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Impedance Spectra for a 2-D Conductor-Insulator Composite by Computer Simulation

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Abstract. Using a computational methodology, ac impedance spectra of macroscopic mixtures of conducting and insulating hard spheres which have random or regular arrangements of the components are studied. These simulations can be used to calculate the ac electrical properties of a multi-component composite using a personal computer.

It is shown in this study that ac impedance spectra are sensitive functions of the filling fraction and the geometrical arrangement of the components, and especially, the impedance spectra of the composite show the abnormal arc originated from the isolated clusters in the composite. From the simulated impedance patterns of the isolated clusters with various length, the abnormal arcs are shown to appear more distinctly when the elongated clusters are arranged along the preferred current line.

Keywords: percolation, impedance, geometrical arrangement, conductivity, simulation

PACS Code: 72.80.T (Composite materials-electrical conductivity)

1. Introduction

A composite is defined as a material made up of two or more different media, which are arranged, in a regular or irregular pattern. It is well known that the conductivity of electrical materials is strongly affected by the atomistic mechanism (charge carrier mobility and concentration, hopping rate etc.) and the microstructure (grain size distribution, grain morphology, porosity etc.). However, the effect of the detailed geometrical arrangement of constituents on the bulk properties of the composites is not known. The theoretical and experimental analyses of the conductivity of polycrystalline composites have been mostly focused on the identification of the underlying atomistic mechanisms and microstructure effects. This is due to the fact that one can hardly get an analytic solution that includes the geometrical arrangement effect. It is difficult to consider the positions of all components in a composite because they will change from sample to sample.

Recently, with the use of the modern frequency analyzer that can do the fast and precise measurements, impedance spectroscopy (IS) is gaining popularity for studying the electrical properties of composite materials. IS goes by various names, including modulus spectroscopy, dielectric spectroscopy, and immittance spectroscopy. Macdonald [1] gives a good overview, including many applications to solid-state phenomena. It should be understood as immittance, i.e., any form of the transfer function of two-terminal systems: impedance Z, admittance $Y = Z^{-1}$, modulus $M = j\omega C_0 Z$ and complex permittivity M^{-1}, where $j = \sqrt{-1}$, ω is angular frequency ($\omega = 2\pi f$) and C_0 is the permittivity of free space. A Nyquist plot (Z'' vs. Z') of two RC parallel circuits (R_1C_1, R_2C_2) connected in series, gives two semicircles with the diameters of R_1 and R_2 whose centers lie on the Z' axis at $R_1/2$ and $R_1 + R_2/2$. Impedance data are often plotted either in Z'' vs. Z', or in M'' vs. M' in order to get the higher resolution. In M'' vs. M' plot, the centers of two semicircles are located at

$1/(2C_1)$ and $1/C_1 + 1/(2C_2)$, respectively. In theory, we can analyze more complex circuits in a similar fashion, as long as the time constants (the RC products of the subcircuits) are sufficiently different from each other to permit deconvolution of the spectrum. When the system is not well defined, however, a researcher resorts to the equivalent circuit analysis, fitting the data by trial and error to the different electrical circuits [2]. In many cases, the analogy rests on the assumptions that it is possible to model the polycrystalline composite with a series-parallel combination of linear passive elements.

The objective of this paper is to study the effects of geometrical arrangement on the ac impedance spectra of polycrystalline composites. The impedance spectra were obtained by computer simulations of 2-D electrical composites. The simulations were made utilizing a modified transfer matrix algorithm for the triangular network. The simulation results were compared with a series circuit model and McLachlan's generalized effective medium theory (GEMT) [3]. For the model of 2-D close packed hard spheres, small spheres of a homogeneous phase are assumed to be mixed with similar articles of a second phase and the two types of crystalline spheres fill the space in a close-packed pattern.

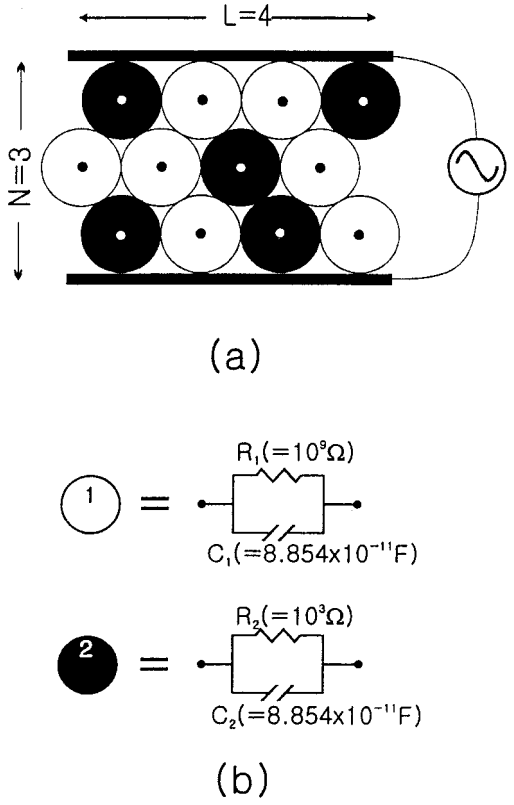

Fig. 1. (a) An example of the close packed hard spheres model of $N=3$ and $L=4$, (b) the values of the resistance and capacitance of one sphere used in this study.

