

# Theoretical Analysis Based on Particle Electro-Mechanics for Au Pearl Chain Formation

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**Abstract** — This paper analyzes the fundamental mechanisms in driving Au Pearl Chain Formation (PCF) based on dielectrophoresis (DEP) force. From experimental results, the PCF process strongly depends on the voltage and the frequency applied on electrodes, but weakly on the sizes of particles, which appears to be contrary to theoretical expectations. To explain the above phenomenon, we estimated the DEP force and the Brownian motion imposed on the Au nanoparticles, and then investigated the AC electro-osmosis force and the electro-thermal force which may possibly affect the PCF rate. Numerical modeling to compare the forces is presented. By matching experimental and numerical results, we validate the scaling laws of the DEP force and electro-mechanics in the PCF of Au nanoparticles.

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

## I. INTRODUCTION

The assembly of colloidal particles into functional structures has attracted significant interest due to its potential nanotechnology applications [1-6], such as sensors, nano-structured films, and wires for electrical circuits. During the last two decades, electric-field-driven movement of particles using effects such as electrophoresis [6], dielectrophoresis [5, 7-9], and electrohydrodynamics [10], has been carried out to assemble nanoparticles in suspensions. Diverse patterns, such as fractal, column, and pearl chain, have been observed, respectively [5, 11] or simultaneously [10], during these assembly processes.

Evidence reveals that different ambient conditions result in diverse pattern formations. For instance, surface properties significantly affect the field-induced pattern formation [12], with fractal and chain patterns formed by coating with conducting and insulating films on the glass particles suspended in liquid, respectively. In assembling gold nanoparticles into wires between coplanar electrodes with micrometer scale gap applied by alternating electric field, the pearl chain wires and the broad and diffusion structures formed depending on the voltage and the frequency of the applied electric field [3, 11].

The underlying mechanism of growth formations due to non-uniform electric fields is considered to be of the Columbic interactions and electrohydrodynamic effects [10, 13, 14]. Experiments have exhibited that fluid flows and dielectrophoresis predominate in certain frequencies of applied AC electric field and certain regions of plate surface, respectively

[15]. In this paper, we present how the frequency of applied AC electric field influences the velocity of gold nanoparticles in a coplanar microelectrode system, which agrees with our experimental observations. Following the scale laws of AC electric-kinetics, we estimated the order of magnitude of the various forces experienced by a particle around a simplified ideal microelectrode structure, and determined the dominating forces that drive the PCF process.

## II. THEORY

Dielectrophoresis (DEP) is the motion of a particle arising from the interaction of a non-uniform electric field with the induced effective dipole moment of the particle [7, 8]. In an electric field  $\vec{E}$ , a dielectric particle behaves as an effective induced dipole with dipole moment  $\vec{p}$  proportional to the electric field, that is  $\vec{p} \propto \vec{E}$ . In the presence of an electric field gradient, the force on a dipole is  $\vec{F} = (\vec{p} \cdot \nabla) \vec{E}$ . For an isolated homogeneous dielectric sphere with loss, the complex effective moment is [7]

$$\vec{p} = 4\pi\epsilon_m f(\omega) R^3 \vec{E} \quad (1)$$

Here,  $\omega$  is the angular frequency of the applied field,  $R$  the particle radius, and  $f(\omega)$  the Clausius-Mossotti factor defined as [7]

$$f(\omega) = \frac{\epsilon_p^* - \epsilon_m^*}{\epsilon_p^* + 2\epsilon_m^*} \quad (2)$$

where  $\epsilon^* = \epsilon - j\sigma/\omega$  is the complex permittivity,  $j = \sqrt{-1}$ , and subscript  $m$  and  $p$  representing the surrounding media and the particle.

