Experimental Realization of Superelasticity near the Percolation Threshold

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An experimental determination of the superelastic exponent near the percolation threshold is present-ed. This exponent s' characterizes the pseudodivergence of the elastic constants of a mixture of very soft material (gel) and a rigid material (alumina and zirconia). From the measurement of the Young's modulus, s' is found to be 0.67 ± 0.05. This value is in agreement with previous numerical simulations in 3D, and this indicates that very likely s' is smaller than the superconductor exponent.

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When one considers a mixture of two materials with very different properties (like a conductor and an insula-tor, a normal metal and a superconductor, a soft and a rigid material, etc.), one observes for a well defined pro-portion of the two components a sharp transition between two distinct states of the composite material. This is the percolation phenomenon, for which, at a specific concen-tration of one components, the transition occurs.

Depending on the problem, one measures a particular property like the electrical conductivity or the elastic con-stants. It is customary to express the variation of this quantity as a power law $|p - p_c|^{\pm a}$ where a is the critical exponent appropriate to the chosen quantity. The nega-tive sign indicates a divergence, such as in the conductivi-ty of a normal metal superconductor mixture, where p is the proportion of the superconductivity component, $p < p_c$. The positive sign indicates a drop to zero as $p \to p_c$.

In this paper, we consider the case of inclusions of a perfectly rigid material (with infinite elastic constants) inside a normally isotropic, elastic, host material. The problem has already been studied theoretically by several workers [1–4], but to the best of our knowledge there has been no experimental realization. The elastic constants of the composite diverge and it is usual to call the ex-ponent of the divergence s'. It is the purpose of this work to present an experimental determination of the exponent s' in 3D.

The first numerical simulation in 2D was made by Feng [1], who found an exponent s' slightly but signifi-cantly lower than the exponent s of the divergence of the conductivity in the normal-superconductor composite. However, using a different model, Bergman [2] concluded that $s' = s$. Milton [5] showed rigorously that $s' \leq s$ such that the results of Feng and Bergman are both consistent with the rigorous result. Limat [3] tried to give an argu-ment in favor of the strict inequality but it is based on a specific model and the general validity of his result is un-clear. Recently Arbabi and Sahimi [4] performed nu-merical simulations to determine s' in 2D and in 3D. They found $s'(2D) = 1.24 \pm 0.03$ and $s'(3D) = 0.65 \pm 0.03$ to be compared with $s(2D) = 1.3$ and $s(3D) = 0.735$. In 2D the difference $s' - s$ is small and thus it is difficult to be conclusive, but in 3D the two exponents s'

and s are clearly different.

Although the earlier conclusion seems well confirmed, some of the models used in the simulations are not free from objections (as first pointed out by Bergman [2]). The homogeneous version of the models (i.e., without infinitely rigid inclusions) used by Feng, Limat, and Ar-babi and Sahimi present a very peculiar property. In some particular directions, the lattice which models the solid has a zero Poisson coefficient. This means that a compression in these directions gives no deformation per-pendicular to the compression. The model of Bergman seems more realistic to describe a solid, in spite of the claim of Limat [6] that all the 2D models are equivalent. Thus, we think that an experimental study of this prob-lem, the superelastic problem as it is sometimes called by analogy with the superconductor problem, is worthwhile.

We require for this experiment two materials whose elastic constants (bulk and shear modulus) differ by several orders of magnitude, so that one is perfectly rigid in comparison with the other. It is not possible to find two such isotropic solids. Thus we use for the "normal" elastic material a gel which has a small shear modulus ($\mu \sim 10^5$ dyn/cm^2) and a bulk modulus K of order of 10^{10} dyn/cm^2. As a "perfectly rigid" material any hard solid suffices as K and μ are about 10^{12} dyn/cm^2. The ratio of the μ is satisfactory for the present purpose (10^{-7}), but the ratio of the K is only 10^{-2}. We rely on the simula-tions of Duering and Bergman [7] who studied in 2D a similar case: a μ ratio equal to 10^{-9} and a variable K ra-tio (from 10^{-9} to 1). They found that the s' exponent of the μ divergence is practically independent of the K ratio. In their study s' was taken equal to $s = 1.30$, but the pre-cision was too coarse to detect a small difference from s. Although Duering and Bergman worked in 2D, we think that one can apply their results to our 3D system and conclude that the exponent we find is really s'.

