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Capacitive noise spectra of a disordered material

I. Balberg
The Racah Institute of Physics, The Hebrew University, Jerusalem 91904, Israel

J. Blanc
RCA Laboratories, Princeton, New Jersey 08540
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We report here the first attempt to test the results of cluster theory on a real, practical composite. For this purpose we have calculated the noise-power spectra of the capacitance between a riding capacitive probe and a conducting composite using results of percolating-cluster theories. Comparison with the experimental results obtained on a carbon-black–polyvinylchloride composite confirms the predictions obtained from the above calculations. In particular it appears that the percolation-correlation length for composites can be estimated from the noise-power measurements.

The present knowledge of cluster statistics and cluster structure[1,2] has not been tested thus far on three-dimensional percolation systems. In particular, microscopic probing of clusters embedded in their matrix has not been reported before. Previous tests of three-dimensional cluster theory were carried out only by computer simulations[1–3] while experimental studies[4] were limited to two-dimensional systems which were specially designed for these studies. We present here the first attempt to examine whether or not cluster theory is consistent with experimental results obtained on real practical composites. The advantage of the method used here over Monte Carlo simulations (in particular, for continuum systems[3]) is that much larger ensembles of clusters can be considered and thus much better statistics can be obtained. The present novel experimental method is based on a capacitive pickup which enables the derivation of information on clusters via the measurement of "geometrical" noise. This work indicates possible utilizations of cluster theory in planning and controlling geometrical noise in practical systems.[5]

The simplest model that one can assume for a capacitive pickup system and a composite material, in which conducting particles are embedded in an insulating matrix, is illustrated in Fig. 1. This picture of the composite is valid

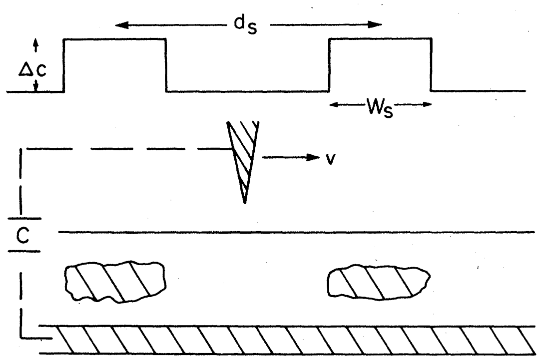

FIG. 1. Schematic illustration of the simple model of the composite system considered in the text and the capacitive pickup response ΔC due to the presence of finite conducting clusters of size *s*.

somewhat away from the percolation threshold where the distance between finite clusters becomes larger than their diameter. As is apparent from the compositions used in the presently studied materials (see below), this picture is applicable here. The capacitive pickup of the system is obtained by a conducting stylus which rides on the surface of the composite. This probe can be looked upon as one "plate" of a capacitor while the "infinite metallic" percolating cluster forms the other "plate." Whenever the probe is over a conducting isolated cluster the capacitance increases due to the decrease of the actual width of dielectric material between the probe and the other "plate." For simplicity we assume the latter "plate" to be parallel to the surface and flat on the average. The assumed parallelism is the intended result of the high-pressure, high-temperature uniform pressing conditions.[6] The flatness simplification is not expected to affect the following results since the percolating cluster has "hills" and "holes" with statistics similar to that of the finite clusters. The infinite cluster may have "arms" that reach the surface. Such arms will lead to spikes of current when approached by the capacitive probe; we have measured such spikes and these occur far too infrequently to contribute to the noise power reported here.[7] The amplitude of the capacitive pickup will depend on the distance between the bulk of the percolating cluster and the surface and on the deviations from the simple ideal system described above. In Fig. 1 we have assumed that between the surface and the percolating cluster there are floating, finite, "metallic" clusters. This picture was borne out by the above infrequent occurrences of spikes. On the other hand, the alternative picture, i.e., that the capacitive pickup has to do solely with the infinite cluster, is expected to yield the same results because of the fractal (or "ramified") nature of this cluster.[8] This yields the property that the hole sizes, the "blob" sizes, and the sizes of the finite clusters embedded in the infinite cluster[8] behave as the sizes of the other finite clusters (e.g., they diverge with the exponent of the correlation length; see below). Under both pictures the capacitance fluctuations between the riding stylus and the percolating-cluster "plate" will yield a sequence of rectangular waves. Since in the present work we measure the power spectra and not the sign of the capacitive pickup, we may use the simplified time series shown in Fig. 1 for the spectral analysis of both pictures. Of course, a much more detailed picture of the cluster sizes and their density in the composite is expected to be obtained by a direct measurement and statistical analysis of the time series itself. This technique which is much more sophisticated than the present one has not been developed yet.