2. Methodology

We have carried out the numerical simulations for the systems of close-packed mixture of hard spheres (Fig. 1a), placing a sample between two flat parallel plates of electrodes. The resistivity (ρ, Ω/sphere) and the permittivity (ε, F/sphere) are assigned as the resistance and capacitance of one sphere, respectively. For the simulation, the values of ρ_1 and ρ_2 are given as 10^9 [Ω/sphere] and 10^3 [Ω/sphere], respectively. Both ε_1 and ε_2 are given as 8.854×10^{-11} [F/sphere]. Two kinds of spheres used in the simulations correspond to two RC parallel circuits as shown in Fig. 1b. The values of spheres were chosen to reflect the case where the conductive particles were introduced into the insulating matrix of the same permittivity.

As shown in Fig. 2a, the simulation system corresponds to the triangular network-site percolation problem. The lattice points correspond to the centers of spheres. Each rectangle connecting the lattice points represents the impedance between the centers of neighboring spheres as shown in Fig. 2b. We used the transfer-matrix algorithm to calculate the conductivity of each triangular network of $N \times L$. The transfer-matrix algorithm calculates the resistance value of new lattice from the known current-voltage relation of old lattice when one column of resistors are added. Old admittance matrix which contains current-voltage relation at each lattice point is updated into the new admittance matrix. The total conductivity is calculated from the element of the inverted admittance matrix. This algorithm, which was originally developed by Derrida and coworkers [4] for the dc resistance calculation of square network-bond percolation problem, is modified for the ac impedance value of triangular network-site percolation problem in this paper. The diagonal admittance matrix is newly introduced for the triangular network, and all elements of matrix are complex numbers for ac impedance simulation. We used Marsaglia's algorithm [5] to generate random numbers. The transfer-matrix algorithm and Marsaglia's algorithm are very simple and

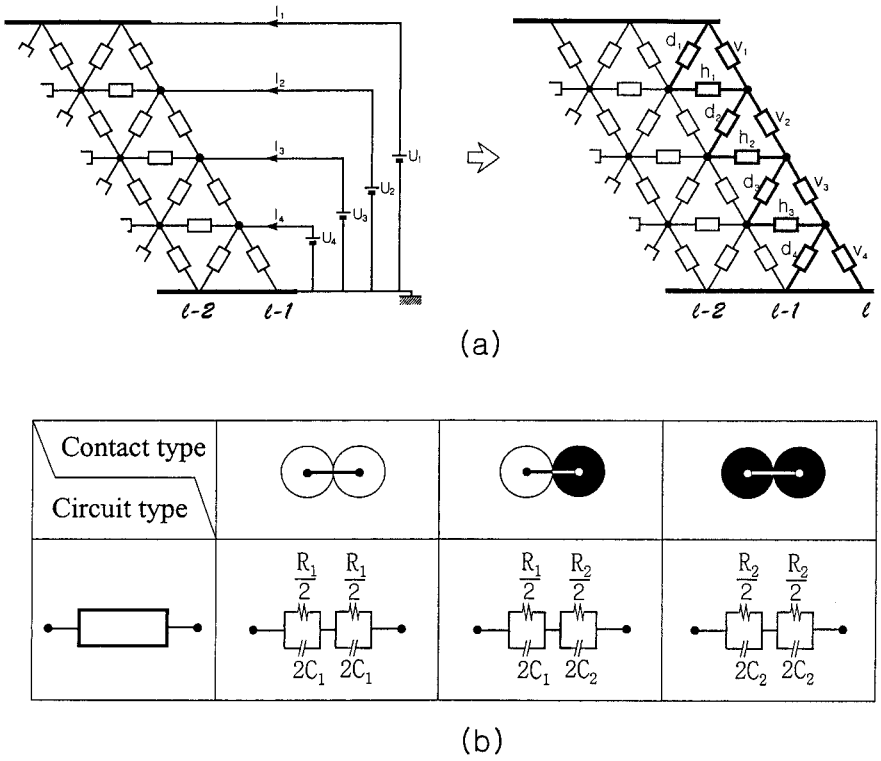

Fig. 2. (a) The triangular lattice corresponding to the model and recursive construction of a strip by adding the horizontal h_i, diagonal d_i and oblique v_i impedances. Black dots indicate the centers of spheres. (b) The h_i, d_i and v_i values between the centers of spheres, which are denoted as the rectangular boxes in (a), are determined by the types of contacting spheres.

need less memory so that they make the ac impedance simulation possible on the personal computer. In this study, all simulations are made over a mesh of 30×100 spheres by an IBM compatible personal computer.