We choose as the host material polyacrylic acid gels because they are very easy to prepare. We follow the procedure indicated in Ref. [8]. The gels are prepared by radical polymerization of acrylic acid in aqueous solution and copolymerization by means of methylene bisacrylam-ide. The two reactions take place together and are ini-tiated by ammonium peroxysulfide. The sample is heated up to 70°C for at least 6 h. We choose a concentration
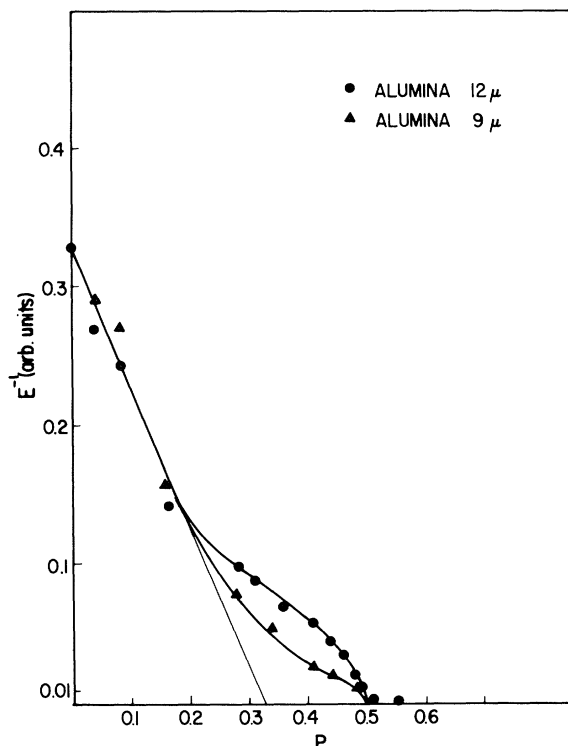
FIG. 1. Inverse of the Young's modulus E^{-1} vs the concentration p of the filler (alumina powder). The line is a guide for the eyes, like in the other figures.

FIG. 2. Variation of the Young's modulus with the composition for the samples of Fig. 1, in the vicinity of the percolation threshold.

of polymer of 10% and a content of cross-link which gives a Young's modulus $E = 3\mu$ of about 10^5 dyn/cm^2. The rigid materials used in the present study are alumina and zirconia powders.

There are two major problems in preparing the samples: getting a distribution in the size of rigid clusters, and avoiding sedimentation of the powders. There is a large number of works concerning gels charged with small particles (sizes from 1 to 10 μm) [9,10], but with the exception of one recent paper [11] there is no mention of a pseudodivergence of Young's modulus. In these works, the gels are charged with monodisperse spherical particles. The theoretical analysis [12] which agrees very well with the experiments [9] assumes that the particles are always isolated and do not form aggregates. We have to stress that even in the case of aggregation of spherical particles in clusters, it is not certain that such clusters will be rigid because of the possibility of relative displacement of the particles belonging to the same clusters under application of an external stress. Thus we choose powders with particles with different sizes and poorly defined shapes, alumina and zirconia powders used for crystal polishing. Because of the crystalline nature of the particles, their shape is very irregular, as was checked by optical microscopy. Furthermore, the size distribution is characterized by a maximum value of the sizes, 9 and 12
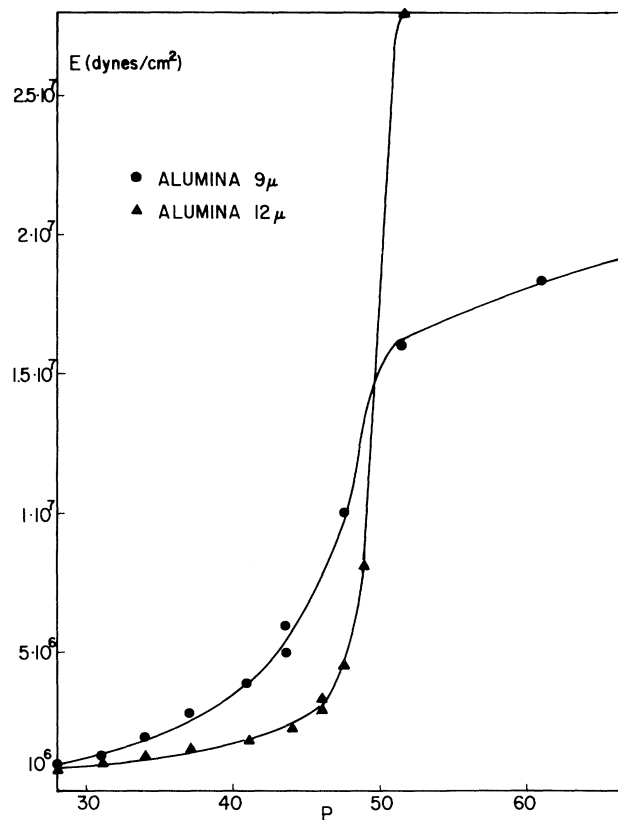
μm for two different alumina powders and 12 μm for the zirconia powder. In such conditions we expect formation of rigid clusters, with different sizes.

