Microcolumn formation between electrodes in a narrow channel from metallic colloidal suspension through induced-charge electrophoresis

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It is desirable to achieve the self-organization of a microcolumn between electrodes in a flow channel because the microcolumn can be used as a biosensor with high sensitivity. A direct simulation of a dispersed system of metallic particles in water is performed to show that a microcolumn between electrodes is formed by the application of an ac electric field. By the multiphysics coupled simulation technique between fluidics and electrostatics based on the boundary element method along with the double layer approximation, we find that microcolumns are formed by the growth of clusters perpendicular to the electrodes under the condition that the number density of particles is larger than the percolation threshold. Further, we propose a simple model that efficiently explains the time dependence of the probability of the formation of a microcolumn by considering standard collision theory and percolation theory. By this analysis, we can greatly contribute to developments in studies on the self-organization of microcolumns and biosensors.

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I. INTRODUCTION

Patterned colloidal structures formed from dispersions of particles have many potential applications [1], thus, they have been researched extensively [2–5]. In particular, because of its high aspect ratio, micro- or nanocolumn or wire between electrodes in a flow channel can be used as a biosensor with high sensitivity. Trau *et al.* [2] reported the formation of multicolloidal columns by generating electrohydrodynamic flow in a suspension of spherical $BaTiO_3$ by the application of a dc electric field $E_0=50-200$ kV/m. Further, Hermanson *et al.* [3] reported the formation of microwires from gold nanoparticle suspensions between gold electrodes through dielectrophoresis by the application of an ac electric field $E_0 \approx 25$ kV/m. Their methods are similar in the sense that they formed microstructures between electrodes from colloidal particle suspensions by the application of ac or dc electric fields. In both these studies, it is pointed out that the electro-osmotic flow plays a major role in the assembly process; however, their findings are not directly predicted by theory and to the best of our knowledge, a direct simulation of a colloidal multiparticle system has not been performed. Electrophoretic deposition, which can be used to form films on an electrode from colloidal suspensions by the application of dc electric fields, is known to be a related phenomenon and has been studied extensively [4–6].

Recently, Bazant and Squires [7–9] showed that an induced-charge electrokinetic phenomenon (ICEP), which includes induced-charge electro-osmosis and electrophoresis, is a key concept for understanding behaviors of metallic colloidal suspensions and flows around a metal post; e.g., it has been found that conductors in an ionic solution with a broken symmetry generate a large net flow velocity (of the order of a few millimeters per second in an electric field of approximately 10^4 V/m) due to an ICEP [7–15]. An ICEP is different from classical electro-osmosis and electrophoresis because it is caused by the interaction between an electric field and ions in an electric double layer formed by the polarizing effect of the electric field. Moreover, it can be driven by ac electric fields; therefore, problems due to a dc electric field can be avoided. In this study, from this unified viewpoint, i.e., ICEP, we focus on the self-assembly process of a microcolumn in a narrow channel from metallic colloidal suspensions and elucidate the effect of application of an electric field to a metallic dispersion system in water in a microfluidic channel.

II. THEORY

Figure 1 shows the schematic view of our simulation of the self-assembly process of a microcolumn. As shown in Fig. 1, we consider a dispersion system of circular metallic particles of radius c (=0.08w), with N (=18) number of particles between electrodes in a rectangular channel of length L (=2.25w) and width w (=100 μm). To evaluate the probability of the formation of a microcolumn, we generate random positions at $t=0$ ms by considering random number for metal particles; i.e., we define regular lattice positions (X_i, Y_j) and then consider irregular lattice positions $(X_i$

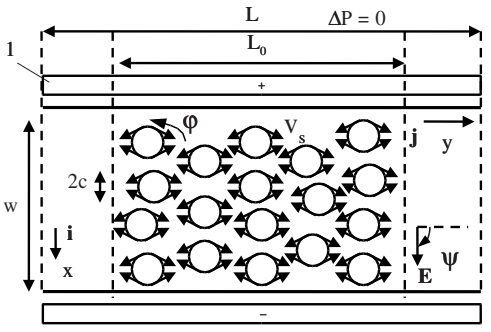

FIG. 1. Schematic view of metallic particle dispersion system (in water) used for the simulation of microcolumns. 1: pair of electrodes. Here, length $L=2.25w$ and width $w=100$ μm.