The time-average DEP force on an isolated homogeneous lossy sphere is given by [7]

$$\langle \vec{F}_{DEP} \rangle = 2\pi\epsilon_m R^3 \text{Re}[f(\omega)] \nabla E_{rms}^2 \quad (3)$$

where  $E_{rms}$ , a function of position, is the root-mean-square (RMS) magnitude of the imposed AC electric field. The real component of the Clausius-Mossotti factor,  $\text{Re}[f(\omega)]$ , determines the frequency dependence of the average DEP force. This frequency dependence, which depends upon the parameters of the particle and the suspending medium, defines the DEP spectrum and the motion of the particle. When the real

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part of factor is positive, particle moves toward higher electric field regions, and this is termed *positive dielectrophoresis*. When it is negative, the particle moves toward smaller electric field regions, and this is termed *negative dielectrophoresis*.

For a metallic nanoparticle in aqueous suspensions  $\text{Re}[f(\omega)] \approx 1$ , which leads to positive dielectrophoresis. As an excellent conductor, gold nanoparticles exposed to non-uniform field will be attracted to intense electric field regions and accumulate together to form fractal and chain patterns [5, 10, 11]. We note here that the washed gold nanoparticles mainly formed fractal pattern, and less dependent on the frequency of applied fields [5]. Whereas, the purchased gold nanoparticles that are directly used for the assembly of wires presented more frequency-dependent and formed fractal or chain patterns in different space regions [10].

Generally, gold nanoparticles are 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. This means that the gold nanoparticles can not be treated as homogeneous conductive spheres because of their coating. In order to explore the frequency-dependent characterization of gold nanoparticles in the manipulation of DEP, we select the *thin surface layer model* [7] to calculate the DEP spectrum.

### III. SINGLE SHELL MODEL

Consider a particle with a very thin outer layer shown in Figure 1. The particle consists of a core sphere with radius  $R$ , permittivity  $\epsilon_c$ , and conductivity  $\sigma_c$ , which is covered by a uniform layer of thickness  $\Delta \ll R$ , permittivity  $\epsilon_s$ , and ohmic conductivity  $\sigma_s \ll \sigma_c$ . The particle is modeled in terms of surface capacitance  $c_s (= \epsilon_s / \Delta, \text{ in } \text{F}/\text{m}^2)$  and surface transconductance  $g_s (= \sigma_s / \Delta, \text{ in } \text{S}/\text{m}^2)$ .

The effective complex permittivity of the particle can be expressed as [7]

$$\epsilon_2^* = \frac{c_s^* R \epsilon_c^*}{c_s^* R + \epsilon_c^*} \quad (4)$$

where  $c_s^* = c_s - jg_s / \omega$  is the complex capacitance per unit area. Assumed that the transconductance is small enough to be ignored, the expression for the effective permittivity can be rewritten as [7]

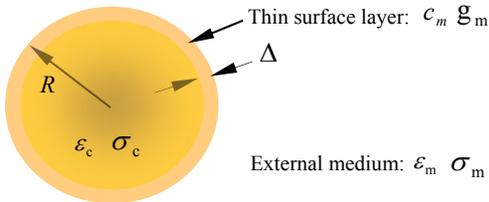


Figure 1 Single shell model of gold colloid.

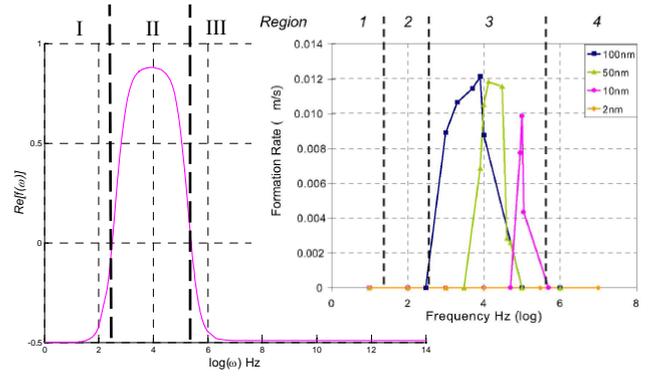


Figure 2 DEP spectrum of single shell sphere (Core gold particle:  $\epsilon_c = 1 \epsilon_0$ ;  $R = 100 \text{ nm}$ ;  $\sigma_c = 2.4 \times 10^{-4} \text{ S/m}$ . Thin surface layer:  $c_s = 0.25 \text{ F/m}$ ;  $g_s = 0$ . Deionized water:  $\epsilon_m = 80.18 \epsilon_0$ ;  $\sigma_m = 5.5 \times 10^{-6} \text{ S/m}$ ). The inset shows the experimental results.