To evaluate the capacitive fluctuations let us consider first the expected contribution of clusters of size s (containing s conducting particles[1]). If the average distance between two such clusters is d_s and the average diameter of these clusters is $w_s = 2R_s$, then the time sequence of waves obtained for a stylus which rides at a velocity v will have the period d_s/v. The time-dependent part of the capacitance wave shown in Fig. 1 can be presented by its Fourier series:

$$C(t) = \sum_{n=1}^{\infty} [a_n \cos(\omega t) + b_n \sin(\omega t)] \ , \tag{1}$$

where $\omega = 2\pi n v/d_s$ and a_n and b_n are the amplitudes of the superimposed waves. The power $P_\omega(s)$ at any discrete frequency ω will be given[9] by $P_\omega(s) = a_n^2 + b_n^2$ yielding

$$P_\omega(s) = (8A^2 v^2/\omega^2 d_s^2)[1 - \cos(\omega w_s/v)] \ , \tag{2}$$

where A is the amplitude of the capacitive pickup.

The simplicity of Eq. (2) leads to immediate conclusions regarding the power spectra due to one kind of cluster. It is apparent that at low frequencies ($\omega w_s << v$) the power will be frequency independent with an amplitude $4A^2 w_s^2/d_s^2$, while at higher frequencies the power will decrease as $1/\omega^2 d_s^2$. Since different-size clusters are assumed to be uncorrelated, the power spectral due to many types of clusters is expected to be the sum of the power spectra of all clusters. Hence, the observed power spectrum is expected to be

$$P_\omega = \int P_\omega(s) ds \ , \tag{3}$$

where the integration is over the finite clusters.

Following the above discussion and the predictions of cluster theory[1,2] we may anticipate some features of the power spectra. For example, if N is the concentration of conducting particles in the composite and N_c their concentration at the onset of percolation, then w_s is a weakly decreasing function of $N - N_c$, while the cluster concentration N_s ($\propto d_s^{-D}$ where D is the dimensionality of the system) is a relatively stronger decreasing function of $N - N_c$. Since this qualitative behavior is common to all clusters, we can predict from Eq. (2) the following: (a) the measured noise power will be independent of frequency at low frequencies and then decrease at higher frequencies; (b) the larger the $N - N_c$, the smaller the w_s, and the larger the transition frequency ω_T which characterizes the "crossover" from the low-frequency to the high-frequency regimes; (c) since A^2 is determined primarily by the distance between the surface and the percolating-cluster "plate," it is expected to increase with $N - N_c$ and to oppose the decrease of the $(w_s/d_s)^2$ term with $N - N_c$. While we do not have a quantitative electrostatic model for A^2, we can determine experimentally (see below) its effect and we can evaluate whether $(w_s/d_s)^2$ decreases with $(N - N_c)$ as predicted by cluster theory. Various other predictions and their experimental confirmation will be reported later.

To test these predictions we have carried out power-spectra measurements on a carbon-black–polyvinylchloride (PVC) composite. The composite which has been described in detail before[6,10] has been shown[10] to follow percolation-theory predictions such as the dependence of the conductivity on the weight percent M above its critical value M_c. For the composite materials prepared for this study ($M = 9$, 11, 13, 15, 17, and 19 wt.% of carbon black) resistivity measurements (described in Ref. 10 for a composite of a different carbon black) yield a value of $M_c = 10.4$ wt.%. Since this composite is easily pressed (in its molten state) into circular grooved disks[5,6] (so that the capacitive stylus can be guided) and since the capacitance pickup technique for such disks is well developed,[5] we could measure the capacitance power spectra by introducing two modifications to the system described previously.[5,6] The first was the preparation of special Selectavision Videodiscs,[5] consisting of an area of no intentionally impressed information and of an area on which sinusoidal signals at selected frequencies were impressed. The second modification was that the output of the pickup circuit was fed into a spectrum analyzer in order to obtain the P_ω dependence. To verify that the noise is associated with spatial variations, we have confirmed that the spectra have the expected linear dependence on stylus velocity.[11]

The results for the noise spectra on the area with no impressed information are shown in Fig. 2. It is clearly seen that the low-frequency noise power is independent of frequency and then drops at higher frequencies. It is further seen that the transition frequency ω_T is lower for the lower M as predicted above. The fact that the transition between the two frequency regimes is smeared is not surprising in view of the fact that the transition for each set of clusters, with a common s, depends on s [see Eqs. (2) and (3)]. To test the third cluster-theory prediction made above concerning the decrease of $(w_s/d_s)^2$ with $N - N_c$ (or with $M - M_c$), we have singled out the effect of the percolating-cluster "plate" (or of A^2) by measuring the power at the frequencies 0.7, 2, 5, and 8 MHz on the area of the disk where the corresponding sinusoidal signals were impressed. It was found that this power increases with $M - M_c$ faster than the