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$+\delta x_{ij}, Y_j+\delta y_{ij})$, where δx_{ij} and δy_{ij} are uniform random numbers in the ranges $|\delta x_{ij}|<w/8-c$ and $|\delta y_{ij}|<L_0/10-c$, respectively. Here, $X_i=(i+1/2)w/4$ for $i=0,1,2,3$ if $j=0,2,4$, $X_i=(i+1)w/4$ for $i=0,1,2$ if $j=1,3$, and $Y_j=(j+1/2)L_0/5+(L-L_0)/2$ for $j=0,1,2,3,4$. It should be noted that we introduce a limitation length L_0 to obtain samples that differ in number density under the same particle number N since number density is defined as N/L_0w. Further, we assume that particles aggregate in the direction of x if $r_{k\lambda}<2c+d_0$ and $|x_{k\lambda}|<(2c+d_0)/2$, where $r_{k\lambda}$ is the distance between particles, $d_0=0.02w$, and $|x_{k\lambda}|$ is a distance in the x direction. By considering this connection in the x direction, we define an average cluster size of each sample arrangement Λ as $S_{x,\Lambda}\equiv\sum_{s=0}^{s=\infty}sP_s$, where s is the cluster size, $P_s=sn_s/N$ is the probability that one particle belongs to the cluster whose size is s, n_s is the number of clusters whose size is s, and N (=18) is the number of particles. Further, if particles belonging to the same cluster come in contact with upper and lower electrodes at the same time, we can conclude that percolation occurs between electrodes and at least one microcolumn is formed between electrodes. We set $G_\Lambda=1$ when percolation occurs and $G_\Lambda=0$ when no percolation occurs.

By considering standard collision theory and percolation theory [16], we propose a simple scaling model that explains $\langle S_x\rangle\equiv\sum_{\Lambda=1}^{\Lambda=N_s}S_{x,\Lambda}/N_s$ and $\langle G\rangle\equiv\sum_{\Lambda=1}^{\Lambda=N_s}G_\Lambda/N_s$ as follows:

$$\langle S_x\rangle \approx 1+(S_x^{\max}-1)(1-e^{-t/\tau_1}), \tag{1}$$

$$\langle G\rangle \approx P(L_0)\left[1-\frac{1}{e^{(t-\tau_2)/\tau_3}+1}\right], \tag{2}$$

