and L_0 are the mass, volume, and size of the individual particles making up the structure. In the present case, the occupied volume fraction of the Cab-O-Sil clusters is ~ 0.1 and $\bar{d} = 1.7$; therefore, $(L/L_0)^{-1.3} \sim 0.1$ or $L \sim 6 L_0$. For the 140 Å particles used for the fractal analysis,

$L \sim 10^{-1} \mu\text{m}$ and agrees very well with the median cluster size shown in Fig. 3. In this regard, the Cab-O-Sil beams are probably similar to the silica aerogel (22) and colloidal silica (23), with fractal structure up to a length of ~ 10 particle diameters and Euclidian structure beyond that.⁵ The different fractal dimensions merely reflect the different growth processes.

This structure of the Cab-O-Sil and silica aerogel must be responsible for the elasticity exponent $\tau = 2.9 \pm 0.2$, which is significantly larger than the conductivity, or scalar Born elasticity model, exponent $t = 2.0$, but which is also significantly smaller than the minimum exponent $\tau = 3.55$ of the bond-bending elasticity model. Gronauer *et al.* (21) have measured Young's modulus for a series of silica-aerogel samples in the range $0.032 < f < 0.12$. By forcing a fit to the Young's modulus of bulk silica, the best fit to the results corresponds to an elasticity exponent $\tau = 3.7$. However, if only the aerogel results are fitted, $\tau = 2.9$ gives a much better representation of the data.⁶ Recent theoretical work on the application of the bond-bending model of elasticity to *continuum* percolation systems shows that the elasticity exponent should be significantly larger than for lattice-based percolation systems (27); it is, therefore, unlikely that the exponent 2.9 arises from continuum effects. One possible origin of the exponent is that within the "nodes, links, blobs" picture of percolation (28), with the nodes being occupied lattice sites, the links being connections between the nodes, and the blobs being regions encompassing multiple connectivity and dangling bonds, the nodes of the silica systems are fractal clusters rather than single particles.

Another perhaps more likely possibility is that the attractive force between a significant number of neighbouring clusters is predominantly a central force; that is, some pairs of the clusters can freely rotate about their point of contact (29). This is unlike the case of the sintered metal powder, where a definite bond between particles is formed by surface diffusion during the sintering procedure. In such a case of a mixture of central forces and bond-bending forces, an elasticity exponent between the Born and bond-bending limits would not be unexpected.

A final comment concerns the dynamics of Cab-O-Sil. Several years ago, a measurement of the specific heat of pressed 7 nm Cab-O-Sil ($f \sim 0.5$) (10) showed an anomalous specific heat that was linear in temperature and an order of magnitude larger than the well-known low-temperature linear specific-heat capacity of amorphous solids (30). Rutherford *et al.* (31) postulated localized vibrational modes for a packed powder, spread over a frequency range with a constant density of states, to explain millikelvin Kapitza resistance measurement. As evidence for these modes, they showed that the calculated specific heat for the packed Cab-O-Sil powder had the same temperature dependence as the measured specific-heat anomaly and was within a factor of two in numerical agreement. Since that time, it has been found that packed powders

⁵This does not mean that the beams are homogeneous on a length scale larger than 10 particle diameters. Homogeneity sets in only beyond the correlation length ξ , or the size of the largest pore. This length scales with occupied volume fraction as $(f - f_c)^{-\nu}$ with $\nu \sim 0.9$ (1, 25).

⁶It is worth noting that the line shown in Fig. 5 extrapolates to $1 \times 10^{11} \text{ N}\cdot\text{m}^{-2}$ at $f = 1$, which is considerably smaller than Young's modulus of bulk silica ($7 \times 10^{11} \text{ N}\cdot\text{m}^{-2}$) (26). Similarly, the extrapolation of the sintered silver-powder modulus (7) to bulk silver gives a Young's modulus of 25% of the measured bulk-silver value. It is not known if these observations are significant, because the percolation models are applicable only close to the percolation threshold.

can be described by percolation theory, and theory has been extended to include dynamical effects. If the elasticity of the percolation system is described by the scalar Born (balls and springs) model, then the Alexander–Orbach conjecture (32) is that the density of vibrational modes varies as $\nu^{1/3}$. On the other hand, if the elasticity is described by the more realistic bond-bending model, then the density of vibrational modes varies as $\nu^{-0.1}$ (33). The elasticity exponent $\tau = 2.9$ for Cab-O-Sil suggests some form of bond-bending elasticity and therefore the postulate of Rutherford *et al.* of a frequency-independent density of modes has received a striking confirmation.

5. Conclusions

Cab-O-Sil is an aggregated form of small silica spheres. The individual clusters show fractal dimensionality over almost two orders of magnitude in linear dimension with $d = 1.71 \pm 0.05$. This is in good agreement with the cluster-aggregation growth model. Beams of pressed Cab-O-Sil powder behave according to percolation theory with a percolation-threshold occupied volume fraction $f_c = 0.017 \pm 0.002$ and an elasticity exponent $\tau = 2.9 \pm 0.2$. The exponent is larger than that calculated for the scalar Born model ($\tau = 2.0$) but is smaller than the lower limit of the bond-bending model ($\tau = 3.55$). The low percolation threshold is attributed to the fractal aggregate character of the powder. The similar low percolation threshold and elasticity behaviour for pressed Cab-O-Sil powder and silica aerogel suggest that they have very similar form; fractal structure up to about 10 particle diameters, percolation structure up to the correlation length, and homogeneity beyond that. The correlation length is not yet known.

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