Computer simulation of electrical conductivity of colloidal dispersions during aggregation

N. I. Lebovka,[1] S. Tarafdar,[2] and N. V. Vygornitskii[1]
[1]*F. D. Ovcharenko Biocolloid Chemistry Institute, 42 Vernadsky Av., Kyiv, Ukraine*
[2]*Condensed Matter Physics Research Centre, Physics Department, Jadavpur University, Kolkata 700032, India*
(Received 1 October 2005; revised manuscript received 15 December 2005; published 7 March 2006)

The computation approach to the simulation of electrical conductivity of colloidal dispersions during aggregation is considered. We use the two-dimensional diffusion-limited aggregation model with multiple-seed growth. The particles execute a random walk, but lose their mobility after contact with the growing clusters or seeds. The two parameters that control the aggregation are the initial concentration of free particles in the system p and the concentration of seeds ψ. The case of $\psi=1$, when all the particles are the immobile seeds, corresponds with the usual random percolation problem. The other limiting case of $\psi=0$, when all the particles walk randomly, corresponds to the dynamical percolation problem. The calculation of electrical conductivity and cluster analysis were done with the help of the algorithms of Frank-Lobb and Hoshen-Kopelman. It is shown that the percolation concentration ϕ_c decreases from 0.5927 at $\psi=1$ to 0 at $\psi\to 0$. Scaling analysis was applied to study exponents of correlation length ν and of conductivity t. For all $\psi>0$ this model shows universal behavior of classical $2d$ random percolation with $\nu\approx t\approx 4/3$. The electrical conductivity σ of the system increases during aggregation reaching up to a maximum at the final stage. The concentration dependence of conductivity $\sigma(\phi)$ obeys the general effective medium equation with apparent exponent $t_a(\psi)$ that exceeds t. The kinetics of electrical conductivity changes during the aggregation is discussed. In the range of concentration $p_c(\psi)<p<0.5927$ the time of percolation cluster formation τ_c decreases with increasing ϕ.

DOI: 10.1103/PhysRevE.73.031402 PACS number(s): 61.43.Hv, 64.60.Ak, 72.60.+g, 83.80.Hj

I. INTRODUCTION

Conductometric techniques are frequently used in the study of composite colloids, suspensions, and emulsions [1]. The conductance behavior is a complex function of particle concentration, their size, form and geometrical arrangement, particle-to-medium conductivity ratio σ_p/σ_m, degree of aggregation, temperature, and many other factors [2].

A quantitative prediction of the effective electrical conductivity σ of such systems is a difficult problem dating back to work by Maxwell [3]. For binary systems considered in this paper in the vicinity of percolation threshold $p\approx p_c$ the effective conductivity behaves as a power law [4]

$$\sigma=\sigma_m[(p_c-p)/p_c]^{-s} \quad \text{at } p_c>p, \tag{1}$$

and

$$\sigma=\sigma_p=[(p-p_c)/(1-p_c)]^t \quad \text{at } p_c<p, \tag{2}$$

where p is the filling fraction of the particles with conductivity σ_p, p_c is the critical percolation concentration, s and t are the electrical conductivity exponents, $s=t\approx 4/3$ in $2d$, and $s\approx 0.73$, $t\approx 2.0$ in $3d$ [4].

For fitting of conductivity data in the entire composition range, $0\leqslant p\leqslant 1$, the empirical model [5] based on combination of the mean-field and percolation theories is commonly used. This model is applicable to systems with strong percolation effects and it gives the *general effective medium* (GEM) equation:

$$\frac{(1-p)(\sigma_m^{1/s}-\sigma^{1/s})}{\sigma_m^{1/s}+A\sigma^{1/s}}+\frac{p(\sigma_p^{1/t}-\sigma^{1/t})}{\sigma_p^{1/t}+A\sigma^{1/t}}=0, \tag{3}$$

where $A=(1-p_c)/p_c$.