respectively, where τ_1 is a clustering time, τ_2 is a threshold time of the formation of a microcolumn, τ_3 is a width of the threshold, $S_x^{\max}$ is the maximum value of $\langle S_x\rangle$, $P(L_0)\equiv 1/[e^{(L_0-L_0^{\rm th})/\Delta L_0}+1]$ is the percolation probability between electrodes, $L_0^{\rm th}$ is the threshold of P, and ΔL is the width of the threshold of P. Although Eq. (1) seems to be complex, it is just the reaction equation of the first order with a time constant τ_1 in a random system, except that it is modified so that $\langle S_x\rangle$ is one at the initial time and becomes $S_x^{\max}$ at the final time because of the physical limitation of the cluster in our random system. Similarly, Eq. (2) is just the phenomenological equation that describes the phenomenon that $\langle G\rangle$ glows at $t\simeq\tau_2$ with the ambiguity time τ_3, except that it is designed so that $\langle G\rangle$ becomes the percolation probability P at the final time. It should be noted that percolation theory provides the probability to form clusterings that connect to infinite or finite regions in various random systems and can be used to explain a macroscopic conductance [16,17]. Thus, Eq. (2) is an appropriate equation that describes our random system as a first attempt. Basically, all the parameters are determined so that numerical results fit into Eqs. (1) and (2); i.e., from simulations, we set $\tau_1=4\tau_0$, $\tau_2=3\tau_0$, $\tau_3=0.6\tau_0$, $L_0^{\rm th}/w=1.35$, $\Delta L_0/w=0.3$, $U_0^{\rm eff}=U_0/7$, and $S_x^{\max}\approx 2.4+1.8(L_0-2.2)^2$, where $\tau_0=1/[4cU_0^{\rm eff}(N/L_0w)]$ is a collision time, $4c$ is a collision cross section, N/L_0w is a number density of the particles, $U_0(=\epsilon cE_0^2/\mu)$ is a standard representative velocity, and $E_0(=V_0/w)$ is a representative electric field between electrodes. It should be noted that we have derived Eqs. (1) and (2) by considering random collisions between particles that move randomly with average velocity $U_0^{\rm eff}$. In the random system, it is reasonable that $\langle S_x\rangle$ is subject to the reaction equation of 1 order with $\tau_1=4\tau_0$, since clustering in the x direction occurs with the probability of 1/4. Note that clustering is apt to occur from a lower or upper electrode owing to attractive forces between a particle and a wall and attractive forces in the x direction between particles; i.e., a cluster grows in the one x direction only when a particle collides with the particle that positions at the edge of the cluster opposite to the wall. Of course, if particles collide with each other in the y direction, clustering does not occur because repulsive forces due to an induced-charge electro-osmosis (ICEO) flow around particles work between particles. Further, it is reasonable that the stable value of $\langle G\rangle$ is an ordinary percolation probability for a random configuration problem of a finite number of particles in a finite size under the condition that $\Delta L_0\neq 0$ and $\langle G\rangle$ has a time threshold that is strongly related to τ_1.

Numerically, we consider a two-dimensional (2D) quasi-static Stokes flow without Brownian motion: i.e., we consider the limit in which the Reynolds number Re tends to zero and the Peclet number is infinite. We assume the posts of the metal cylinder to be polarizable in an electrolytic solution under a dc or ac electric field. The motion of the surrounding fluid must satisfy Stokes equations modified by the inclusion of an electrical stress. However, by using matched asymptotic expansion [18], we can reduce them to the classical Stokes equations as follows:

$$\mu\nabla^2\boldsymbol{v}-\boldsymbol{\nabla}p=0,\quad \boldsymbol{\nabla}\cdot\boldsymbol{v}=0, \tag{3}$$

$$\text{On } S_p^{+(j)}:\quad \boldsymbol{v}^{(j)}=\boldsymbol{U}^{(j)}+\boldsymbol{\Omega}^{(j)}\times\boldsymbol{x}^{(j)}+\boldsymbol{v}_s^{(j)}, \tag{4}$$

$$\int_{S_p^{+(j)}}\boldsymbol{f}^{(j)}dl+\boldsymbol{F}_t^{\text{ext},(j)}=0,\quad \int_{S_p^{+(j)}}\boldsymbol{x}^{(j)}\times\boldsymbol{f}^{(j)}dl+\boldsymbol{T}_t^{\text{ext},(j)}=0, \tag{5}$$

where $S_p^{+(j)}$ denotes the surface defined as the outer edge of the double layer, $\boldsymbol{U}^{(j)}$ is the translational velocity, $\boldsymbol{\Omega}^{(j)}$ is the rotational angular velocity, $\boldsymbol{f}^{(j)}$ is the traction vector, and $\boldsymbol{F}_t^{\text{ext},(j)}$ and $\boldsymbol{T}_t^{\text{ext},(j)}$ are the total external force and torque, respectively, on the j's metal cylinder ($j=1,2,\ldots,N$). Further, $\boldsymbol{x}^{(j)}(=-\sin\varphi\ \boldsymbol{i}+\cos\varphi\ \boldsymbol{j})$ is the surface position of the j's metal parameterized by φ, $\boldsymbol{i}$ and $\boldsymbol{j}$ are orthogonal unit vectors in the Cartesian coordinate system, μ ($\sim$1 mPa s) is the viscosity, $\boldsymbol{v}$ is the velocity, and p is the pressure. Under a wide range of conditions, the local slip velocity $\boldsymbol{v}_s^{(j)}$ is given by the Helmholtz-Smoluchowski formula