$$\epsilon_2^* = c_s R \frac{j\omega\tau_c + 1}{j\omega(\tau_s + \tau_c) + 1} \quad (5)$$

Here,  $\tau_s = c_s R / \sigma_c$  and  $\tau_c = \epsilon_c / \sigma_c$ . Combining Equation (5) and Equation (2), the complex Clausius-Mossotti factor becomes [7]:

$$f(\omega) = -\frac{\omega^2(\tau_m \tau_s - \tau_c \tau_m') + j\omega(\tau_m' - \tau_m - \tau_s) - 1}{\omega^2(2\tau_m \tau_s + \tau_c \tau_m') - j\omega(\tau_m' + \tau_m + 2\tau_s) - 2} \quad (6)$$

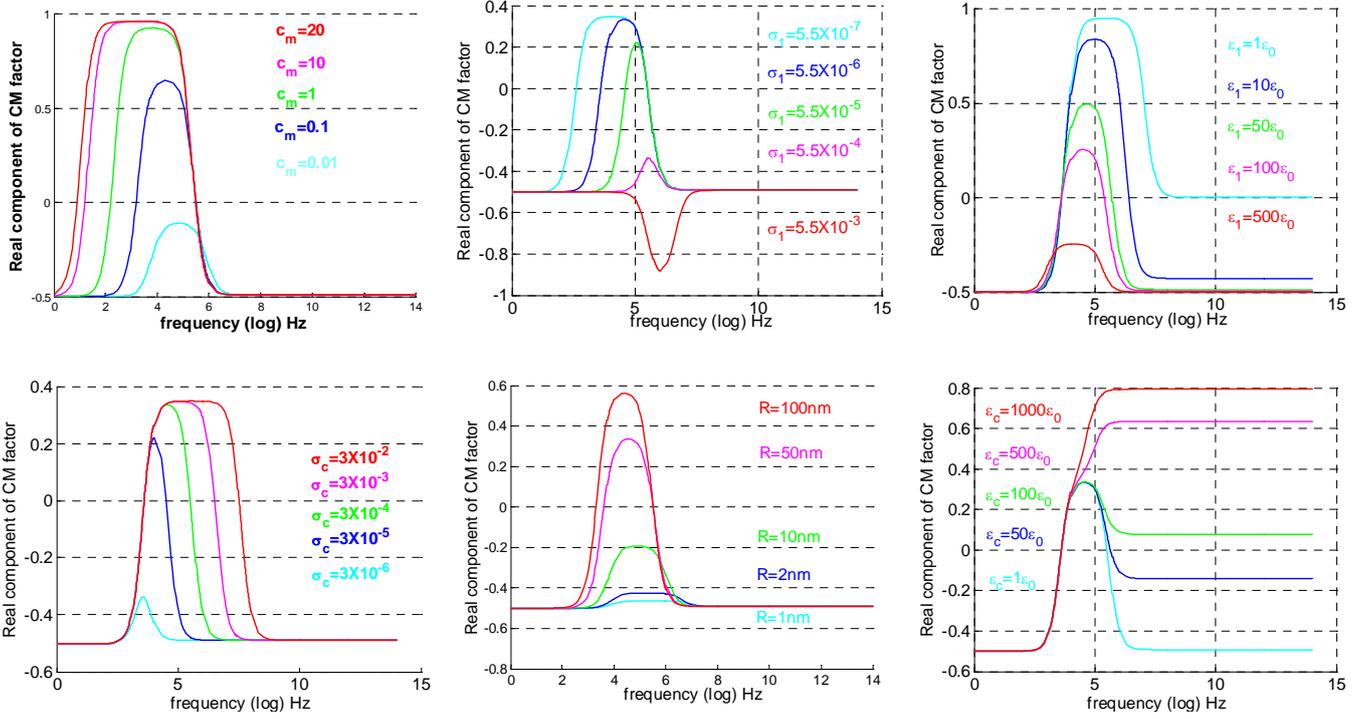
Here,  $\tau_m = \epsilon_m / \sigma_m$  and  $\tau_m' = c_s R / \sigma_m$ . To determine the frequency dependence of the DEP force acting on the particle, it is necessary to obtain the real part of Equation (6).