Modifications for the GEM equation for anisotropic systems are discussed in Ref. [6]. The different aspects of the electrical conductivity of heterogeneous systems are comprehensively reviewed in Ref. [7]. The major restriction of the GEM equation is in the neglecting of the real geometrical arrangement and aggregation of the particles. The introduction of the percolation theory in the calculations accounts for the network formation in the systems. But percolation parameters of the model s,t,p_c are empirically fitted to the experimental data [5] and do not have a clear correlation with the real microstructural geometrical arrangement of the particles. It is well known that interaction between particles influences the value of the percolation threshold p_c [8] and long-range correlations result in nonuniversality of critical exponents dependent on a parameter that characterizes the nature of the correlations [9]. The dependence of the electrical conductance σ versus concentration p may reflect the existence of interparticle interactions and their aggregation in correlated-percolation model [10]. Experimentally the influence of aggregation on conductance was studied in only a limited number of works [11,12]. A simplified model describing changes in electrical conductivity during irreversible aggregation of colloidal systems was previously reported in Ref. [11].

The purpose of this paper is to analyze the electrical conductivity for a two-dimensional multiple-seed diffusion-limited aggregation (DLA) model [13] and to demonstrate a correlation between the character of the σ vs p curves and the parameters that control aggregation.

II. AN AGGREGATION MODEL AND THE DETAILS OF CALCULATION

In this work we used the two-dimensional model of diffusion-limited aggregation at multiple growth sites that is similar to those proposed in Ref. [13]. This model generates clusters with fractal structure on short length scales and a uniform structure on long length scales. Initially the $N=pL^2$ particles are randomly placed on a square lattice of size $L\times L$. The concentration of particles is defined as $p=N/L^2$, $0<p<1$. A fraction of particles $N_s=\psi N$, where ψ is the concentration of immobile seeds ($0\leqslant\psi\leqslant 1$) are identified as growth sites and kept fixed. The other particles are mobile and execute random walks until they come in contact with one of the growing clusters or seeds. The initial number of mobile particles $N_m=N(1-\psi)$ continuously decreases until complete aggregation for the system. Each attempt of the particle to move is one time step, denoted by $d\tau=1/N_m$. During the simulations periodic boundary conditions are used.

When the initial concentration of particles is higher than some critical value p_c the different clusters coalesce and a percolation cluster spanning the lattice is formed. The case of $\psi=1$, when all particles are immobile seeds, corresponds to the usual random percolation problem [4]. The other limiting case $\psi=0$, when the particles continuously undergo random walks, corresponds to the dynamical percolation problem [14].

In order to identify clusters and determine the percolation concentration p_c, we used a cluster numbering algorithm by Hoshen and Kopelman [4,15]. The value of p_c for a single configuration was determined to a precision of $1/L^2$. The percolation threshold for the infinite system p_c^∞ was estimated using the finite-size scaling relation [4]

$$p_c(L) = p_c^\infty + aL^{-1/\nu}, \tag{4}$$

where a is a constant and ν is a correlation length exponent.

The value of ν was estimated by analyzing the scaling behavior of standard deviation of percolation concentration, $\Delta p_c=\sqrt{\langle p_c^2\rangle-\langle p_c\rangle^2}$,

$$\Delta p_c \propto L^{-1/\nu}. \tag{5}$$

The electrical conductivity of the system was calculated as follows. The lattice sites were replaced by equivalent resistors as shown in Fig. 1. For studying strong percolation effects we suppose that particles are conductors and their electrical conductivity σ_p is very high compared to the electrical conductivity of the medium σ_m (these are empty sites on the lattice). In this work the ratio of electrical conductivities $f=\sigma_p/\sigma_m$ was 10^9. For calculating the conductance of lattices we used an algorithm by Frank and Lobb [16] and data are averaged over 100 different initial configurations.

III. RESULTS AND DISCUSSION

A. Percolation threshold p_c

Figure 2 presents the dependences of the standard deviation Δp_c versus size of lattice L obtained for the different values of ψ. The dashed lines correspond to the classical correlation length index $\nu=4/3$ of a $2d$ random percolation problem [4]. As follows from presented data in the limit of large systems, $L\to\infty$, the classical scaling behavior with index $\nu=4/3$ is observed for different ψ. For small systems deviations from scaling law of Eq. (4) are evident. This behavior can be explained by the influence of the lattice size on the regime of isolated cluster growth in the model of multiple growth sites. This regime is important when the separation between growth sites is large [13].