The following is the brief explanation of the transfer-matrix method for the triangular lattice. The matrix A_{l-1} gives, by definition, the currents I_i as functions of the potential U_i

$$\begin{pmatrix} I_1 \\ I_2 \\ \vdots \\ I_{N+1} \end{pmatrix} = A_{l-1} \begin{pmatrix} U_1 \\ U_2 \\ \vdots \\ U_{N+1} \end{pmatrix} \tag{1}$$

In the transfer-matrix algorithm, the admittance matrix A_{l-1} is updated to a new matrix A_l when horizontal impedances h_i, diagonal impedances d_i, and oblique impedances v_i are inserted. Three values of the inserted resistors are determined by the types of neighboring spheres as shown in Fig. 2b. Then, the matrix A_l has the recursion relation with $A_l - 1$:

$$A_l = (A_{l-1} + D)\{1 + H(A_{l-1} + D)\}^{-1} M + P \tag{2}$$

and the matrixes H, D, M and P are given:

$$H = h_i \delta_{i,j} \tag{3}$$

$$D = \left(\frac{1}{d_{i-1}}\right)\delta_{ij} - \left(\frac{1}{d_i}\right)\delta_{i+1,j} \tag{4}$$

$$M = \delta_{i,j} + \left(\frac{h_i}{d_{i-1}}\right)\delta_{i,j+1} \tag{5}$$

$$P = \left(\frac{1}{d_i} + \frac{1}{v_i} + \frac{1}{v_{i-1}}\right)\delta_{i,j} - \left(\frac{1}{d_{i-1}} + \frac{1}{v_{i-1}}\right)\delta_{i,j+1} - \left(\frac{1}{v_i}\right)\delta_{i+1,j} \tag{6}$$

Here, $\delta_{i,j}$ is the Kronecker delta:

$$\delta_{i,j} = \begin{cases} 0; & i \neq j \\ 1; & i = j \end{cases}$$

The formalism remains valid for $i = 1$ when one takes $h_1 = 0$, $1/d_0 = 0$ and $1/v_0 = 0$. This recursive process is iterated up to the end of lattice, L. Then, we can aquire the total conductivity (σ_{tot}):

$$\sigma_{tot} = \left(2A_L^{-1}(1,1)\right)^{-1} N/L \tag{7}$$

Here, the total conductivity σ_{tot} is normalized and defined as the conductance of one sphere.

3. Results and Discussion

The impedance spectra are presented in M-plots because M-plots have better resolution than Z-plots when the difference of the time constants is due to the difference of the resistance values. The frequency in simulation ranges from 10^{-2} Hz to 10^{2} MHz and reflects the frequency range of many impedance analyzers.

The simulated impedance spectra with completely-random patterns of two spheres are given in Fig. 3. Figure 4 shows the calculated impedance spectra of a series circuit model and the generalized EMT (GEMT) which are often used to analyze the electrical components of ploycrystalline materials. The equations generating the impedance spectra are as follows: When σ_1 and σ_2 are the conductivities of the basic constituent 1 and 2, respectively, and p_2 is the volume fraction of the constituent 2, the series circuit model gives the following equation:

$$\sigma_{tot}^{-1} = (1 - p_2)\sigma_1^{-1} + p_2\sigma_2^{-1} \tag{8}$$

where σ_{tot} is the real or complex conductivity of the composite. McLachlan and coworkers have presented a GEMT, which takes into account an effective percolation threshold (p_{eff}) and a critical exponent (t) into Bruggeman's effective medium theory (BEMT) formula [6]:

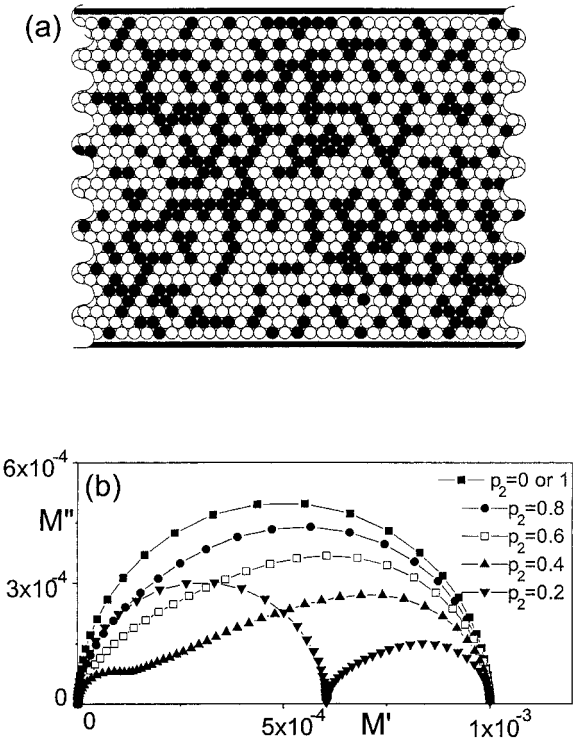

Fig. 3. (a) An example of completely-random patterns with $N = 30$, $L = 100$. Here, p_2 is about 0.35. (b) Simulated M-plots for completely-random patterns at various p_2.

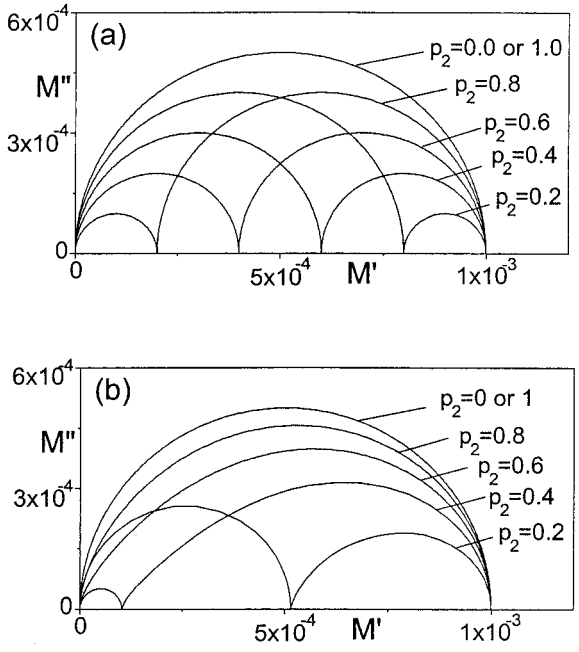

Fig. 4. M-plots calculated by the analytical equations of (a) series circuit model, and (b) GEMT with $p_{eff} = 0.47$ and $t = 1.2$.