$$\boldsymbol{v}_s^{(j)}=-\frac{\epsilon\zeta^{(j)}}{\mu}\boldsymbol{E}_S^{(j)}, \tag{6}$$

where $\boldsymbol{E}_s^{(j)}$ is the tangential component of the electric field, ϵ ($\sim 80\epsilon_0$) is the dielectric permittivity of the solvent (typically water), and ϵ_0 is the vacuum permittivity. Here, a zeta-potential $\zeta^{(j)}$ around the j's metal is generally defined as

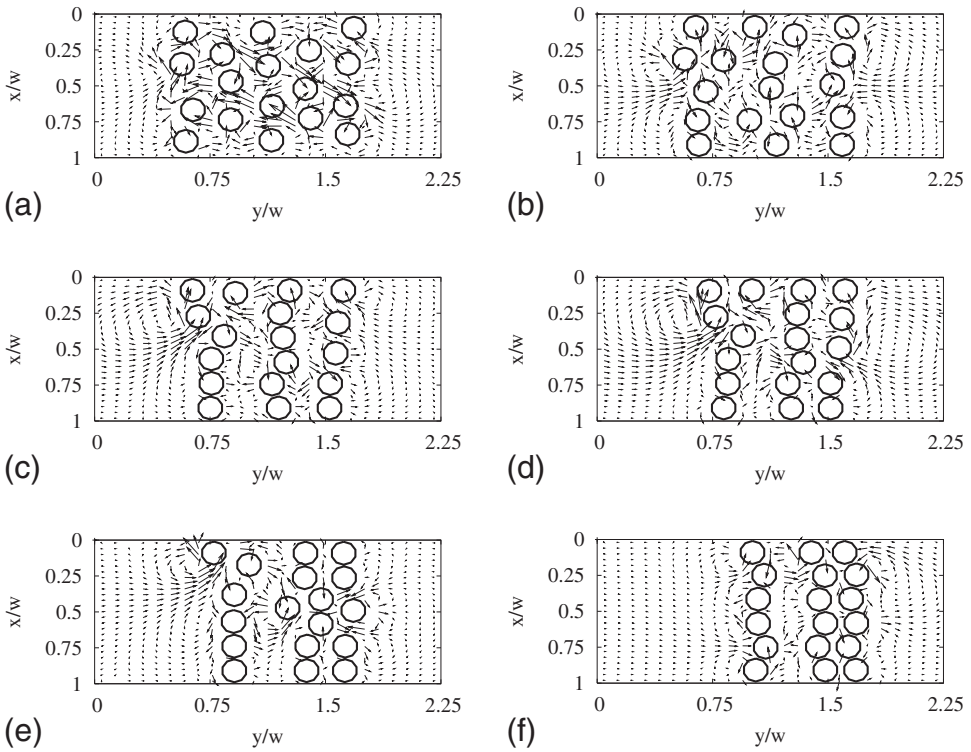

FIG. 2. Formation of microcolumn and ICEP flow fields of metallic particle dispersion system by a full coupled simulation. Here, $L_0/w=1.3$, $c/w=0.08$, $\Delta P=0$, $\tau_0=79.1$ ms, $U_0=2$ mm/s, $U_0^{\text{eff}}=U_0/7$, and $E_0=18.8$ kV/m.

$\zeta^{(j)}=\phi_i^{(j)}-\phi_f^{(j)}$, where $\phi_f^{(j)}$ and $\phi_i^{(j)}$ are final and initial potentials, respectively.