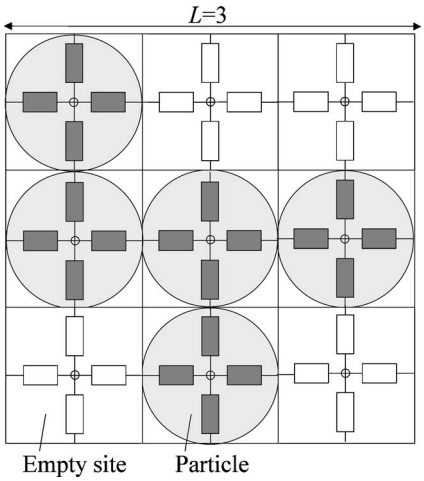

FIG. 1. On the calculating the conductance of lattice. Each site is substituted by four resistances. It is assumed that the particles represent more electrically conductive phase with conductivity σ_p (shown in a gray color) and conductivity of a matrix σ_m is low (shown in a white color).

For systems of small size, $L<L_c\approx 1/\sqrt{p\psi}$, the number of growth sites is limited that is illustrated by the patterns presented in Fig. 2 for $L=64$ (1 growth site) and for $L=256$ (28 growth sites)

Figure 3 presents percolation threshold p_c^∞ versus concentration of immobile seeds ψ. At $\psi=1$ the model under con-

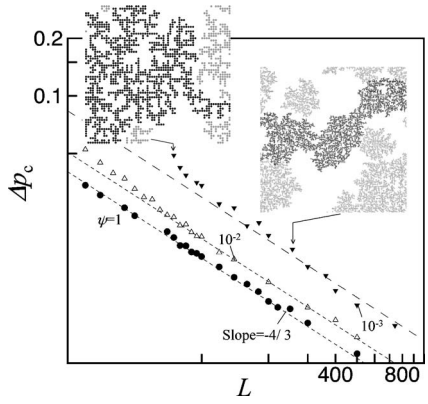

FIG. 2. Standard deviation of percolation concentration Δp_c versus lattice size L at different values of immobile seed concentration ψ. Dashed lines correspond to the slope $-3/4$. Patterns display cluster structures at $L=64$ and $L=256$ for $\psi=10^{-3}$ at the percolation point. The percolation clusters are shown in black color and other clusters in gray. The values of Δp_c are calculated for the simulation of 1000 different starting configurations.

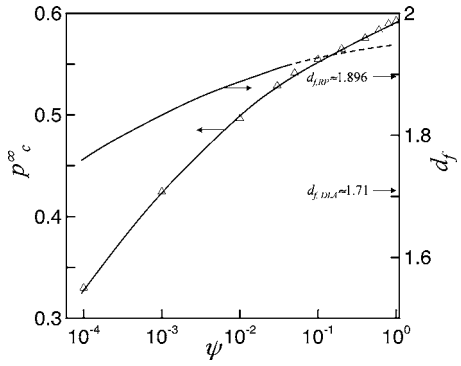

FIG. 3. Percolation threshold p_c^∞ and effective fractal dimensionality of clusters d_f vs concentration of immobile seeds ψ. Arrows show the values of $d_{f,RP} \approx 1.896$ (see Ref. [4]) for random percolation and $d_{f,DLA} \approx 1.71$ (see Ref. [17]) for DLA model, respectively.

sideration is equivalent to the model of random percolation for which $p_c^\infty \approx 0.5927$. The percolation threshold p_c^∞ decreases with decreasing ψ. So, the model of diffusion-limited aggregation with multiple growth sites represents a variant of the correlated-percolation model when the percolation threshold p_c^∞ depends on a parameter characterizing the nature of correlations, namely ψ [8].

The character of p_c^∞ vs ψ dependence may be qualitatively estimated, at least at small ψ, from the following considerations. At $\psi \ll 1$ the separation between growth sites is large and in early stage of aggregation the isolated clusters grow at different seeds. As the percolation threshold is approached, the clusters come into contact and form a continuous network of connected particles.

At the percolation point the mean distance between seeds is of order

$$r \approx (\psi p_c^\infty)^{-1/d}, \tag{6}$$

where $d=2$ is the Euclidian dimension.