$$\frac{(1-p_2)(\sigma_1^{1/t}-\sigma_{tot}^{1/t})}{\sigma_1^{1/t}+\left(\frac{1-p_{eff}}{P_{eff}}\right)\sigma_{tot}^{1/t}} + \frac{p_2(\sigma_2^{1/t}-\sigma_{tot}^{1/t})}{\sigma_2^{1/t}+\left(\frac{1-p_{eff}}{P_{eff}}\right)\sigma_{tot}^{1/t}} = 0 \tag{9}$$

The effective percolation threshold p_{eff} is generally defined as the filling fraction at which a percolating cluster connects the top to the bottom of the sample for the first time. In the real system, however, it was difficult to determine whether the composite was percolated, or not, by this definition. Thus, we proposed the new definition of p_{eff} as the filling fraction at which the variance of the properties of the system had maximum values, and determined p_{eff} of the present system (the triangular lattice with the size of 30×100) to be 0.47 in a previous study [7]. The value of t is determined to be 1.2 which best fits the impedance spectra of completely-random patterns.

The simulated ac impedance spectra of completely-random patterns (Fig. 3b) are similar to those of the GEMT (Fig. 4b). The ac impedance of completely-random pattern is expected to be similar to those of the GEMT since both patterns are based on the configuration of two interspersed spherical components.

However, a few impedance shapes of random patterns show a clear difference from the GEMT patterns at filling fractions away (about $p_2 = 0.2 \sim 0.4$) from p_{eff} in a sense that they show more overlapped semicircles. Figure 5 shows the detailed ac impedance spectra of completely-random patterns in the region $p_2 = 0.1 \sim 0.5$. As shown in Fig. 5, the third semicircle with the peak frequency of ω_3, which is about $10^{-1} \times \omega_2$, grows as the filling fraction p_2 increases. Thus, it is shown that the apparent third semicircle appears for a two-component system at certain compositions. The observation of three semicircles for a two-component system is not clear but may be explained as follows. The size of the clusters composed of black spheres increases as p_2 increases from 0 to p_{eff}, and some clusters span from the bottom to the top of the sample at p_{eff}. The number of isolated clusters, however, decreases as p_2 approaches p_{eff}, and only one or a few clusters exist at p_{eff}. The isolated clusters of very different size and shape exist in the sample at filling fractions away from p_{eff}. The new semicircle may appear in impedance spectra due to these isolated clusters of different size and shape. This interpretation is verified in the following simulations.

When the distribution of spheres has no-contact random patterns as shown in Fig. 6a, ac impedance spectra can be analyzed by a two-component series circuit model as shown in Fig. 6b. In no-contact random patterns, black spheres are distributed

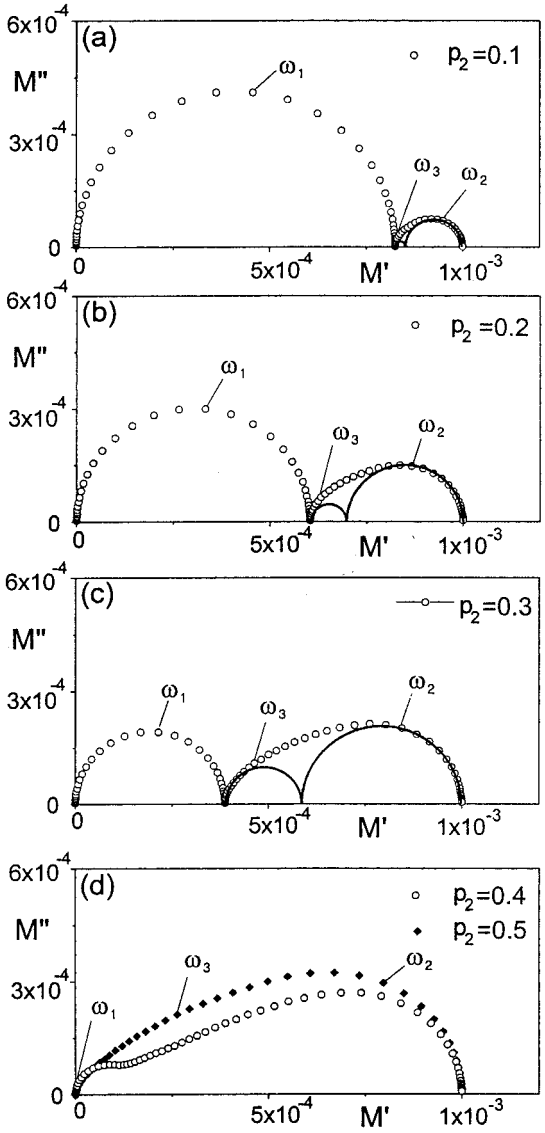

Fig. 5. Simulated *M*-plots for the completely-random patterns of $N = 30$, $L = 100$: The bold semicircles are for the arcs analyzed by the equivalent circuit model. ω_1 and ω_2 are the peak angular frequency (the inverse of time constant) for sphere 1 and sphere 2, respectively. $\omega_1/2\pi$ and $\omega_2/2\pi$ are about 2 Hz and 2×10^6 Hz, respectively. ω_3 is the peak angular frequency of the third semicircle, and $\omega_3/2\pi$ is about 2×10^5 Hz.

