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## An experimental model for studying the effect of anisotropy on percolative conduction

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**Résumé.** — Nous présentons des mesures préliminaires de la conductivité électrique d'un matériau composite formé de particules conductrices cylindriques dans une matrice isolante réalisant un milieu modèle pour l'étude de la percolation anisotrope en fonction du rapport longueur sur diamètre des particules. Dans la limite expérimentale des grandes valeurs de ce rapport, un argument géométrique permet d'interpréter nos résultats, en particulier la faible valeur du seuil de percolation.

**Abstract.** — We present preliminary measurements of the electrical conductivity of a composite made of small conducting rods in an insulating matrix. It constitutes a model material for studying the effect of anisotropy on percolation as a function of particle length to diameter ratio. We can interpret our results, especially the lowering of threshold respective to isotropic systems, by means of a geometrical argument when the ratio is high as in our experiments.

**1. Introduction.** — Among the various aspects of percolation studies, the influence of anisotropy on the results established for the classical isotropic case has recently received an increasing interest [1, 2]. The main features studied refer to critical concentration, critical behaviour, crossover effects and, as a consequence, to the principle of universality. It has long been shown [3] that there exists an intimate connection between percolation and the problem of the onset of conductivity in an inhomogeneous material as far as there exist no tunnelling effects. Apart of experimental results on real materials where anisotropy is important like organic conductors [4] or multifilamentary superconducting wires [5] there exist few publications concerned with the influence of anisotropy on percolative conduction. We can quote a computer monitored experiment by the Marseille group [6] and electrical measurements on heterogeneous metallic films [7]. The results of both these studies on 2D systems are still ambiguous.

In real heterogeneous solids, e.g. conducting particles in an insulating matrix, there are several ways of introducing anisotropy, keeping, for simplicity, the matrix isotropic. As recalled by Shklovskii, [8] the particles can be either spherical with anisotropic conductivity or of non spherical shape with isotropic conductivity. Besides, in both cases two limiting situations are to be considered depending on whether the axes of symmetry of the particles are oriented at

random (disoriented case) or along macroscopic directions (oriented case). All the studies quoted above belong to the *oriented* case. We present in this Letter an experimental model essentially suitable for studying a *disordered* case, which should, hopefully, be extended next to an *oriented* case.

**2. The experimental model and preliminary results.** — Carbon polymer composites have been shown [9] to be good model materials for studying the (isotropic) percolative conduction when spherical carbon particles (carbon black) are used. For introducing anisotropy, other kinds of carbons can be chosen relating the composite material to any of the cases discussed above. We have decided to start studying the influence of particle shape on percolation by using short carbon fibres as the particles, the length of which being varied as desired in the millimeter range, and oriented at random.

The polymer is an epoxy resin ARALDITE with hardener HY from CIBA GEIGY Cy; its resistivity is higher than  $10^{10} \Omega \cdot \text{cm}$ . Carbon fibres are high modulus AG fibres from LE CARBONE LORRAINE Cy. Their diameter is  $10 \mu$  and conductivity  $10^2 \Omega^{-1} \cdot \text{cm}^{-1}$ . The fibres are cut with calibrated razor blades; it has been checked that a fairly narrow length distribution is obtained. The fibres are mixed carefully in appropriate concentration with the viscous resin before polymerization. The samples are

let to harden several hours at room temperature while they are constantly and slowly rotated in order to prevent sedimentation. The strong diamagnetic anisotropy of a fibre (of the order  $10^{-5}$  emu.cgs.g $^{-1}$  [10]) offers a simple way of testing the disorientation of the rods : samples with more than 5 % difference of diamagnetic susceptibilities measured on a small parallelepiped along three perpendicular axis by a Faraday method are rejected. Despite a macroscopic isotropic susceptibility it could happen that, locally, fibres would orient themselves due to steric effects. Such an effect is likely to be present in strongly concentrated samples. However, examination under microscope of our samples with low concentration showed that if orientation does exist, it only concerns a very small part of the fibres. The actual concentration in fibres is controlled by density measurements as the densities of the fibres and of the resin are respectively 1.91 and 1.16. The samples are cut and electrodes for four leads electrical measurements are placed by means of a silverpaste. The minimum size of the sample to be used for these measurements is an important point to be discussed here. As an experimental model for percolative conductivity studies, our material is demanded to be large enough for the definition of a threshold and critical behaviour be meaningful (*thermodynamic* limit). The solid under study must be large compared to the coherence length of the phenomenon in order to avoid size effects [11]. On an experimental ground, such effects show up as scatter in the data obtained on different samples. We have in a few cases varied the ratio  $L/l$  of the sample length to a given fibre length between 5 and 40 and we have found  $L/l \simeq 20$  as the limit above which the scatter of the data lays within experimental uncertainty. All the data given in this letter were obtained in such a condition. We verified on a few samples that Ohm's law is obeyed.

