Limitations of Au Particle Nano-Assembly using Dielectrophoretic Force ——A Parametric Experimental and Theoretical Study

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***Abstract*—When a gold colloids suspension is subjected to AC electric field, "gold pearl chains" will form due to the dielectrophoretic (DEP) force. Our latest experiments show that the rate of gold pearl chains formation is dependent on the applied field frequency, which tends to zero at high and low frequency limits and has a maximum at a narrow mid range of frequency. This letter analyzes the frequency-dependent DEP manipulation of gold colloid suspensions using the protoplast model. Simulated results show that the relationship curve between the frequency of applied field and the velocity of gold colloids motion due to DEP agrees with our experimental observations. In addition, the orders of magnitude of the velocity due to various effects in our experimental system, such as DEP force, Brownian motion, gravity, and fluid flows induced by electric field, were also estimated. The result implies that the DEP-based manipulation of less than 2nm gold colloids is extremely difficult to be controlled.**

***Index Terms*—Dielectrophoresis, Gold Nano-particles, Nano-assembly, Nano-manipulation, Pearl Chain Formation**

I. Introduction

THE assembly of gold colloidal particles into functional structures has attracted significant interest due to its potential nanotechnology applications, such as sensors, nano-structured films, and wires for electrical circuits [1]-[6]. During the last two decades, electric-field-driven movement of particles using effects such as electrophoresis (EP) [3], dielectrophoresis (DEP) [4]-[9], has been carried out to assemble colloids in suspensions. When subjected to AC electric fields, particles suspended in fluid exhibit a motion arising from various forces, including DEP force, gravity, and drag forces due to the electrothermal flow and AC electro-osmosis flow, and from the Brownian motion [10]. Investigations both in theory and experiments reveal that DEP force can dominate the particle motion under certain conditions, i.e., specific material used to build the micro electrodes, electrode geometry, and solution medium in which the particles are in, etc.

Experiments in [11] reveal that the surface conductivity of microparticles significantly controls the field-induced pattern formed by microparticles. The fractal-chain transition was demonstrated by a further experiment with glass microspheres coated with conducting and insulating films. Detailed experimental observation indicates that the suspended chains will further aggregate to form column under high field condition. Gold colloids subjected to AC electric fields are capable of forming diverse patterns, such as fractal [6], [8], [9], column [4], [7], and pearl chain [2], [7]. Obviously, conductive gold particles assembled to pearl chains or columns must have a certain insulating film coating on their surfaces.

The gold colloids used in the above experiments are generally produced by the method of liquid chemical reduction. To prevent the particles from aggregating, some sort of stabilizing agent that sticks to the nanoparticle surfaces is usually added [12]. Considering that the stabilizing agent film of gold colloids can be regarded as membrane, which possesses capacitance along the normal direction of the film, and that the gold particle core as cytoplasm, the protoplast model [13] can be used to derive the effective dipole moment of gold colloids in dielectric medium.

In this letter we analyze the relationship between the frequency of applied field and the DEP force exerted on the gold colloid in dielectric medium. Simulated results show that the relation curve has a reverse-bell-shaped profile and tends to zero at high and low frequency limits, which agrees well with our experimental data in [14]. The scaling laws in our simplified experimental system were also surveyed. The result implies that the DEP-based manipulation of less than 2nm gold colloids is extremely difficult to be controlled.

II. Protoplast Model

Consider a protoplast-like spherical particle with radius R, permittivity ε_2 and conductivity σ_2, which is covered by a uniform layer of thickness $\Delta << R$, permittivity ε_m and

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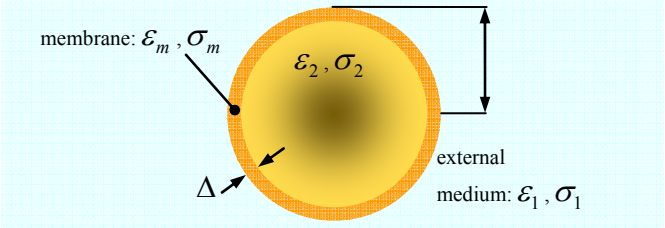

Fig. 1. A protoplast-like spherical particle with radius R, permittivity ε_2 and conductivity σ_2, which is covered by a uniform layer of thickness $\Delta << R$, permittivity ε_m and conductivity $\sigma_m << \sigma_2$, and is surrounded with a solution, permittivity ε_1 and conductivity σ_1.