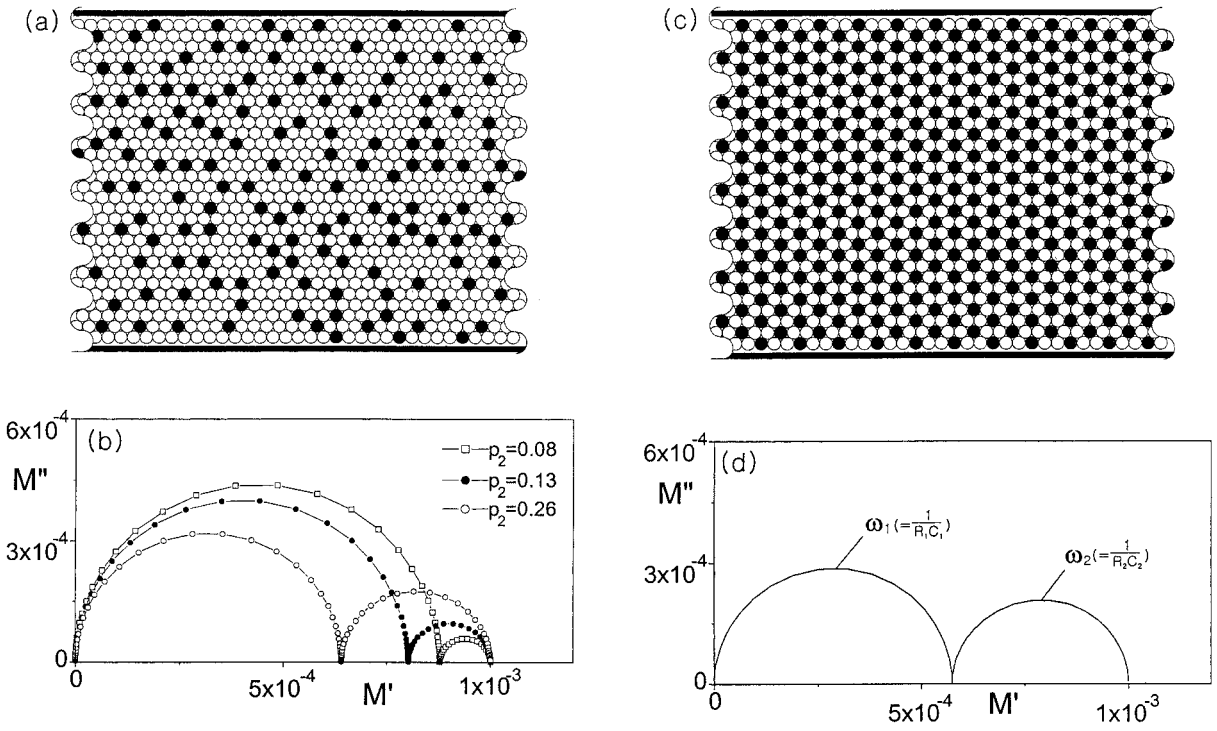

Fig. 6. (a) An example for no-contact random patterns where black spheres are randomly distributed but prohibited from contacting each other ($N = 30$, $L = 100$). Here, p_2 is about 0.26. (b) Simulated M-plots for no-contact random patterns. (c) Typical ordered distribution and (d) simulated M-Plots for the ordered distribution ($N = 30$, $L = 100$). p_2 is 0.335.

randomly, but forbidden to contact each other, thus no black clusters form. The frequencies at the apexes of the semicircles are those expected from the semicircles representing white and black spheres, i.e., $\omega_1(=1/R_1C_1)$ and $\omega_2(=1/R_2C_2)$. The third semicircle is not observed although the filling fraction, p_2 reaches as high as 0.26. When the filling fraction increases further, the distribution loses randomness since the number of sites, which may be occupied by black spheres without contacting each other, is limited. The distribution of black spheres needs an ordered arrangement as shown in Fig. 6c in order to get the higher filling fraction on the condition of no contact between black spheres. The third semicircle is not observed in Fig. 6d. These impedance spectra which do not show the third semicircle can be analyzed very well by the series circuit model (Fig. 4a).

When the branched clusters, which imitate the isolated clusters formed in the completely-random patterns, are arranged obliquely as shown in Fig. 7a, the third semicircle (ω_3) appears clearly as shown in Fig. 7b. From these observations, the third semicircle seems to originate from the clusters formed in the composite, and the morphology of the clusters seems to play a major role in generating the third semicircle.