To consider a multiparticle problem under a bounded condition, we solve the electric potential at every time step before calculating a flow field by the boundary element method based on the following Laplace's equation, $\nabla^2\phi=0$. On one hand, we use the Dirichlet boundary condition for the upper and lower walls (electrodes); i.e., $\phi=+0.5V_0$ at $x=0$, $\phi=-0.5V_0$ at $x=w$, where V_0 is an applied voltage across the channel. On the other hand, we use the Neumann boundary condition for the left and right walls; i.e., $\boldsymbol{n}\cdot\nabla\phi=0$ at $y=0$ and L, where $\boldsymbol{n}$ is the surface-normal unit vector. In addition to those boundary conditions, to obtain a final potential, we also use the Neumann boundary condition (i.e., $\boldsymbol{n}\cdot\nabla\phi=0$) on the metal surface. Further, to obtain an initial potential, we use the condition that j's metal particles have an unknown surface potential $\phi_i^{(j)}$ and require the electrical neutral condition that $\oint_{(j)}(\boldsymbol{n}\cdot\nabla\phi)ds=0$. Thus, we can numerically calculate a flow field for a bounded domain. It should be noted that we use the boundary condition that the velocity on the wall of the channel is zero and that the pressures of the inlet and outlet are P_1 and P_2, respectively. (Here, $P_1=P_2=0$ and $\Delta P=P_2-P_1=0$.) On the basis of Eqs. (3)–(6), we calculate the flow fields of the ICEP multiparticle system for a bounded domain by the boundary element method.

Further, we consider a short-range repulsive velocity $\mathbf{u}_{\text{col}}(r_{ik})$ that prevents unphysical overlapping between particles; i.e., at every time step, we move particles from $\mathbf{x}_i^{\text{before}}$ to $\mathbf{x}_i^{\text{after}}$ as $\mathbf{x}_i^{\text{after}}=\mathbf{x}_i^{\text{before}}+\mathbf{u}_{\text{col}}(r_{ik})\Delta t/10$ until all the distances r_{ik} become larger than $2c+d_1$, where $d_1=0.01w$ ($<d_0$), Δt (=1 ms) is a time interval of the numerical simulation, $\mathbf{u}_{\text{col}}(r_{ik})=0$ if $r_{ik}>2c+d_1$, $\mathbf{u}_{\text{col}}(r_{ik})=-2U_0\mathbf{x}_{ik}/r_{ik}$ if $r_{ik}<2c$, and $\mathbf{u}_{\text{col}}(r_{ik})=-2U_0\exp[-(r_{ik}-2c)/d_1]\mathbf{x}_{ik}/r_{ik}$ if $2c\le r_{ik}\le 2c+d_1$. Here, $\mathbf{x}_{ik}=(x_{ik},y_{ik})$. Note that unphysical overlapping between particles occurs mainly because particles move relatively large distances during Δt. Thus, a small factor, such as 1/10, is needed to remove unphysical overlapping. To the best of our knowledge, our developed simulator is the only tool that can directly analyze ICEP multiparticle flow automatically by considering hydrodynamic and electrostatic wall-cylinder interactions.

III. RESULTS

Figure 2 shows an example of the formation of a microcolumn due to ICEP by a full couple simulation when $L_0/w=1.3$, $c/w=0.08$, $\Delta P=0$, $\tau_0(=L_0w/4aNU_0^{\text{eff}})=79.1$ ms, $U_0=2$ mm/s, $U_0^{\text{eff}}=U_0/7$, and $E_0=18.8$ kV/m. Here, the applied voltage $V_0=1.88$ V for $w=100$ μm is reasonable for an ICEP caused by an ac voltage. In fact, such strong electric fields have been used in previous experiments [2,3,10]. Metal particles that are placed at random positions at $t=0$ ms generate a complex flow field, as shown in Fig. 2(a), and move in a complex manner due to an attractive force parallel to the electric field and a repulsive force perpendicular to the electric field between particles. Figure 2(b) shows an image of particles and flow fields at $t=80$ ($\approx 1.0\tau_0$) ms. Because of the attractive force that is parallel to the electric field, particles have a tendency to aggregate in the direction of the electric field and form clusters. As shown in Fig. 2(c), a microcolumn is formed first at $t=195$ ($\approx 2.5\tau_0$) ms; i.e., there is no microcolumn formation in the period $t<195$ ms. There is a tendency that the system keeps to form a microcolumn or multicolumns even though there is movement as shown in Figs. 2(d)–2(f). It should be noted that we cannot observe a remarkable flow toward the electrodes and a deposition of particles on the electrodes.