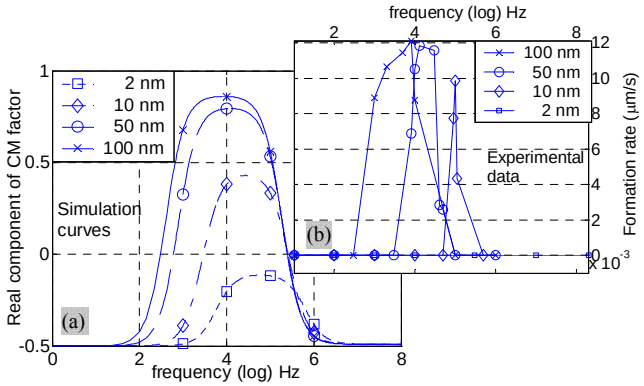

Fig. 2. (a) Real component of the factor f_{CM} versus frequency for the following model parameters: gold core: $\varepsilon_2 = 1\varepsilon_0$, $\varepsilon_0 = 8.85\text{e-}12$ F/m, $\sigma_2 = 2.4\text{e-}4$ S/m, R = 2, 10, 50, 100 nm; membrane: $c_m = 0.25$ F/m^2; medium: $\varepsilon_1 = 80.18\varepsilon_0$, $\sigma_1 = 5.5\text{e-}6$ S/m. (b) The formation rate versus frequency with 2nm, 10nm, 50nm and 100nm gold colloids in our experiment.

conductivity $\sigma_m << \sigma_2$, and is surrounded with a solution, permittivity ε_1 and conductivity σ_1, as shown in Fig. 1. When the particle is subjected to an AC electric field, the effective complex permittivity of the particle can be expressed as [13]

$$\varepsilon_2^* = c_m R(j\omega\tau_c + 1)/[j\omega(\tau_m + \tau_c) + 1] \quad (1)$$

Here, the quantity c_m is the surface capacitance of the layer, defined as ε_m/Δ, and ω is the angular frequency of applied field, while $\tau_m = c_m R/\sigma_2$ and $\tau_c = \varepsilon_2/\sigma_2$ and j is the square root of -1. Furthermore, the membrane conductivity is neglected.

For an isotropic homogeneous dielectric spherical particle, the time-averaged DEP force exerting on a particle that is subject to an AC electric field with no variation in phase is

$$\langle F(\omega)\rangle = \pi\varepsilon_1 R^3 \,\mathrm{Re}[f_{CM}(\omega)]\nabla E^2 \quad (2)$$

where E is the magnitude of the AC electric field, the factor f_{CM} is the well-known Clausius-Mossotti factor defined as [13]

$$f_{CM}(\omega) = (\varepsilon_2^* - \varepsilon_1^*)/(\varepsilon_2^* + 2\varepsilon_1^*) \quad (3)$$

Here, ε_2^* has been defined in (1), and $\varepsilon_1^* = \varepsilon_1 - j\sigma_1/\omega$ is the complex permittivity of the medium. To determine the frequency dependence of the DEP force acting on a gold colloid, it is necessary to obtain the real part of (3). Fig. 2(a) plots Re[f_{CM}] for a set of parameters of a gold colloid suspended

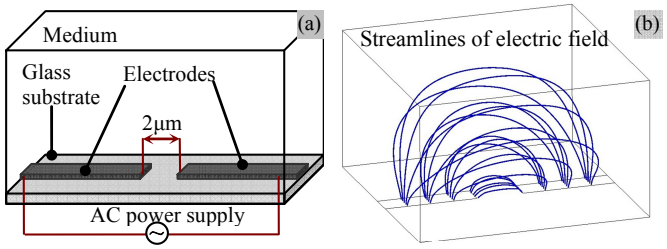

Fig. 3. (a) Schematic diagram of the experimental system in [14]; (b) The electric field distribution in three-dimensional space.

in the deionized water, which has the curve trend similar to our experimental data shown in the Fig. 2(b).

