Electrical-Conductivity Fluctuations near the Percolation Threshold

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$1/f$ noise near the percolation threshold X_c of carbon-wax mixtures was carefully studied. The noise spectral density was found to diverge with a power-law dependence on $X-X_c$. Our results might be qualitatively explained by carrier-number fluctuations, produced by tunneling conduction, in infinite clusters.

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$1/f$ noise has been observed in almost all electric-current–carrying devices; however, even for the simplest conductive devices such as metal films, the origin of $1/f$ noise remains controversial.[1-4] One of the reasons for the controversy is that it is difficult to characterize the nature of the noise-producing mechanism and the structure of the device studied. To circumvent these difficulties, several authors studied the electrical-conductivity fluctuations in rather unconventional systems, such as systems near their second-order phase-transition point.[5,6] There are several advantages of systems near the second-order phase-transition point; for example, (a) the conductivity fluctuations are large, (b) the correlation length is so large that the microscopic structure in the system might be unimportant in the production of noise near the transition point, and (c) the systems can be characterized by few variables as a result of the universal scaling laws.[7]

Ketchen and Clarke[5] studied the excess noise in superconductive metal films near the superconducting transition, and found that the noise arose from temperature fluctuations in the superconducting films. Kim *et al.*[6] measured the electrical-conductivity fluctuations in a binary mixture near the critical point and found that the observed noise was generated by the fluid flow. However, the noise spectra in these studies were not of $1/f$ type. Both temperature fluctuations and the flow noise are realized not to be the cause of the ordinary $1/f$ noise.[6,8] A possible reason for the observation of unusual noise spectra in the above-mentioned conductors might be that the systems were susceptible to external perturbations near their transition point, and hence, exhibited noise spectra characterizing the relaxation processes of the external perturbations.

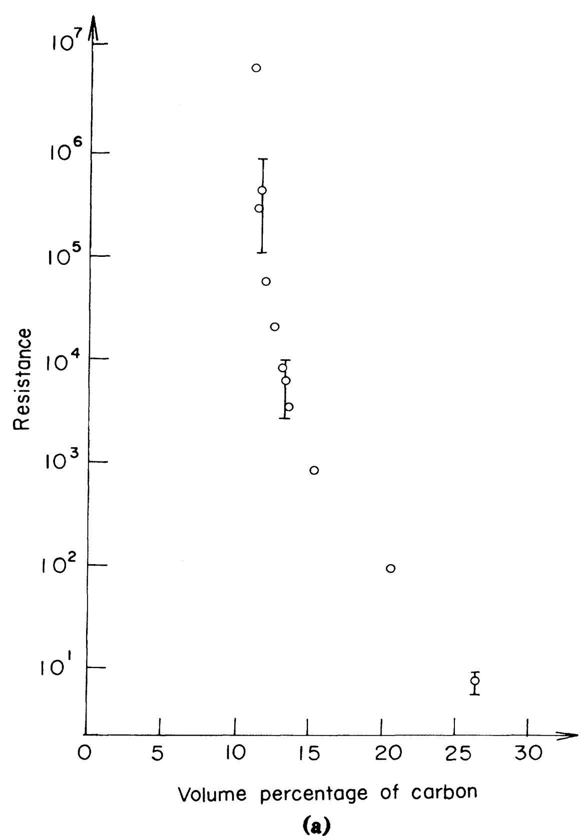
Recently, properties near the percolation threshold have attracted much research interest.[9-11] In this Letter, we report studies of $1/f$ noise in a system near the percolation threshold. The reasons for this research are (1) to add some insight to $1/f$ noise through the study of the critical behavior of $1/f$ noise in a percolative system, and (2) to provide valuable information about electronic conduction near the percolation threshold. In addition, the percolation transition is known to be a kind of second-order phase transition,[12] and hence, the above-mentioned advantages remain.

The system that we studied was a carbon-powder–wax mixture, which Bueche[13] found to exhibit the percolation type of conductivity transition. The advantages of this system are that the conduction mechanism is known to be tunneling and this system can be easily handled and reproduced. The noise was found to diverge near the percolation threshold and to follow a simple power law.