When the horizontal-clusters are introduced as shown in Fig. 8a, the third semicircle is not observed as shown in Fig. 8b. The ratio of two diameters of the semicircles is equal to the ratio of two volume fractions ($p_1 = 0.818$, $p_2 = 0.182$). So, this impedance spectrum is analyzed nicely by the two-phase series circuit model (Eq. (8) and Fig. 4a). However, the overlapping third semicircle appears as shown in Fig. 9b when the oblique-clusters are introduced (Fig. 9a). The diameter of the third semicircle decreases (Fig. 9b and 9d) as the length of oblique-clusters decreases as shown in Fig. 9a (23 spheres-long) and 9c (5 spheres-long). For the very small clusters (two spheres form one cluster as shown in Fig. 9e), the effects of clusters are also very small as shown in Fig. 9f. If there are no contacts between black spheres (Fig. 9g), impedance spectra are well separated again into two semicircles (hereafter, ω_1 and ω_2 semicircles) having peak frequencies at ω_1 and ω_2 without showing the third semicircle, as shown in Fig. 9h.

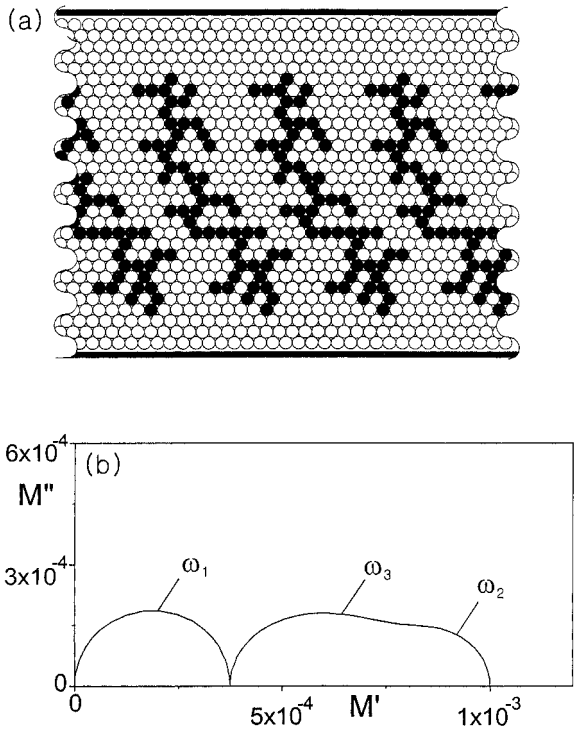

Fig. 7. (a) The branched clusters are distributed obliquely. (b) Simulated *M*-Plots for the branched cluster pattern of p_2 equal to 0.2.

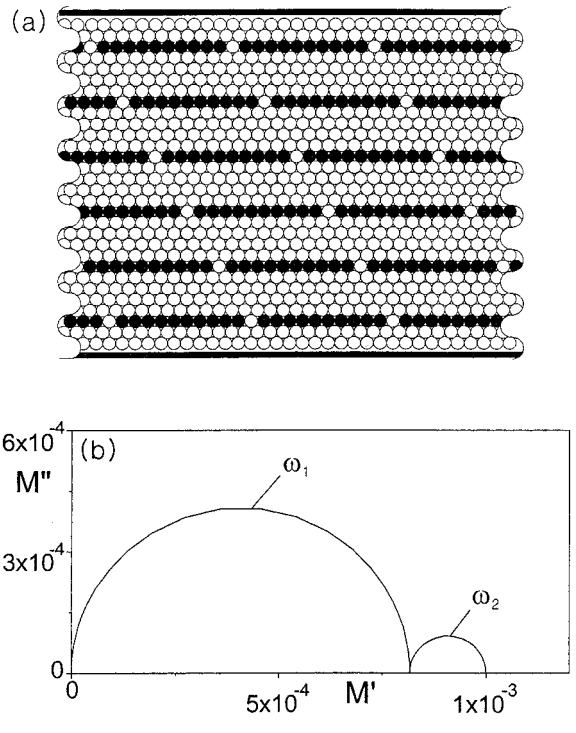

Fig. 8. (a) Ten black spheres are horizontally distributed. (b) Simulated *M*-Plots for the horizontal distribution. Here, p_2 is about 0.182.

The length of the oblique-clusters also affects the diameter of ω_1 semicircle. The difference between the diameter ratio and the filling fraction ratio increases as the length of oblique-clusters increases. As shown in Fig. 9b, the filling fraction of white spheres, estimated by using the ratio of the diameter of ω_1 semicircle to the entire $\omega_1\omega_2\omega_3$ diameter, is only $p_1 = 0.33$ although the filling fraction is actually $p_1 = 0.872$. These simulation results imply that the filling fraction may be estimated incorrectly from the radius ratio of semicircles in many experiments. Only for the composite with no cluster (Fig. 6) or the horizontally layered cluster (Fig. 8), the filling fractions of components may be estimated directly from the ratio of two diameters of the semicircles in the impedance spectra.

The analysis of various patterns suggests that the appearance of the third semicircle is due to the elongated clusters oriented in the direction of the preferred current line. The preferred current line is defined, here, as the shortest current path between two electrodes. In the present lattice, the shortest path between two electrodes is the oblique direction. However, in most real materials, the preferred current line is perpendicular to the electrodes. Thus, it is expected that the clusters arranged perpendicular to the electrodes generate the clearer third semicircle in real systems. The effects of the elongated clusters on the ac impedance spectra shown in these simulatins are also expected to be observed in real composites, such as the film with the included conducting whisker, or the bulk composites with the included conducting plates.