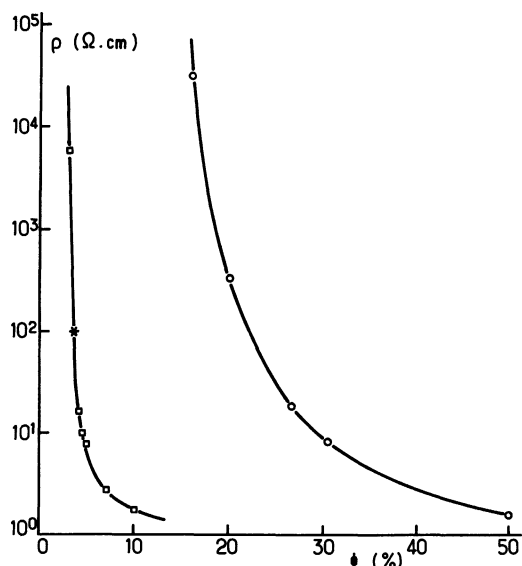


Fig. 1. — Plot of the resistivity  $\rho$  dependence with volume fraction  $\phi$  for fibres length  $l = 1.1$  mm ( $\square$ ). The star (\*) is for  $\phi = 0.035$ . Also shown for comparison  $\rho(\phi)$  for spherical particles ( $\circ$ ) (from ref. [9]).

Figure 1 shows the volume concentration dependence of the electric conductivity at constant fibre length  $l = 1.1$  mm. The drop of  $\rho$  occurs for about 3 % by volume of fibres in the material. This low figure for the critical concentration is to be compared to the value  $\phi^* = 0.17$  as obtained for spheres in a 3D heterogeneous solid [9]; the corresponding  $\rho(\phi)$  curve [9] is also plotted on figure 1 for comparison. This result was expected [12] since the surface of an elongated particle ( $l/d = 110$  in this case) is much larger than that of the sphere of equal volume so numerous contacts can occur on a single fibre and an infinite chain can form easily. The critical volume fraction [12] is no longer an invariant.

Figure 2 shows the effect of varying the (shape) anisotropy of the particles at constant volume concentration on resistivity. A sharp decrease is also evidenced in the  $\rho(l)$  plot, that is consistent with a decreasing critical concentration as the length of the fibres increases.

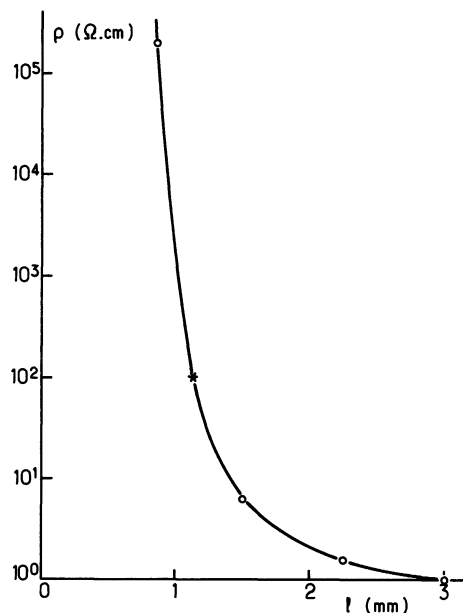


Fig. 2. — Plot of the resistivity  $\rho$  dependence with fibres length  $l$  at constant volume fraction  $\phi = 0.035$ . The star (\*) is for  $l = 1.1$  mm.

**3. Geometrical aspects.** — The onset of electrical conduction is related to the existence of an infinite chain of connected particles. In the case of spheres, there is a limited number of possible contacts per particle. When considering long disordered rods this number can be very high depending on the  $l/d$  ratio,  $d$  being the diameter of the rods. We then assume that for a given number of particles per unit volume  $N$  the possibility of forming an infinite chain depends only on  $l$ .