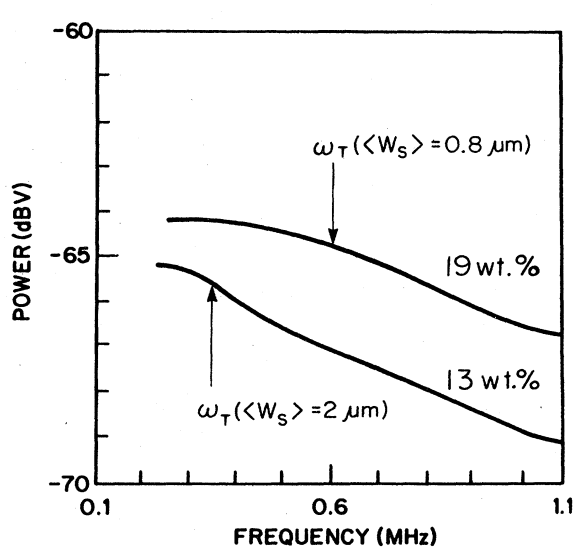

FIG. 2. Power spectra of carbon-black–PVC composites with two different carbon-black loadings. The frequency ω_T designates the transition from the low- to the high-frequency regimes. Also indicated is the corresponding distance $\langle w_s \rangle = 2\pi v/\omega_T$ along the stylus path. (0 dBV = 1 V rms.)

noise power (as obtained for the same frequencies on the area where no signal was impressed). This means that if we normalize the power spectra, shown in Fig. 2, by the signal power (the A^2 effect) in order to determine the "pure" noise [or the $(w_s/d_s)^2$] effect, we find that indeed the $(w_s/d_s)^2$ amplitude decreases with $M-M_c$.

Following the above qualitative confirmations we may try to deduce quantitative information from the experimental results. Reexamination of Fig. 2 suggests that quantitative conclusions can also be drawn from the data. The integral in Eq. (3) may be considered as the average $\langle 1-\cos(\omega_T w_s/v)\rangle$ or the average $\langle w_s^2\rangle$ with a weighting function $1/d_s^2$ ($\propto N_s^{2/D}$). On the other hand, the percolating correlation length ξ is given[2] by another average of w_s:

$$\xi^2=\sum_s N_s s^2 (w_s/2)^2 \Big/ \sum_s N_s s^2 \ , \qquad (4)$$

where the summation is over the finite clusters. It appears then that ξ and $\langle w_s\rangle$ are closely related and that $\langle w_s/2\rangle$ approaches ξ when the distribution of the d_s (or N_s) values is not too broad, i.e., when M departs from M_c. Hence, the transition frequency ω_T which is observed experimentally and which is related to $\langle w_s\rangle$ by the condition $\langle w_s\rangle = 2\pi v/\omega_T$ yields the approximation $\omega_T\xi \approx v$. This relation is also expected from the simple argument[4] that crossover behavior of a physical quantity in a percolating system is associated with crossing a distance of length ξ.

In the present results we found (Fig. 2) that for $M=13$ wt.%, $\omega_T/2\pi=0.25$ MHz. Since $\langle w_s\rangle = 2\pi v/\omega_T$, where $v=5$ m/sec is the velocity of the stylus, $\langle w_s\rangle = 2$ μm. Similarly for $M=19$ wt.%, $\omega_T=0.6$ MHz and $\langle w_s\rangle = 2\pi v/\omega_T = 0.8$ μm. Considering the fact that the carbon particles are 0.1 μm long and their aspect ratio is about 4, these values of $\langle w_s\rangle$ are very reasonable approximations of ξ for the corresponding $M-M_c$ values. Monte Carlo simulations of such a system[3] confirm this conclusion. To further check this suggestion we have plotted in Fig. 3 $\langle w_s\rangle = 2\pi v/\omega_T$ as a function of $M-M_c$ in order to find whether or not it is consistent with the expected[1] $\xi \propto (M-M_c)^{-\nu}$ behavior. While our present data are not good enough to derive the value of ν it is (as can be seen in Fig. 3) in good agreement with the expectations due to percolation theory,[1] i.e., that $\nu=0.85$ in three dimensions.

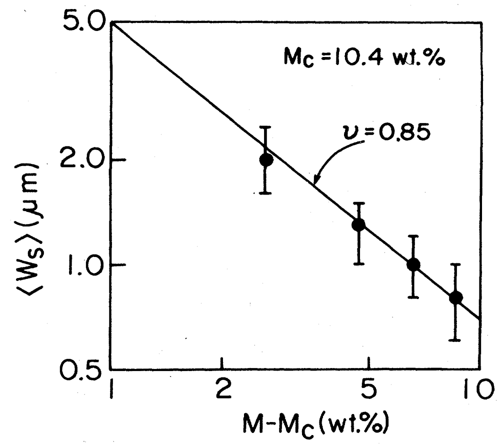

FIG. 3. Dependence of the distance $\langle w_s\rangle$ on the carbon-black loading, M. It is shown that the data are consistent with a correlation length type dependence $(M-M_c)^{-0.85}$.

In conclusion, predictions of percolation-cluster theory were confirmed, for the first time, on a three-dimensional composite. We have further shown that the capacitive noise-power spectra can yield information regarding the structure of the composite.

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