The maximal radius of a fractal aggregate is of order

$$R_c \approx (p_a)^{-1/(d-d_f)}, \tag{7}$$

where $p_a \approx p_c^\infty$ is the mean concentration of particles inside the aggregate and d_f is an effective fractal dimension.

At the percolation threshold where $r \approx R_c$ we have

$$p_c^\infty \approx b\psi^{d/d_f - 1}, \tag{8}$$

where b is a constant.

Using relation $d_f \approx d/(1+\partial \ln p_c^\infty / \partial \ln \psi)$, that follows from Eq. (8) the effective fractal dimensionality of clusters d_f vs ψ was calculated (Fig. 3). The value of d_f decreases with decreasing ψ approaching the value $d_{f,DLA} \approx 1.71$ characteristic for the DLA model [17] in the limit of $\psi \to 0$. This is reasonable, because in limit of $\psi \to 0$, the growth of isolated clusters by the DLA is the dominating mechanism. The value of d_f is equal to 1.896 in the other limit of usual random percolation [4], $\psi \to 1$. But Eq. (8) is unsuitable for estimation of d_f at a high value of ψ, because in this case clusters begin to coalesce at an early stage of aggregation.

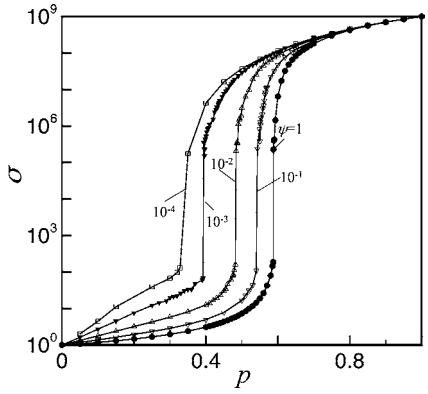

FIG. 4. Conductivity σ vs concentration of particles p at different concentrations of immobile seeds ψ. The size of lattice is $L=512$.

B. Percolation of conductivity

For our model we observe that the electrical conductivity increases during the course of aggregation to a maximal value at the final stage of aggregation. Figure 4 shows the dependences of the maximal conductivity σ on the concentration of particles p at different concentrations of immobile seeds ψ and lattice size $L=512$. These dependences are typical for strong percolation behavior and the abrupt increase of conductivity occurs exactly at percolation threshold $p=p_c$ ($L=512$).

The scaling behavior of maximal conductivity σ at concentration $p \geqslant p_c$ is illustrated in Fig. 5. Near the percolation threshold, at $p-p_c \ll 1$, a power law of Eq. (2) with $t \approx 4/3$ is fulfilled at different values of ψ. That means the considered model displays the same class universality of conductivity exponent t as for random percolation model [16]. Note, that power law of Eq. (2) is satisfactorily fulfilled in the full composition interval up to $p=1$ at high seeds concentration, $\psi \approx 1$, but this composition interval decreases with decreasing of ψ (Fig. 5).

For testing the possibility of application of the GEM equation for fitting of $\sigma(p)$ curves as in Ref. [18] we introduce the percolation connectivity defined as:

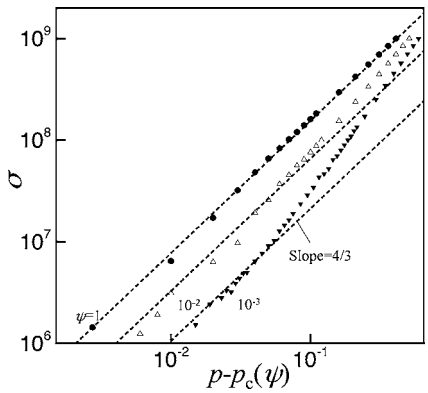

FIG. 5. The maximal conductivity σ vs deviation from threshold concentration $p-p_c(\psi)$ at different concentration of immobile seeds ψ. The slopes of dashed lines are 4/3. The size of lattice is $L=512$.