The preweighed carbon powder and white wax (melting temperature $T_m = 58\,°\mathrm{C}$) were mixed at a temperature slightly higher than T_m. The mixture was very viscous at the mixing temperature and could be thoroughly stirred for a long period without precipitation of carbon powder due to the difference in density between carbon powder and wax. The mixtures were then filled into a rectangular ($10\times6\times2$ mm^3) cell. The diameter of individual carbon particles was less than 1 μm. The samples were annealed at 54 °C for 50 h to smooth out the possible irregular structures in the samples. The resistance and noise measurements were made by the four-probe method. The electric contacts were made by means of pressed indium wires. The current was provided by a constant-current source containing a battery and a series wire-wound resistor with resistance a factor of 10 higher than the sample resistance. The noise was amplified by a low-noise preamplifier (PAR 113) and Fourier analyzed by a spectrum analyzer (ONO SOKKI CF-500). Spectra were averaged 1024 times and stored in a microcomputer.

The percolative behavior of the resistance of the wax-carbon mixture was studied first. Figure 1(a) shows the dependence of the resistance of mixtures on the volume percentage of carbon powder. An abrupt drop of the sample resistance was found to occur at a critical value, $X_c = (10.8 \pm 0.1)\%$, of the carbon volume percentage X, which is a characteristic of percolative behavior as observed in other conductor-insulator mixtures.[12] This value of X_c is consistent with that from a least-squares fit of a power-law dependence of the measured sample resistance and noise spectral density on $X-X_c$, where X_c and individual exponents were treated as variable parameters. The data points were the average resistance of ten individually mixed samples. The error bars in Fig. 1(a) were determined by measurement of the standard deviation of the resistances of sixty samples of the same carbon composition. The error bars are larger for the samples close to the percolation threshold; this fact is consistent with the large fluctuations in the nature of samples near the percolation threshold and with a sensitive dependence of resistance on the carbon composition. An Ohmic behavior was found to be followed very well by our samples for applied voltages between 0.01 and 4 V, which is the range of interest. The resistance measurements could be fitted with a power-law dependence $R \propto (X-X_c)^{-t}$, where t is a critical exponent. Figure 1(b) shows a logarithmic plot of resistance vs $X-X_c$, for $X_c = (10.8 \pm 0.1)\%$. Our data show that $t = 2.3 \pm 0.4$. The X_c value is higher than what Beuche observed. We believe that this difference is due to the different methods of preparing the samples. The observed exponent t is consistent within error bars with the published data of other three-dimensional percolation systems.

The noise spectral density $S_v(f)$ was measured in the frequency range $0.1\ \mathrm{Hz} \leq f \leq 1\ \mathrm{kHz}$. The power spectra, $S_v(f)$, for the samples with resistance less than 500 kΩ were found to be proportional to V^2/f^α, where $\alpha = 1.1 \pm 0.1$, and V is the voltage drop across the sample. Hence, the electrical noise in this system was due to resistivity fluctuations in the mixture when a dc current flowed through the sample. Near the percolation threshold, the noise spectral density diverged very fast. Figure 2 shows the full logarithmic plot of $S_v(1\ \mathrm{Hz})/V^2$ against $X-X_c$ of the carbon-wax mixtures. The error bars were determined with the same method as for those in Fig. 1. The noise spectra were found to follow reasonably the power-law relation $S_v(f) \propto (X-X_c)^{-a}$, with $a = 5 \pm 1$. To our knowledge, this is the first time that the electric noise in such a disordered, random system has been observed to follow a simple functional dependence on a macroscopic parameter $(X-X_c)$ of the system. It will be clear later that this strong $X-X_c$ dependence can be



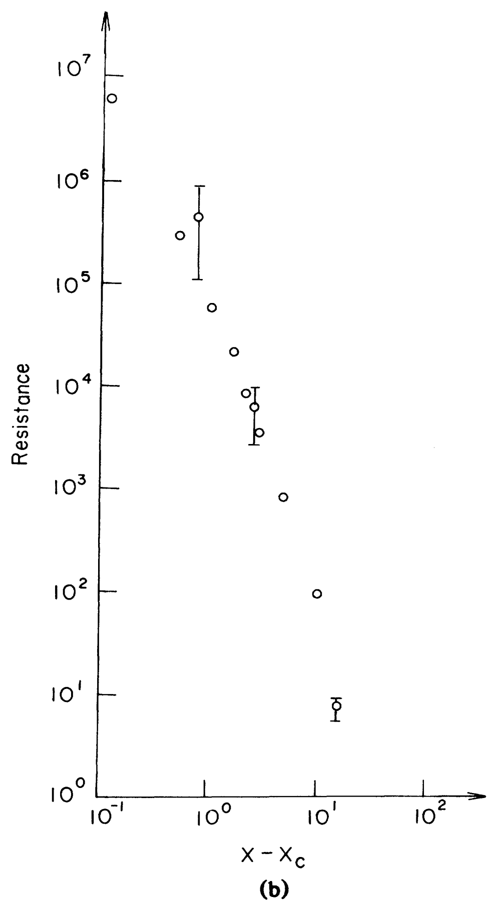


FIG. 1. (a) The dependence of the resistance of mixtures on the volume percentage of carbon powder. The critical carbon volume percentage $X_c = (10.8 \pm 0.1)\%$. (b) Logarithmic plot of resistance vs $X-X_c$.