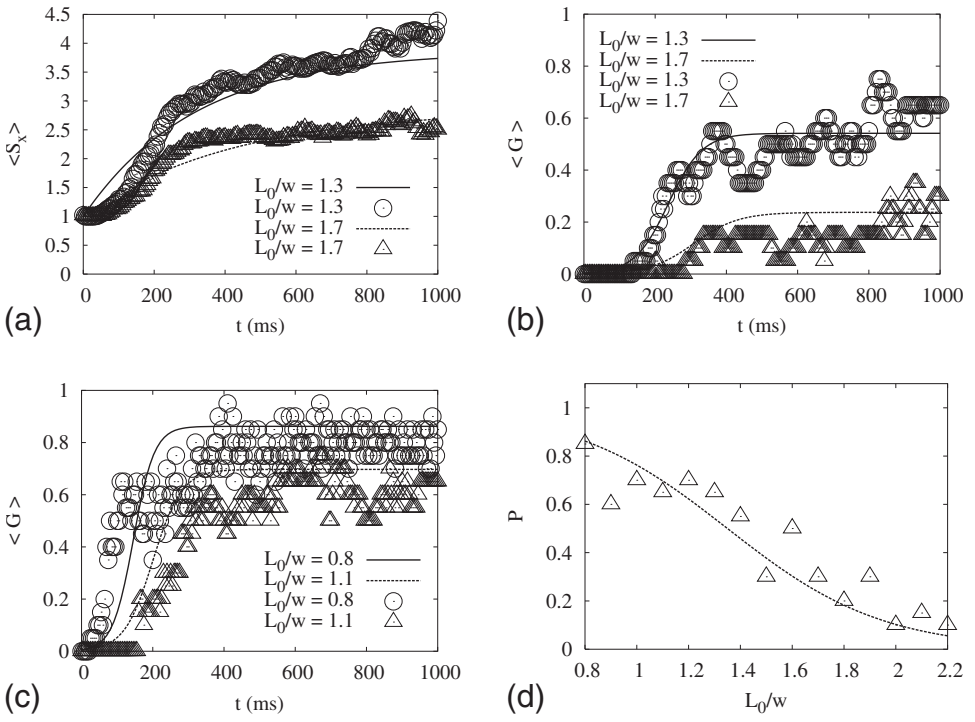

FIG. 3. Results of clustering analysis by a full coupled simulation. Here, $L/w=2.25$, $\Delta P=0$, $U_0=2$ mm/s, and $E_0=18.8$ kV/m. Lines show analytical results obtained by Eqs. (1) and (2). Symbols show numerical results obtained by the boundary element method.

Figure 3 shows the results of clustering analysis by a full coupled simulation for N_s (=20) initial arrangements when $L/w=2.25$, $U_0=2$ mm/s, and $E_0=18.8$ kV/m. Figure 3(a) shows the time dependence of $\langle S_x \rangle$. As shown in Fig. 3(a), the time evolution of $\langle S_x \rangle$ is described by Eq. (1), which is similar to the reaction equation of 1 order, derived from random collisions. Figures 3(b) and 3(c) show the time evolution of $\langle G \rangle$. As shown in Figs. 3(b) and 3(c), microcolumns form and then stabilize; i.e., we cannot observe a decay of $\langle G \rangle$. Figure 3(d) shows the dependence of P on L_0/w. Here, P is defined as $P=\langle G \rangle_{t=1000\ \mathrm{ms}}$. As shown in Fig. 3(d), microcolumns are well formed in the range $L_0 < L_0^{\mathrm{th}}(=1.35w)$, although the width of the threshold of P is rather wide; i.e., $\Delta L_0/w=0.3$. Thus, at a specific initial arrangement of particles, the formation of microcolumn is not merely a coincidence. Further, from Fig. 3, we can observe that the analytical results of $\langle S_x \rangle$, $\langle G \rangle$, and P agree fairly well with the numerical results.