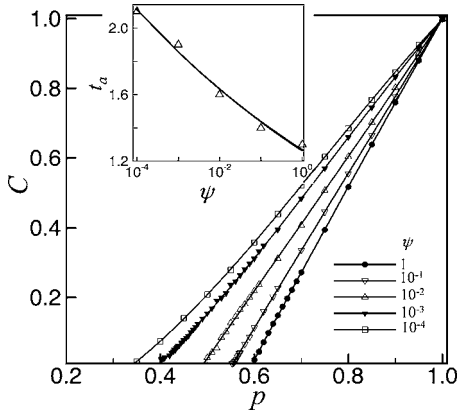

FIG. 6. Percolation connectivity C [Eq. (9)] vs the concentration of particles p at different ψ. Symbols represent the simulation data. Solid lines correspond to the fitting of simulation data with the GEM equation [Eq. (3)] for $2d$ systems. The inset shows the apparent conductivity exponent t_a vs concentrations of immobile seeds ψ. The size of the lattice is $L=512$.

$$C = (\sigma^{1/t} - \sigma_m^{1/t})/(\sigma_p^{1/t} - \sigma_m^{1/t}). \tag{9}$$

The value of C is dimensionless, monotonic in p, varies from 0 to 1 and is a function of the conductance ratio $f=\sigma_p/\sigma_m$. Equation (3) in the limit $\sigma_p/\sigma_m \to \infty$ has the simple solution

$$C = (p - p_c)/(1 - p_c) \quad \text{at } p \geqslant p_c. \tag{10}$$

So, the GEM equation predicts that the connectivity C is linear in p for $p \geqslant p_c$. For the present model the linear relation in Eq. (9) gives a satisfactory fit to $C(p)$ curves at different ψ (Fig. 6).

Noticeable deviations are observed only in the vicinity of the percolation threshold for small values of ψ. The inset in Fig. 6 shows apparent conductivity exponent t_a versus the concentration of immobile seeds ψ calculated by fitting of experimental data with the GEM equation [Eq. (3)]. The apparent conductivity exponent t_a is nonuniversal and increases with decreasing of ψ. This nonuniversality reflects only the influence of details of aggregates structure on the connectivity C versus concentration p behavior described with the help of the GEM equation. This equation is satisfied in the wide range of concentration $p_c \leqslant p \leqslant 1$, through near the percolation threshold, in the limit $p \to p_c$, the considered model belongs the random percolation universality. The difference between conductivity t and apparent conductivity t_a exponents is related with different intervals of p used for estimations of these values. Note, that in experimental estimations the wide composition interval $p_c \leqslant p \leqslant 1$ is commonly used for estimation of conductivity exponent and the reported values of t_a are considerably higher than universal value of t for random percolation [19]. We suppose that observed nonuniversality of the apparent conductivity exponent estimated from data in a wide composition interval $p_c \leqslant p \leqslant 1$ may reflect the influence of the details of geometrical arrangement or aggregate structure on the conductivity behavior.

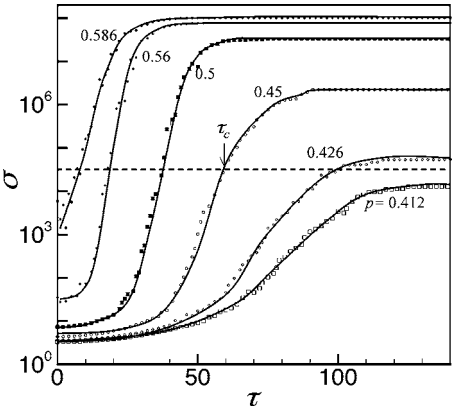

FIG. 7. Electrical conductivity σ vs time of aggregation at different initial concentrations of particles p. The size of lattice is $L=128$ and concentration of immobile seeds is $\psi=10^{-3}$.

C. Conductivity changes during the aggregation

Figure 7 shows the variation of the typical electrical conductivity σ versus time τ during aggregation. The presented data correspond to the lattice size of $L=128$, concentration of immobile seeds $\psi=10^{-3}$, and percolation concentration $p_c=0.413$.