In our experiments [14], gold colloids were manipulated by AC electric field to bridge the 2 μm gap of electrodes with constant voltage of $6V_{pk\text{-}pk}$. The frequency of applied field extremely influences the motion of gold colloids. Particles are attracted to the electrodes to form pearl chains in an ideal mid frequency region，as shown in the Fig. 2(b), where the mid frequency regions of particles less than 100nm belong to 0.3 kHz - 0.3 MHz. In the lower and higher frequency regions, however, no pearl chains are formed. This can be illustrated with the Fig. 2(a), where the frequency changes the sign of the Re[f_{CM}] factor. The negative sign of the factor in lower and higher frequency regions represents the *negative* DEP force, which repels the particle away from the highest electric field intensity. The positive one in the mid frequency region, in contrast, represents the *positive* DEP force, which attracts the particle to the highest field, i.e., the electrodes.

III. Scaling Laws

Our experimental microelectrodes structure consisted of two coplanar parallel strip electrodes, with a 2 μm gap between two electrode tips. A simplified illustration of our experimental system is shown in Fig. 3a. For the sake of a simplified analysis, the electric field lines between the electrodes, which were simulated in three-dimensional space in Fig. 3b, can be considered semicircular, especially in the vertical section. The magnitude of the electric field is approximatively given by $E = V/\pi r$, where V is the amplitude of the applied voltage and r is the distance to the centre of the gap.

As stated previously, various forces in the system influence the motion of the particle subjected to AC electric field. Reference [15] summarized the displacement equations in a given time t (utilized to estimate the order of the magnitudes), which are rewritten as velocity equations in the Table I. With the set of parameters of deionized water and assuming the Re[f_{CM}] factor of 1, the magnitudes of the velocities of a particle in such system, at a distance r (= 1 μm) from the centre, can be estimated and intercompared. Fig. 4 shows the velocity of a particle plotted as a function of particle radius. Note that at 0.1 MHz DEP dominates over electro-osmosis for particles with diameters above 2 nm, while at 1 kHz the crossover occurs at a radius of 100 nm. However, the DEP can not manipulate the particles of radius less than 2 nm, which was demonstrated in our experiments [14]. Forming 2 nm particles chains is

TABLE I
THE EQUATIONS TO ESTIMATE VELOCITIES FOR A PARTICLE IN THE SIMPLIFIED EXPERIMENTAL SYSTEM WITH A SET OF PARAMETERS DESCRIBED IN THE CONTENT

FORCES	ESTIMATED EQUATIONS
Dielectrophoresis:	$0.03R^2\cdot\varepsilon_1\cdot V^2/\eta/r^3$;
Gravity:	$0.2R^2\cdot\rho_m\cdot g/\eta$;
Brownian:	$[k_B\cdot T/(3\pi\cdot R\cdot\eta\cdot t)]^{1/2}$;
Electrothermal ($\varepsilon\omega/\sigma \ll 1$):	$5\times10^{-4}\cdot\varepsilon_1\cdot\sigma_1\cdot V^4\cdot\lvert\beta\rvert/(\eta\cdot r^3\cdot k)$, $\beta = \partial\sigma_1/\partial T/\sigma_1$;
Electrothermal ($\varepsilon\omega/\sigma \gg 1$):	$2.5\times10^{-4}\cdot\varepsilon_1\cdot\sigma_1\cdot V^4\cdot\lvert\alpha\rvert/(\eta\cdot r^3\cdot k^1)$, $\alpha = \partial\varepsilon_1/\partial T/\varepsilon_1$;
Buoyancy:	$2\times10^{-2}\cdot\sigma_1\cdot V^2\cdot g\cdot r^2\cdot(\partial\rho_m/\partial T)/(\eta\cdot k)$;
AC electro-osmosis:	$0.1\Lambda\cdot\varepsilon_1\cdot V^2\cdot\Omega^2/[\eta\cdot r\cdot(1+\Omega^2)^2]$, $\Omega = \Lambda\cdot\omega\cdot\varepsilon_1\cdot\pi\cdot r/(2\cdot\sigma_1\cdot\lambda_D)$, $\Lambda = C_S/(C_S+C_D)$;