To solve the problem of sedimentation we proceed in the following manner. We mix the acrylic acid with the solvent (water), the cross-linking agent (methylene bisacrylamide), the catalyst, and the desired amount of powder. The mixture is poured into a cell of radius 11 mm and length 30 mm. To avoid sedimentation, the cell is rotated at a rate of 5 rpm during heating. To verify that the samples are homogeneous, we cut a sample into three thinner samples and measured their Young's moduli. We found the same values, taking into account experimental uncertainties.

The Young's modulus is measured by imposing a known deformation to the sample and determining the pressure by means of a piezoelectric sensor. From the linear region of the strain-stress curve, it is possible to deduced the Young's modulus.

In Fig. 1, we present the curve E^{-1} as a function of p for the case of two alumina powders. The value of the threshold is near 0.5. The pseudodivergence of E is very well seen in Fig. 2, where E vs p is plotted for p larger

than 0.29. The behavior of E for the third series (zirconia) is shown in Fig. 3. In this case the threshold is located between 0.40 and 0.41. One notes that near p_c the values of E are 100–1000 times the value of E of the gel. Our results are very different from those obtained with monodisperse spherical particles as filler: There is no singularity in the curve of $E(p)$, even for p as high as 0.6. We believe that our experiments, where a singularity is clearly observed, can be analyzed as a percolation phenomenon.

First we consider the regime of small p, where the results can be compared with the predictions of the effective medium theory (EMT). This theory [13] predicts that E^{-1} decreases linearly when p increases and goes to zero for p_c calculated in this approximation. In the case of spherical rigid inclusions $p_c = 0.33$ but in general the threshold is shape dependent. In Fig. 1, one can see that the behavior of E^{-1} with p is effectively linear for $p < 0.15$ and the extrapolation of the straight line gives $p_c^{EMT} = 0.34$. This value seems to indicate that the rigid inclusions behave almost as spherical inclusions in spite of their very irregular shape. This is the first direct verification of the EMT theory in the case of the superelastic problem.

