Scaling Approach to Sintering of Fractal Matter

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A simple model for the sintering of materials made of connected fractal aggregates, such as aerogels, is proposed. The densification at small scales is described by an increase of the lower cutoff length accompanied by a decrease of the upper cutoff length, in order to conserve the total mass of the system. General scaling laws are derived which relate the structural characteristics to the mean bulk density. The theory explains quite satisfactorily a large number of experiments on gradually densified silica aerogels.

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Sintering is of major importance in materials science and technology since it is widely used as a strengthening process in the fabrication of common materials such as metals, glasses, ceramics, etc. It generally proceeds by heating, sometimes with the aid of pressure. Starting from a sample generally made of an assembly of fine particles, sintering produces internal toughening by gradually decreasing the total surface energy with rising temperature [1]. In the solid state, this decrease of energy may be indicated either by a change in whole surface of the material or by a change in the nature of the interface interactions. Sintering can be due to different kinds of mass transfers: evaporation/deposition, surface diffusion, viscous flow of matter, etc., but, in the case of glasses and gels, sintering is essentially due to viscous flow of matter and it is accompanied by a shrinkage of the sample; hence the material densifies.

Several theoretical models have been proposed to describe the shrinkage rate as a function of time [1-5]. The old theory of Frenkel [2], which considers couples of tangent spheres, can only explain the first few percent of shrinkage. The model of Mackenzie and Shuttleworth [3], which considers a medium consisting of closed pores of identical sizes, applies well to the last stages of sintering. More recent theories by Scherer, which consider cylinders [4] or other geometrical shapes [5], are more convincing since they intend to cover the full range of densities and have been successfully applied to glass sintering. However, these theories, due to their geometrical restrictions, are sometimes hard to extend to complex disordered structures.

Fortunately, several low-density materials, such as aerogels, exhibit very interesting scaling invariance. They are probably the best example of fractal geometry [6] in materials science, as demonstrated by their dynamical [7] and structural [8] properties. We now believe that they are made of connected fractal aggregates or "blobs" that have been grown by cluster-cluster aggregation [9]. Scaling occurs in a range of length scales extending from the mean size a of the subunits (of which the aggregates are made) up to the mean connecting distance ξ between the aggregates.

In this Letter, we present a novel theoretical approach to sintering which is intended to model the densification of aerogels. This approach has the advantage of being general in the sense that only global symmetries of scale invariance and mass conservation are used. Therefore the model can ignore the detailed characteristics of the material such as surface energy, viscosity, etc. Furthermore, it does not require knowledge of the densification rate. With respect to these features, our approach appears to be more general than the previous ones. The main approximation is that the blob picture remains valid and that its general topology is not destroyed during the densification process. As a result of our scaling approach, the fractal dimension of the blobs remains unchanged but the smaller and the larger cutoffs a and ξ vary in opposite directions and tend to each other; the extension of the fractal regime is thus gradually reduced during sintering. Several scaling laws are established and we show, in this Letter, that they are able to explain quite satisfactorily a wide range of experiments on partially densified silica aerogels.

Our reasoning is based on simple scaling ideas. Imagine that, at a given stage of sintering, the cutoffs of a typical fractal blob are a and ξ [case (a) of Fig. 1]. At a later stage, the sintering process leads to a new structure for this blob, characterized by $a' > a$ and $\xi' < \xi$ [case (c) of Fig. 1]. The increase of the lower cutoff results from the smoothing of the internal surface of the aggregate due to local transfers of matter from large curvature to small curvature regions and reinforcements of thinner arms. Consequently, there should be a decrease of the larger cutoff in order to ensure the mass conservation of the whole system. If there is not too much dispersion of the blob sizes, the length contraction ξ'/ξ of a given aggregate should be equal to the overall length contraction of the bulk and the following "trivial" scaling should hold:

$$\xi \sim \rho^{-1/3}, \tag{1}$$

where ρ is the bulk density.

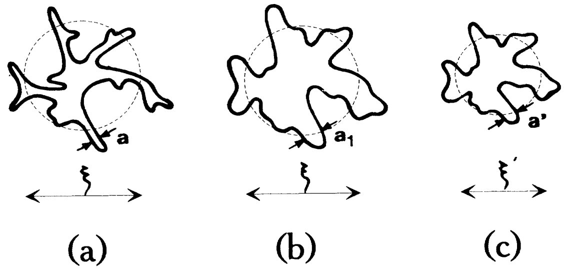

FIG. 1. A two-dimensional sketch of an aggregate at two successive stages of sintering, (a) and (c), where the cutoffs vary from a and ξ to $a' > a$ and $\xi' < \xi$. The intermediate aggregate (b) is obtained by enlarging aggregate (c) by ξ/ξ'.