IV. DISCUSSION

When $c=8$ μm, a root mean square of Brownian motion is $\sqrt{6Dt}=\sqrt{k_BTt/\pi\mu c}=0.13$ μm ($\ll 8$) even for $t=100$ ms, where k_B is the Boltzmann constant and T (=300 K) is a temperature. Therefore, we can neglect Brownian motion even though our proposed system is colloidal. Thus, we have an idealized system of particles that is subject to whatever external forcing we can impose. Further, the threshold value of L_0/w for P is approximately 1.2–1.6, which corresponds to $q \approx 0.38-0.29$, where q is the occupied ratio defined as $q=4c^2N/L_0w$. Since the threshold of bond percolation for a 2D triangular lattice problem is approximately 0.35, we think that the current microcolumn is formed because of the percolation occurring when the percolation threshold is exceeded in the case of narrow channel. Thus, the formation mechanism of our microcolumn is different from that of other microcolumns that can be explained by the concentration of electric fields on the top of the growing tip of the microcolumn. Furthermore, though our system is not driven by dielectrophoresis, a lot of similarities may exist between an electrorheological (ER) fluid [19] and a multiparticle system of ICEP since the phenomenon of organizing particles in a plane normal to electrodes is common. In an ER fluid, the formation of chains and columns parallel to the field is accompanied by a dramatic increase in the apparent viscosity of the suspension. Thus, we expect that an ICEP can be used to create a new high-performance ER fluid in the future. Further, the random configuration of particles in our system will induce a nonuniform electric field and a nonuniform slip velocity around particles. Thus, although it might not be in the unified viewpoint of ICEP, if the phenomenon seen in the relative motion of suspensoid and medium resulting from polarization forces produced by an inhomogeneous electric field is widely defined as "dielectrophoresis" [20], we may need to say that a kind of "dielectric" effect also would be automatically taken into account in our calculations through the nonuniform slip velocities resulting from a nonuniform electric field. Note that we assume that $F_t^{\mathrm{ext},(j)}$ and $T_t^{\mathrm{ext},(j)}$ are zero in Eq. (5) by considering that the electrostatic force is screened by the existence of counter ions; i.e., we consider that direct electrostatic interactions between particles do not exist in perfectly polarizable solutions, as far as we use the boundary condition that $\boldsymbol{n}\cdot\nabla\phi=0$ on $S_p^{+(j)}$ to obtain a steady electric field because the boundary condition means that there is no net charge to interact with.

V. CONCLUSION

In conclusion, we have proposed the formation of microcolumns between electrodes in a narrow channel through

an ICEP and percolation phenomena and numerically examined their characteristics. By full coupled simulations, we observe the following. (1) The formation of clusters and a microcolumn in the direction of an applied electric field proceed within the time that is approximately 4–5 τ_0 ($=L_0 w/2aNU_0^{\mathrm{eff}}$). (2) A microcolumn is formed under the condition that the occupied ratio of metal particles is larger than approximately 0.35; this value approximately agrees with the threshold of bond percolation on a 2D triangular lattice. (3) The time dependence of the probability of the formation of the microcolumn is characterized by a simple scaling model that considers standard collision theory and percolation theory. (4) In a full coupled simulation that considers precise boundary conditions, there is no remarkable flow toward electrodes and the effective velocity becomes slower than an ordinary characteristic velocity. We believe that our method for the formation of microcolumns will revolutionize the design concept of biosensors.

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