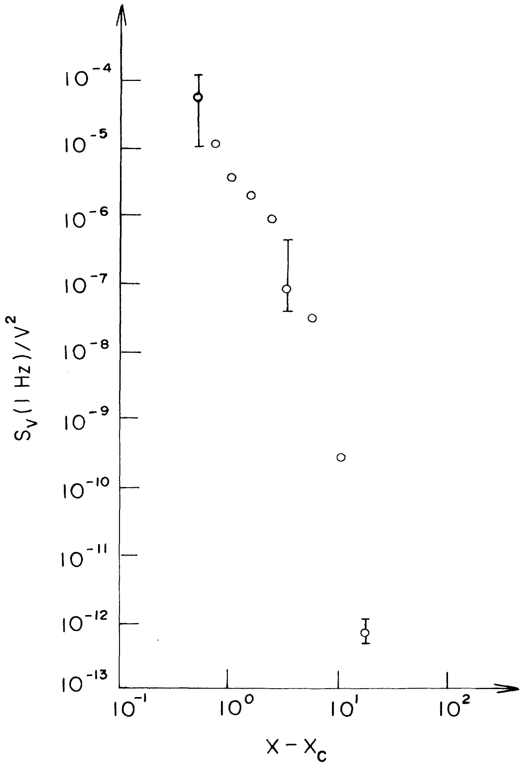


FIG. 2. Full logarithmic plot of $S_v(1\ \mathrm{Hz})/V^2$ against $X-X_c$ of the carbon-wax mixtures.

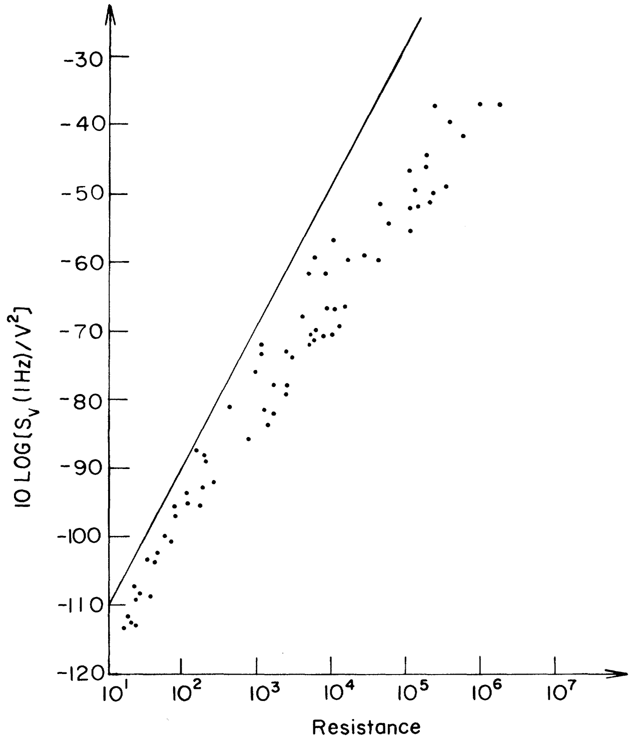


FIG. 3. Full logarithmic plot of the noise spectral density $S_v(1\ \mathrm{Hz})/V^2$ vs the sample resistance. The solid line denotes an R^2 dependence.

attributed to the fluctuations in the number of carriers in the infinite clusters in the percolative system.

For samples very close to the percolation threshold, the resistance is larger than 1 MΩ and the noise spectra usually decreased faster than the $1/f$ frequency dependence at high frequencies. This might be due to the capacitive effect of the anomalous dielectric constant near the percolation threshold.[14] Also observed were occasional bursts in the time-domain noise signals. Very close to the percolation threshold, only a few paths (infinite clusters) are formed for current conduction. Hence the current density in these paths is very high. The observed bursts might be attributed to the breaking of links between carbon clusters by local heating. In our measurements for the samples of high resistance (>30 kΩ), the applied currents were kept to a very low level (<0.1 μA) to avoid the unwanted bursts.