Now, let us imagine a hypothetical intermediate stage [case (b) of Fig. 1], where the final aggregate has been enlarged by the factor ξ/ξ' in all three space directions to fit the size of the original aggregate. The lower cutoff at this intermediate stage is $a_1 = a'\xi/\xi'$. The aggregate (b) can be considered as a coarse-grained version of aggregate (a). Details of lengths ranging from a to a_1 have been erased, as done in standard real-space renormalization-group methods [10]. Thus both the size and the fractal dimensions of aggregate (b) are the same as those of aggregate (a) but its lower cutoff is larger. Using the definition of the Hausdorff-Besicovitch fractal dimension D [6], one can estimate that the minimum number N of balls of size a necessary to cover the aggregate (a) is related to the corresponding number N' of balls of size a_1 in case (b) by

$$\frac{N'}{N} \sim \left(\frac{a_1}{a}\right)^{-D} \sim \left(\frac{a'\xi}{a\xi'}\right)^{-D} . \tag{2}$$

Furthermore, to ensure mass conservation between (a) and (c),

$$Na^3 \simeq N'a'^3 . \tag{3}$$

Combining Eqs. (2) and (3), it can be seen that

$$\frac{a'}{a} = \left(\frac{\xi'}{\xi}\right)^{-D/(3-D)} . \tag{4}$$

Then, from (1) and (4), one can find how a scales with ρ:

$$a \sim \rho^{D/3(3-D)} . \tag{5}$$

We have used spherical balls to cover the aggregate, but apart from some corrections to scaling, any object of different shape could have been used. As a consequence, the results do not depend on the precise topology of the local external surface of the aggregate, as long as its lower cutoff a is well defined (in average). This underlines the very general character of our reasoning. Obviously our theory is not more valid when a approaches ξ. At this stage it remains holes of all the same mean size (a or ξ) and the densification mechanism becomes similar to that of standard porous materials. Moreover when a becomes close to ξ, the existence of a size distribution of blobs should induce some corrections to scaling due to the fact that smaller blobs are completely densified earlier and do not participate further to the bulk contraction. However, before introducing such refinements, it can be enlightening to compare our conclusions with experiments.

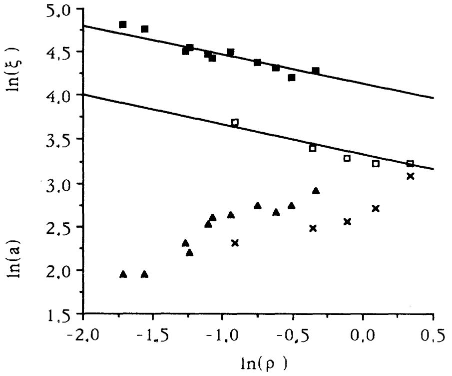

FIG. 2. Log-log plots of the two cutoffs a and ξ versus the bulk density ρ for two different aerogel samples A (▲,■) and B (×,□), as deduced from an analysis of small angle neutron scattering intensity. Straight lines of slope $-\frac{1}{3}$ have been drawn through the data for ξ.

Small angle neutron scattering (SANS) experiments have been performed on gradually densified silica aerogels. These samples, which can be characterized by their mean density ρ, have been obtained by starting from similar materials (resulting from the same sol-gel process) but stopping the heating process at different temperatures. The smaller and larger cutoffs have been estimated from the experimental scattering intensity curve $I(q)$ by locating the limits of the linear fractal regime in a log-log plot. This has been done quantitatively by means of the so-called "Teixeira formula" [11]. The results are given in Fig. 2 for two different series of samples A and B which correspond to different starting aerogels, prepared using different conditions during geling and hypercritical drying (A and B are respectively called $N26$ and $N46$ in previous papers [12]). These samples have been chosen because their fractal regime is quite large. Their fractal dimensions have been estimated to lie in the range 2.2–2.4. In Fig. 2, a straight line of slope $-\frac{1}{3}$ has been drawn through the data for ξ to show that Eq. (1) is qualitatively well verified by experimental results, giving support to the assumptions of our model. The fit of $\ln a$ versus $\ln\rho$ by a straight line gives a slope of order 0.7 ± 0.2 in both cases. According to Eq. (5), this would lead to $D = 2.0 \pm 0.2$, a value slightly smaller but not so far from what is already known.