Here, η and ρ_m are respectively the dynamic viscosity and the density of solution, and k is the thermal conductivity of solution. g is the acceleration of gravity, k_B Boltzman's constant, T the absolute temperature, C_S the capacitance of the Stern layer, C_D the capacitance of the diffusion layer, and λ_D the Debye length (≈10nm [10]), with $C_D = \varepsilon_1/\lambda_D$.

For deionized water in room temperature, approximately, k = 0.6 J/m/s/K, ρ_m = 1 g/cm^3, α = -0.4% K^{-1}, β = 2% K^{-1}, $\partial\rho_m/\partial T/\rho_m = 10^{-4}$ K^{-1}, C_S is set to ≈0.02 F/m^2 in our experimental results.

important because it could allow much smaller nano-devices to be developed in the future. Fig. 5 shows the velocity vs. the applied voltage. This diagram implies that the movement of 2nm sized particle by DEP at low frequencies (~ 1 kHz) is almost impossible owing to AC electro-osmosis, and suggests that a mid voltage in the range 8-40 V is supposed to be an optimum manipulation condition based on DEP. However, the optimum condition needs to be rigidly controlled because only small magnitude differences exist between the velocities of the DEP and the other forces.

IV. CONCLUSION

Our theoretical analysis reveals that the frequency spectrum of DEP can be estimated by the protoplast model of gold colloids. In assembling gold colloids into microstructures using DEP, the positive DEP force rests with the optimum frequency and relevant Re[f_{CM}]. Therefore, it is necessary to explore how the parameters in protoplast model influence the DEP force, which competes with the drag forces due to the thermal effects and electric-field-induced fluid flows. In addition, the conditions to form pearl chains with 2nm gold colloids in AC electric field should be further explored as our analysis showed that the particle velocities induced by electrothermal and electro-osmotic forces are close to the velocity induced by DEP through a wide-range of applied voltage. Hence, manipulation of 2nm Au particles using DEP should be very difficult, which was validated in our laboratory.

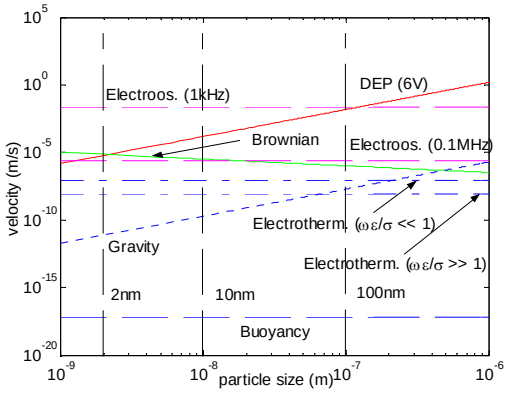

Fig. 4. Particle velocity versus particle radius.

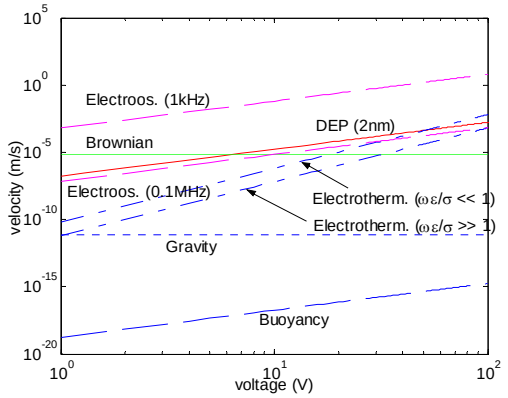

Fig. 5. Velocity of 2 nm particle versus applied voltage.

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