To our knowledge, there are no theories that explicitly deal with the electrical-conductivity fluctuations near the percolation threshold. Shklovskii[15] calculated the $1/f$ noise spectrum in lightly doped semiconductors by assuming that the conduction mechanism in this material is hopping, and proposed that his theory was applicable to systems near the percolation threshold. Shklovskii assumed that $1/f$ noise was due to fluctuations of the number of electrons in infinite clusters, caused by exchange of electrons between infinite clusters and nearby isolated finite clusters. With an $(X-X_c)$-dependent relaxation time of fluctuations, Shklovskii found that the relation between the spectral density of the current noise $S_I(f)$ and $X-X_c$ was $S_I(f)/I^2 \propto (1/P^2)\,dP/dX$, where $P(X)$ is the fraction of donors belonging to infinite clusters: $P(X) \propto (X-X_c)^\beta$ for $(X-X_c) \ll X_c$ and $P(X) \propto 1-e^{-X}$, for $X \gg X_c$. The $X-X_c$ dependence of $S_I(f)$ should be applicable to the voltage-noise spectral density $S_v(f)$; hence, $S_v(f) \propto (X-X_c)^{-1.4}$, with $\beta = 0.4$ for three-dimensional percolative systems.[12] This theory predicted too mild an $X-X_c$ dependence to explain what is shown in Fig. 2. The reason for this inconsistency might be that, in real systems, the number fluctuations of current carriers in the infinite cluster themselves dominate the noise-production mechanism.

Figure 3 shows the full logarithmic plot of the noise spectral density $S_v(f)/V^2|_{1\ \mathrm{Hz}}$ vs the sample resistance. Over a wide range of resistance, the relation between $S_v(f)/V^2|_{1\ \mathrm{Hz}}$ and R can be fitted by $S_v(f)/V^2|_{1\ \mathrm{Hz}} \propto R^b$ with $b = 1.7 \pm 0.2$. The noise spectral density $S_v(f)$ in the mixture system shows different character from Hooge's empirical formula for continuous metal films, which requires $S_v(f)/V^2 \propto 1/N_c \propto R$ for a given sample configuration. The observed relation between $S_v(f)$ and R shown in Fig. 3 is consistent with the data presented in Figs. 1 and 2, because from the data in Figs. 1 and 3 $S_v(f)/V^2 \propto R^{1.7 \pm 0.2} \propto (X - X_c)^{-4 \pm 0.6}$, which is within error bars of the results shown in Fig. 2. The observed resistance dependence can be reasonably explained by the fact that the electronic-conductive mechanism in the mixture system is tunneling, and the voltage noise in the system is due to the number fluctuations of charge carriers in the infinite clusters.[16] A phenomenological theory[16] of the noise in discontinuous metal films based on the tunneling mechanism predicts that $S_v(f)/V^2 \propto S_R(f)/R^2 \propto S_N(f)/N^2 \propto R^2$, where a McWhorter[17] type of distribution of the relaxation times is assumed. The R^2 dependence is just outside the error bar of the observed $R^{1.7 \pm 0.2}$ dependence of $S_v(f)/V^2$. We believe that this discrepancy is due to the fractal structure of our sample being different from the structure of discontinuous metal films.[10] Another possibly applicable theory is Pellegrini's theory[18] for the noise spectra of islands of conducting media. Pellegrini, on the basis of tunneling conduction, found that the carrier-number dependence of $S_v(f)$ was $S_v(f) \propto n_m^e/N$, where N is the total number of free carriers, $n_m = N/\Omega$, Ω is the sample volume, and the exponent e depends on the exponent of the frequency dependence of $S_v(f)$. In our experiments, $-\frac{5}{6} \leq e \leq 0.4$. Assuming $N \propto 1/R \propto (X - X_c)^{+a}$, one gets $S_v(f)/V^2 \propto (X - X_c)^{-d}$ with $d \approx 3.7 \pm 1$, which is consistent with our experiments only to the extent of overlapping error bars.

In summary, we have observed $1/f$ noise near the percolation threshold of carbon-wax mixtures. The noise spectrum $S_v(f)$ followed a simple power-law dependence on $X - X_c$, with $S_v(f) \propto (X - X_c)^{-5 \pm 1}$. The observed resistance dependence of $S_v(f)$ and the critical exponent for $S_v(f)$ suggest that $1/f$ noise in this mixture system might be generated by carrier-number fluctuations in the infinite clusters, and that the dominant noise-producing mechanism is tunneling conduction. Hence, the tunneling of charge carriers between clusters of conductors should be considered when one investigates the electronic properties of a percolative system. A detailed theoretical investigation of conductivity fluctuations near the percolation threshold is needed. Noise studies of this kind should provide new information on percolation phenomena.

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