For the simulation described below, gold colloids with the size of 100nm suspended in deionized water are considered. Figure 2 plots  $\text{Re}[f(\omega)]$  for a set of parameters. Note three regions of the frequency spectrum where  $\text{Re}[f(\omega)]$  is roughly constant, separated by two distinct breakpoints, which is similar to our experiments (see reference [16] for detail), as shown in the inset of Figure 2. According to the single shell model of the colloid suspension, the frequency spectrum is controlled by a number of parameters, such as the complex dielectric constant of core particle, of the surface layer, of the suspension medium, and the colloid radius.

We discuss below how various physical parameters influence the value of  $\text{Re}[f(\omega)]$ . The simulation results are shown in Figure 3. Note that these parameters also influence the magnitude of the real part of Clausius-Mossotti factor more or less, in addition to the low or high cross-over frequency.

Table 1 Summary of the parameters affecting the DEP force spectrum. The general trends are given for three growth characteristics within the ranges studied. The characteristics increase ( $\uparrow$ ), decrease ( $\downarrow$ ), or remain constant ( $-$ ) as each parameter is increased. Additional characteristic ( $\uparrow$ ) refers to less trend.

Parameters	$R$	$c_s$	$\sigma_m$	$\epsilon_m$	$\sigma_c$	$\epsilon_c$
$f_{low}$	$\uparrow$	$\downarrow$	$\uparrow$	$-$	$-$	$-$
$f_{high}$	$\uparrow$	$-$	$-$	$\downarrow$	$\uparrow$	$\uparrow$
Magnitude	$\uparrow$	$\uparrow$	$\downarrow$	$\downarrow$	$\uparrow$	$-$



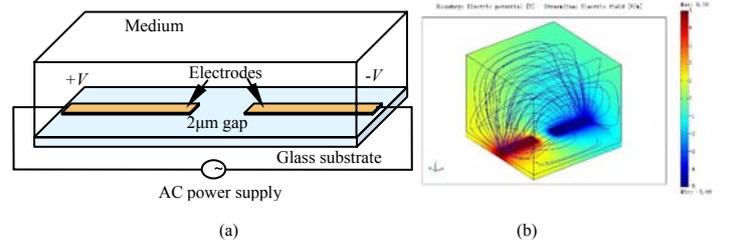
**Figure 3**  $\text{Re}[f(\omega)]$  versus frequency by varying parameters of single shell sphere to show their influences.

The effects of these parameters on the left and right cross over frequency and the magnitude are summarized in Table 1. The surface capacitance and solution conductivity are of major importance to the low critical frequency. The solution permittivity and core particle conductivity mainly have impact on the high critical frequency. The effects of these parameters on the magnitude vary extensively and have some peak maxima.

Manipulating gold colloids using DEP effects to form nanoscale device [3], microwires [5, 13], and gold colloidal crystals [16] have been demonstrated, hence DEP can be regarded as a remarkably simple, highly reproducible, and low cost nano-manipulation technology. The DEP manipulation of micrometer particles has been extensively demonstrated in the past decade, *i.e.*, bioparticles, dielectric particles, and metallic particles could all be manipulated by DEP force. However, the effects of Brownian motion will become greater as the size of the particle is reduced. One procedure to solve this problem is to increase the electric field by reducing the characteristic dimensions of electrode structure. However, the electric-induced fluid flow can be a greater limiting factor than Brownian motion. According to the scaling law in reference [15], it is possible to predict the feasibility of DEP manipulation giving the size of particles.