We now understand that the elongated clusters generate the third semicircle as if there is another component connected in series, in addition to the known two components. It is necessary to explain why the elongated clusters generate the third semicircle with the distinctive time constant in the ac impedance sepctra. The series equivalent circuit model assumes the charge carriers passes through the regions of different time constants sequentially. Therefore, the explaination with the series equivalent circuit model should assume that the charge carriers, in the pattern including the elongated cluster arranged along the preferred current line, should experience three regions

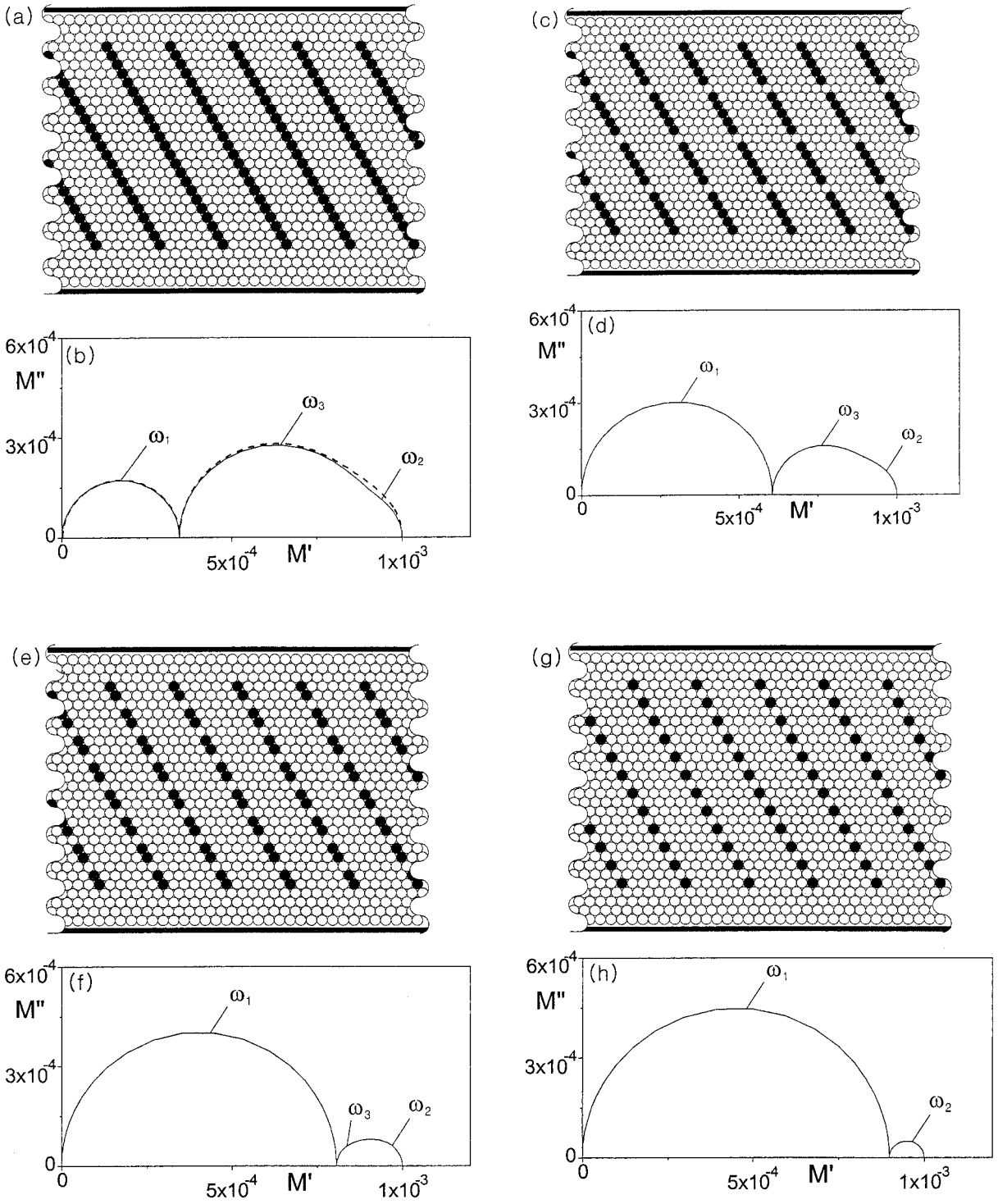

Fig. 9. The distribution patterns (a,c,e,g) which show black-sphere clusters, with various length arranged in oblique direction and the resultant simulated modulus patterns (b,d,f,h) for the corresponding distribution patterns. The elongated clusters are (a) 23 spheres, (c) 5 spheres, (e) 2 spheres and (g) 1 sphere long. The dotted line shown in (b) is the curve fitted by the Eq. 10 with $p_1 = 0.344$, $p_2 = 0.14$ and $p_3 = 0.516$.