In Fig. 3 we give other experimental results. The low frequency Raman spectra have been determined from

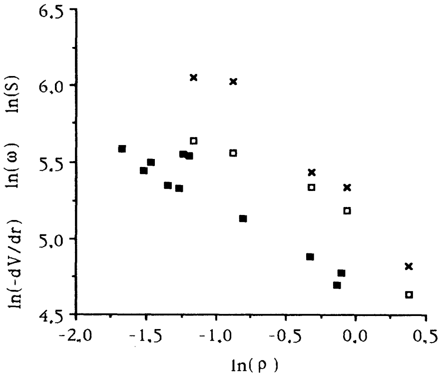

FIG. 3. Log-log plots of the frequency ω (□) of the maximum Raman scattering (sample B), specific surface S (×) as determined from BET experiments (sample B), and the maximum $-(dV/dr)m$ (■) of the pore-size distribution curve (sample A) versus the bulk density ρ.

samples B [13]. They all exhibit a maximum at a characteristic frequency ω which decreases as ρ increases. The data for $\ln\omega$ versus $\ln\rho$ is reported in Fig. 3, exhibiting a mean slope of about -0.7 ± 0.2. If one knows that ω varies as the inverse of a [14], these results are in good agreement with the SANS results on the same samples.

The specific internal surface of pores S has been obtained by nitrogen adsorption (Brunauer-Emmet-Teller) experiments on B samples. Following our scaling reasoning, one should get

$$S \sim Na^2 \sim 1/a \sim \rho^{-D/3(3-D)} . \tag{6}$$

The log-log plot of S versus ρ has a mean slope of -0.8 ± 0.1, in qualitatively good agreement with the preceding results.

We have also performed an investigation of the pore-size distribution of A samples by means of thermoporometry experiments [15]. The curves $-dV/dr(r)$, giving the number of pores of radii lying between r and $r+dr$, have been determined. All these curves exhibit a bell shape with a well defined maximum whose intensity and position vary with density. A simple scaling analysis of the pore-size distribution has already been done [16,17] and leads to the following result for the cumulative volume of pores for an aggregate characterized by the cutoff ξ and the fractal dimension D:

$$V(r) \sim \xi^3 - \xi^D r^{3-D} \tag{7}$$

(this expression can be obtained by dressing the aggregate with balls of radius r and calculating the remaining void volume). This leads to

$$-\frac{dV}{dr} \sim \rho^{-D/3} r^{2-D} . \tag{8}$$

This formula is in principle valid for $a<r<\xi$ and $-dV/dr$ should vanish outside this range. When compared with experiments, a complication arises from the fact that here D is close to 2 and it is not known if the power-law behavior should be attributed to the rising part of the descending part of the experimental curve. Moreover, near the cutoffs, the precise shape of the pore-size distribution cannot be described by the above formula, due to corrections to scaling. However, if it is impossible to fit the entire curve, one can take benefit of formula (8), by observing that the magnitude of $-dV/dr$ near its maximum (where the scaling holds) should scale as $\sim\rho^{-2/3}$ for $D\sim2$. We have plotted the observed maximum value of the pore-size distribution as a function of ρ in a log-log plot in Fig. 3. We find a slope of order -0.6, slightly smaller in absolute value, but quite close to the expected value [18].

For most of the above experimental results, the scaling range is quite small, only a few points are available, and their dispersions are large; therefore the uncertainties on the slopes are important. Moreover, corrections to scaling may enter differently in different cases. However, the wide range of experiments that are accounted for gives strong support to the validity of our scaling approach. The agreement is not so good for other samples where a and ξ are originally too close to each other. It would therefore be very interesting to analyze the corrections to scaling that occur when a becomes of order ξ. This might be done both analytically, by trying to introduce the size distribution of blobs, or numerically, by performing the above described scheme on a computer, starting from simulated aggregates and dressing them in a manner very similar to what was done in [17]. The advantage of numerical studies is that corrections to scaling will show up naturally and that we may be able to reproduce the pore-size distribution curves. It might also be very interesting to extend our analysis by including time in order to set up a "dynamical scaling" approach. However, this cannot be simply done by continuing to ignore the real mechanisms of sintering. Therefore, in parallel to the present global theory, progress in the understanding of detailed microscopic processes is welcomed.

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[18] Thermoporometry does not catch "macropores" (of order 40 nm or more) and it may be that the maximum values of the pore-size distributions are underestimated for smaller densities. This could explain a slope smaller than that expected.