#### IV. SCALING LAWS

Consider a simplified electrode structure, as shown in Figure 4(a). The size of the gap between the coplanar electrodes  $2r$  is 2 micrometer. The three-dimensional electrical field streamlines are also presented in Figure 4(b). At the section perpendicular to the centre of the surfaces of electrodes,



**Figure 4** (a) The schematic diagram of the electrodes. (b) Three-dimensional electric field streamlines across the electrodes.

the electric field lines can be simplified as semi-circular (see the reference [15] Fig. 1 (b)).

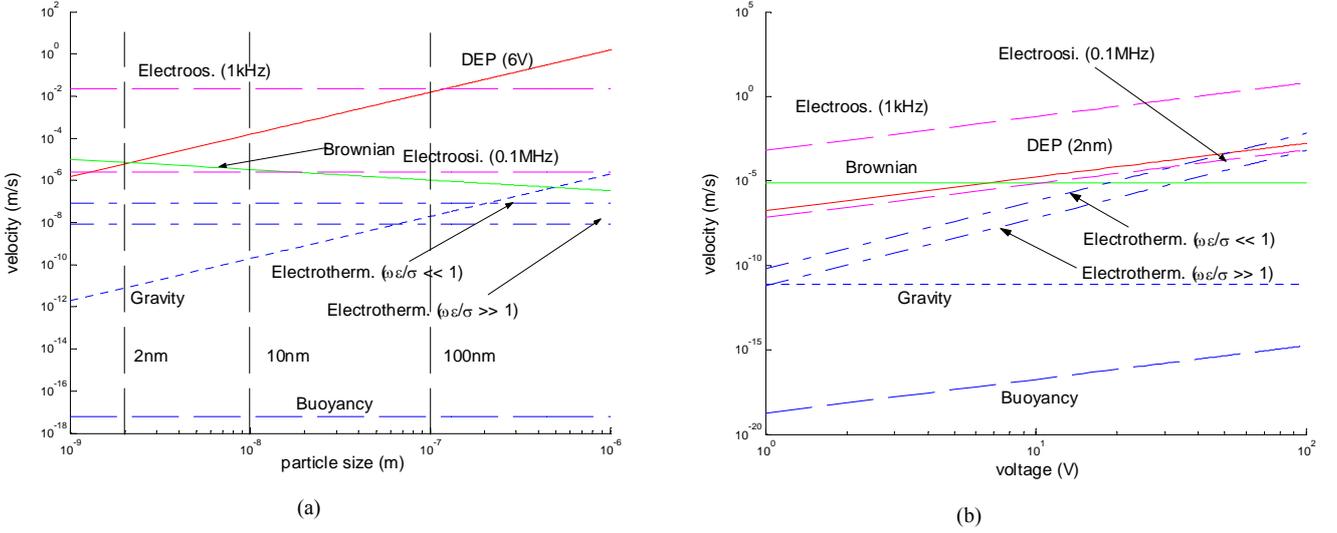
For gold colloids suspending in deionized water, the magnitude of the velocity of a particle in a gravitational field is

$$u_g \approx 0.2 \frac{R^2 \rho_m g}{\eta} \quad (7)$$

where  $\eta$  is the viscosity of water (1cp),  $\rho_m$  the density of water ( $1 \text{ g/cm}^3$ ), and  $g$  the acceleration of gravity ( $9.8 \text{ m/s}^2$ ). Assuming a Clausius- Mossotti factor of 1.0 and an electric field given by  $E = V/\pi r$ , the magnitude of the DEP velocity of a particle, at a distance  $r$  from the centre of gap, is

$$u_{DEP} \approx 0.03 \frac{R^2 \epsilon_m V^2}{\eta r^3} \quad (8)$$

The magnitude of the velocity of a particle arising from Brownian motion can be given by



**Figure 5** The velocity of a particle suspending in DI water versus (a) particle size, and (b) applied voltage ( $r = 1\mu\text{m}$ ).