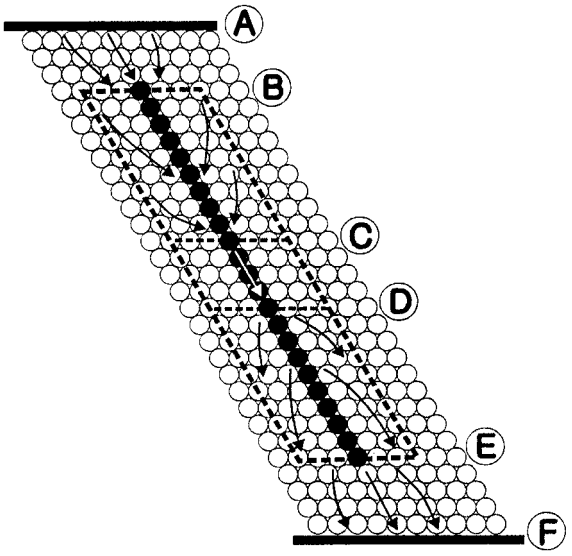

Fig. 10. Some portion of Fig. 9a pattern is shown to explain the proposed equivalent circuit model. Arrows indicate the direction of current flows. The region inside the dotted line may be seen by the charge carriers as the new component.

of different time constants. Fig. 10 shows a portion of Fig. 9a for clarity. When the charge carriers start to flow downwards with the application of potential, they go through a region of white spheres. This A-B region of white spheres is represented as the time constant $1/\omega_1$, or ω_1 semicircle. In the B-C region, the charge carriers bend toward the included elongated clusters of black spheres as shown in the Fig. 10, which are much more conductive than the white spheres. The B-C region inside the dotted line in Fig. 10 resembles a new component with different time constant, and is modeled by the parallel combination of one black sphere and approximately five white spheres. The parallel combination of several R_1C_1 parallel circuits with one R_2C_2 parallel circuit increases the time constant from $1/\omega_2$ to $1/\omega_3$. Thus, the length of the black elongated clusters changes mainly the diameter of the semicircle not the time constant. When charge carriers move through the elongated clusters in C-D region, they generate ω_2 semicircles because they are confined in the more conductive black spheres. Region D-E and E-F are expected to show similar effect of region B-C and A-B, respectively, thus contributing to the generation of ω_3 and ω_1 semicircles.

With the decreasing length of the elongated clusters, the region affected by the bending current is diminished and the region unaffected by this current grows, as indicated by the shrinking ω_3 semicircle and enlarging ω_1 semicircle, respectively, shown in Fig. 9d. and 9f. When M_1, M_2 and M_3 are considered as the three electrical components of the composite with time constants, $1/\omega_1$ $(=R_1C_1)$, $1/\omega_2$ $(=R_2C_2)$ and $1/\omega_3$ $(=R_3C_3)$, respectively, the total modulus of the series connection of three components is given by:

$$M_{tot} = p_1M + p_2M_2 + p_3M_3 \tag{10}$$

Here, p_1, p_2 and p_3 are the fractions of M_1, M_2 and M_3 circuits, respectively. M_3 is represented roughly as the parallel combination of five M_1 circuits and one M_2 circuit. Since $R_1 \gg R_2$ and $C_1 = C_2$, the time constant of ω_3 semicircle is 6 times larger than that of ω_2 semicircle. Thus, ω_2 and ω_3 semicircles overlap in a modulus plot. When Fig. 9b is best fitted with Eq. (10), $p_1 = 0.344$, $p_2 = 0.140$ and $p_3 = 1 - p_2 - p_2 = 0.516$ are obtained. The best fitting curve is shown as the dotted line in Fig. 9b. Thus, the distribution shown in Fig. 9a is seen by the charge carriers as the series combination of 34.4% white spheres, 14.0% black spheres and 51.6% new spheres of intermediate time constant.

We have qualitatively shown that the appearance of the third semicircle is due to the effect of current flow in the insulator-conductor composite. The current distribution effect is pronounced when the elongated clusters are arranged along the preferred current direction. Although we have chosen the modulus (M' vs. M'') plot to show the composite effect on the impedance of a two phase mixture, a similar effect may be shown in the impedance (Z' vs. Z'') plot with the properly adjusted values of the circuit parameters.

4. Conclusions

Impedance plots are useful in determining the appropriate equivalent circuit and estimating the values of the circuit parameters. Although the process is straightforward in some cases, it is not obvious what portion of the equivalent circuit corresponds to what component in materials. These problems are settled by various experimental methods for the given impedance plot. However, until now the effect of geometrical arrangement was hardly considered.

We have numerically simulated the ac impedance spectra of two-dimensional $N \times L$ macroscopic

mixtures of hard spheres, and compared the results with the series circuit model and the effective medium model. These simulations can be used to calculate the ac electrical properties of multi-component composites using a personal computer. They enable us to investigate the effects of geometrical arrangement for both random and regular distributions of the material components.

It is shown in this study, for the first time, that the impedance spectra of the two-component composites may show three arcs due to the geometrical arrangement effects in the vicinity of the effective percolation threshold. It is also proved that the third semicircle originates from the isolated clusters arranged along the preferred current line. The effect of the elongated clusters on the current distribution, and thus on the generation of the third semicircle was explained by a series of simulations using clusters of variable length. Although the series circuit model is widely used for the analysis of impedance of polycrystalline materials to separate grain interior and grain boundary conductivities, the interpretation of impedance spectra for the multi-phase mixture may be used with care.

Finally, it is emphasized that the effects of geometrical arrangement must be seriously considered in the analysis of the electrical properties of composites, especially when the system exhibits percolation phenomena and the filling fraction is near p_{eff}.

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