The percolation time τ_c in all cases was estimated as the time when the mean conductivity of the system is equal approximately to $\sqrt{\sigma_p \sigma_m}$ (dashed line in Fig. 7). At early stages of aggregation the conductivity is the same as for random percolation model, then it increases during the aggregation and in case of $p \geqslant p_c$ the final conductivity exceeds the value of $\sqrt{\sigma_p \sigma_m}$. The percolation time is a decreasing function of the particle concentration p (Fig. 8). In the limit of $p \to p_c(\psi)$ the percolation time $\tau_c \to \infty$, and in the other limit of $p \to p_c(\psi=1) \simeq 0.5927$ (case of random percolation) the percolation time $\tau_c \to 0$.

The percolation time $\tau_c(\psi)$ near the percolation point $p \approx p_c(\psi)$ can be estimated as the time of formation of aggregates with radius R_c as defined by Eq. (7). Initially all

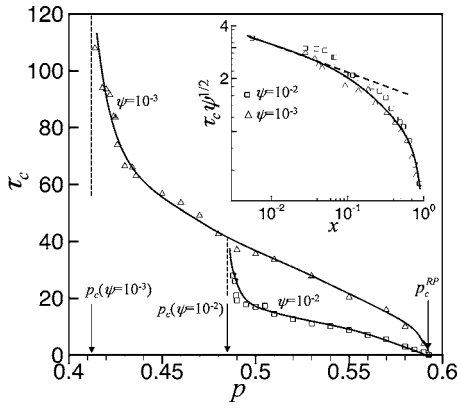

FIG. 8. Percolation time τ_c vs particles concentration p at different concentrations of immobile sites ψ. The dashed vertical lines show percolation concentrations $p_c=0.413, 0.485, 0.5927$ for values of $\psi=0.001, 0.01, 1$, respectively. The inset shows $\tau_c \psi^{1/2}$ vs scaled particles concentration x. The size of lattice is $L=128$.

particles are distributed randomly in space and $\tau_c(\psi)$ is proportional to $R_c(\psi)$. Taking into account Eqs. (7) and (8) we obtain $\tau_c(\psi) \propto \psi^{-1/d} = \psi^{-1/2}$.

We now scale the particle concentration as

$$x = [p - p_c(\psi)]/[p_c^{RP} - p_c(\psi)] \tag{11}$$

in the interval $p_c(\psi) < p < p_c^{RP}$, and look for universal behavior with τ scaled as

$$\tau_c(\psi) = \psi^{-1/2} f(x), \tag{12}$$

where f is an unknown function of x.

This assumption is supported by the inset in Fig. 8, where the data for $\psi = 0.001$ and $\psi = 0.01$, presented as $\tau_c \psi^{1/2}$ vs x, evidently collapse onto a single master curve. We thus find a scaling behavior $\tau_c \propto x^{-\alpha}$ in the limit of $x \to 0$. The dashed line in the inset in Fig. 8 corresponds to a scaling exponent $\alpha \approx 0.2$ but at this stage we have no reasonable explanation for this behavior.

IV. CONCLUSIONS

In this work we have developed a computer simulation approach for study of electric conductivity variation and percolation in a colloidal dispersion during aggregation in two-dimensional systems. The aggregation was simulated with the multiple growth-site DLA model [13]. The concentration of immobile seeds ψ influences the percolation concentration but at all values of $0 < \psi \leqslant 1$ this model shows the universal behavior of classical $2d$ random percolation with $\nu \approx t \approx 4/3$. The present results confirm that the *general effective medium* model can be successfully used for the fitting of conductivity data in the entire composition range. The estimated apparent conductivity index is nonuniversal and increases with decreasing ψ. This nonuniversality reflects only the influence of details of the structure of the aggregate on the connectivity C versus concentration p behavior described with the help of the GEM equation. The experimentally observed nonuniversality of apparent conductivity exponent t_a may be possibly related with the rather wide concentration intervals commonly used for estimation of t_a. We have observed that the time of percolation cluster formation τ_c decreases with increasing of ψ in the particle concentration range of $p_c(\psi) < p < 0.5927$. Further studies are in progress in which the conductivity changes are induced by cluster-cluster diffusion limited aggregation.

ACKNOWLEDGMENTS

N.L. and N.V. thank the NAS of Ukraine for partial financial support under the Projects N 2.16.1.4, 2.16.1.7 and 2.16.2.1.

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