$$u_{Bro} \approx \frac{1}{2} \sqrt{\frac{k_B T}{3\pi R \eta t}} \quad (9)$$

Here,  $k_B$  is Boltzman's constant,  $T$  the absolute temperature 300 K, and  $t$  the period of observation. Consider the electric-induced fluid flows such as electrothermal flow, Buoyancy flow, and AC electro-osmosis flow, the magnitudes of the velocities of a particle are given by

Electrothermal ( $\epsilon_m \omega / \sigma_m \ll 1$ ):

$$5 \times 10^{-4} \frac{\epsilon_m \sigma_m V^4}{k \eta r} \left| \frac{\partial \sigma_m}{\sigma_m \partial T} \right| \quad (10)$$

Electrothermal ( $\epsilon_m \omega / \sigma_m \gg 1$ ):

$$2.5 \times 10^{-4} \frac{\epsilon_m \sigma_m V^4}{k \eta r} \left| \frac{\partial \epsilon_m}{\epsilon_m \partial T} \right| \quad (11)$$

Buoyancy:

$$2 \times 10^{-2} \left( \frac{\partial \rho_m}{\partial T} \right) \frac{\sigma_m V^2 g r^2}{k \eta} \quad (12)$$

AC Electroosmosis:

$$0.1 \Lambda \frac{\epsilon_m V^2}{\eta r} \frac{\Omega^2}{(1 + \Omega^2)^2} \quad (13)$$

$$\Omega = \Lambda \frac{\omega \epsilon_m \pi r}{2 \sigma_m \lambda_D}; \Lambda = \frac{C_S}{(C_S + C_D)} \quad (14)$$

where  $k$  is the thermal conductivity of water,  $C_S$  the capacitance of the Stern layer,  $C_D$  the capacitance of the diffusion layer, and  $\lambda_D$  the Debye length ( $\approx 10$  nm [17]), with  $C_D = \epsilon / \lambda_D$ . For water,  $k = 0.6 \text{ Jm}^{-1}\text{s}^{-1}\text{K}^{-1}$ ,  $(1/\sigma_m)(\partial\sigma_m/\partial T) =$

$+2\%$  per degree,  $(1/\epsilon_m)(\partial\epsilon_m/\partial T) = -0.4\%$  per degree, and  $(1/\rho_m)(\partial\rho_m/\partial T) = 10^{-4}$  per degree [18].

Figure 5 shows the velocity of a particle suspending in deionized water with conductivity  $5.5 \times 10^{-6} \text{ S m}^{-1}$ , plotted (a) as a function of particle radius and (b) as a function of voltage applied between the microelectrodes, using the same characteristic length  $r = 1 \mu\text{m}$ . Figure 5(a) shows that the velocity due to Brownian motion is greater than that due to DEP at 6V for a particle of approximate 2 nm radius in such microelectrodes. This was validated in our experiments [16].

Figure 5(b) suggests that higher voltages and higher frequencies are needed to overcome the effects of Brownian motion and AC electro-osmosis. However, an intensive electric field is impractical for the clearly predominant electro-thermal effect, the electrolysis, and the corrosion of electrodes. In addition, the frequency-dependent real part of Clausius-Mossotti factor may not achieve the max value of 1 due to constraints of electrical properties of gold colloids and suspending solutions. Therefore, it is difficult to directly manipulate a 2 nm gold colloid using DEP. Washing the gold colloids before applying electric field can remove the remnants and stabilizing agents that stick to the colloid surface to make the gold nanoparticles become conductive spheres. However, metallic particles, exposed on non-uniform electric field, will aggregate to form fractal pattern [13], hence the formation of gold particle wires becomes much more difficult to control when the particle size becomes less than 50 nm.

## V. CONCLUSION

The frequency-dependent characteristic of a gold colloid suspending in deionized water manipulated by DEP force was explored. The reverse-bell-shape curve of the frequency characteristic shows that a narrow region of frequency of applied voltage will be the optimal condition to manipulate a

gold colloid, which was demonstrated in our experiments. The order-of-magnitude of the various forces that are experienced by a gold colloid in a simplified ideal system was estimated. Results show that a gold colloid with the size of about 2 nm will be difficult to be directly manipulated by DEP.

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