If  $\phi$  is the volume concentration,  $N = 4\phi/\pi d^2 l$ . We consider the rods as geometrical lines without thickness. If we apply a transformation changing the length scale by a factor  $a$ , the length of each rod becomes  $l' = al$  the distances between the centres

of the rods are also multiplied by  $a$  and the geometry of the system remains unchanged. We now find the same number  $N$  of particles in a volume  $a^3$  so that the new particle density is  $N' = N/a^3$  and the new volumic concentration

$$\varphi' = \pi d^2 l' N'/4 = \varphi/a^2.$$

In particular if  $\varphi$  was the critical volume fraction  $\varphi^*$  for the fibre length  $l$ ,  $\varphi'$  is the critical volume fraction  $\varphi'^*$  for the new fibre length  $l'$  so we write :

$$\varphi'^* = \varphi^*(l^2/l'^2).$$

Noticing that changing both  $l$  and  $d$  so that  $l/d$  remains constant leaves  $\varphi$  unchanged, in such a transformation, we conclude that the critical concentration  $\varphi^*$  must depend, in this limit, quadratically in  $(l/d)^{-1}$ . Let now  $R = \rho(l, \varphi)$  be the resistance of a unit volume cube of material the resistivity of which being  $\rho$ . In the above transformation as  $l$  changes to  $l' = al$  and  $\varphi$  to  $\varphi' = \varphi/a^2$ , the resistance of a single rod is multiplied by  $a$  and so are all the resistances  $r_i$  between two contacts on a fibre of the equivalent random resistor network. The geometry of this network is not changed so the resistance  $R'$  of the new cube of side  $a$  is just  $R' = aR$  and the new resistivity

$$\rho(l', \varphi') = aR' = a^2 R = a^2 \rho(l, \varphi)$$

which can be written

$$\rho(al, \varphi/a^2) = a^2 \rho(l, \varphi).$$

This is an homogeneity relation which can be shown to be satisfied by homogeneous functions of the form

$$\rho(l, \varphi) = l^2 \mathcal{R}(l^2 \varphi)$$

$\mathcal{R}$  being an unknown function of  $l^2 \varphi$  only. This scaling relation predicts that a plot of  $\rho/l^2$  for different values of  $l$  and  $\varphi$  versus the reduced variable  $l^2 \varphi$  should result in a single curve. This has been done on figure 3 taking the data of figures 1 and 2 : it clearly demonstrates the validity of the scaling law in the range of  $(l/d)$  and  $\varphi$  values so far explored experimentally.

The geometrical arguments developed here are clearly valid only when  $(l/d)$  is large enough and/or  $\varphi$  is not too large. More experimental work is needed for giving these limits.

**4. Conclusion and prospects.** — We have presented a model composite material suitable for studying the

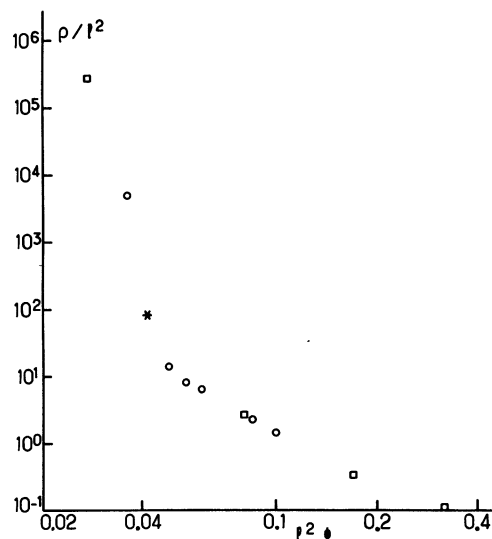


Fig. 3. — Plot of the resistivity to square fibre length ratios  $\rho/l^2$  as a function of the reduced variable  $l^2 \varphi$  : (○)  $l = 1.1$  mm, variable  $\varphi$ ; (□)  $\varphi = 0.035$ , variable  $l$ ; (\*)  $l = 1.1$  mm,  $\varphi = 0.035$ .

effects of particle shape anisotropy on percolative conduction. Preliminary results have been given which partly support predictions of simple geometrical arguments. Work is under progress in order to check the predicted  $(l/d)^{-2}$  dependence of the critical volume concentration for large values of the ratio and to define the range of  $(l/d)$  and  $\varphi$  values over which the limiting behaviour holds. Needless to say much has to be known outside these ranges and especially in the domain of weak anisotropy. The critical behaviour near threshold has also to be studied.

In further experiments we intend to orient the rods inside the matrix so the oriented case could be studied as well.

We believe these experiments to demonstrate for the first time that the concept of a universal critical volume fraction for the onset of electrical conduction in continuous systems with undisperse particles is misleading in the case of long *disordered* particles. That is contrary to the case of oriented particles for which it is believed [8], although not definitely proved [7], that the percolation threshold is not sensitive to anisotropy.

The very low  $\varphi^*$  value obtained for large  $(l/d)$  is an interesting feature which, we believe [13], could help understanding the electrical conductivity of systems like the doped fibrillar  $(\text{CH})_x$  polymers which can be conductors [14] even when obtained as very low density foams.

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