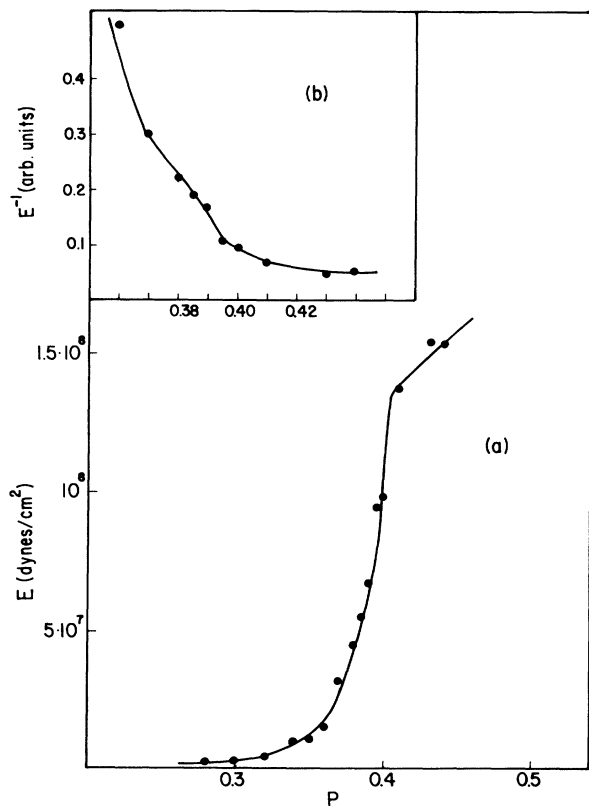Near the threshold, the pseudodivergence of E can be compared with the analytic expression $E \sim (p_c - p)^{-s'}$. To determine the exponent s', the usual method is to plot E vs $p_c - p$ in a log-log plot. However, in the present case, p_c is not precisely known. Taking $p_c = 0.50$ (as suggested by Figs. 1 and 2) for the samples filled with the alumina powders the log-log plot gives straight lines for the smaller values of $p_c - p$ and an exponent $s' \simeq 0.65$. A small change in p_c (between 0.495 and 0.505) gives a slight difference in the value of s'. For each value of p_c, a linear fit is made and the best fit is obtained for $p_c = 0.50$, $s' = 0.64 \pm 0.02$.

The results of the samples filled with zirconia give less precise results. The determination of p_c cannot be made precisely although it is clear that $0.40 \le p_c < 0.41$. We choose several values of p_c between 0.400 and 0.408 and we get from the log-log plot an exponent between 0.640 and 0.720. In Fig. 4, we show the log-log plot of E vs $p_c - p$ for $p_c = 0.402$ and one has $s' = 0.69$. Thus we can adopt the value $s' = 0.67 \pm 0.05$. This relatively large error is due to an inherent difficulty of the problem: The behavior of E is not a true divergence but only a pseudodivergence. This prevents a close approach to p_c, as needed for a good determination of the exponent. Our results give an additional piece of evidence to conclude that $s' < s$. Furthermore, the value of s' we got is in very good agreement with the theoretical one of Arbabi and Sahimi [4].

The values of p_c are relatively large, but this is not the first such observation. Abeles, Pinch, and Gittleman [14]
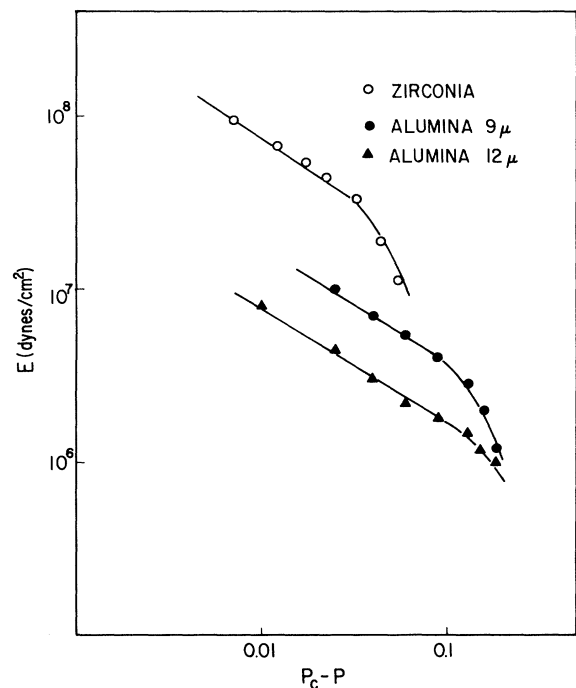

FIG. 3. (a) E vs p in the case of zirconia powder as filler. (b) E^{-1} vs p, near p_c.

FIG. 4. E vs $p_c - p$ in a log-log plot, showing the divergence of E as $(p_c - p)^{-s'}$ with $s' \simeq 0.67$.

have reported a threshold of 0.47 for $W-Al_2O_3$ cermets value which is near what we obtain in our work (0.4 and 0.5). The reason for that is not known but it seems that it does not preclude the use of percolation theory.

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