Dielectrophoretic behaviour of latex nanospheres:

Low-frequency dispersion

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Running title: Stern layer dispersion in dielectrophoresis

Abstract:

The electrostatic manipulation of nanoparticles using non-uniform electric fields (dielectrophoresis) has proved a useful method of investigating the movement of charge around colloidal particles. Whilst previous work has understood many of the ways in which particle behaviour deviates from that predicted by classical Maxwell-Wagner interfacial polarisation theory, there exists an additional, anomalous polarisation mechanism observed in media of high conductivity, causing an unexpected observation of positive dielectrophoresis. Here this is suggested that this may be explained in terms of the polarisation of the Stern layer.

Keywords: Dielectrophoresis, electrokinetics, Stern layer, dielectric

The phenomenon of dielectrophoresis – the imparting of force in a particle suspended in a non-uniform electric field - has been reported for some 100 years and subject to a detailed study for some 50 years by HA Pohl and others (1,2) for the manipulation of cells and other objects on the micrometre scale (1-1000 μ m). However, it is only recently that dielectrophoresis has been applied to the study, manipulation and separation of nanometre scale particles such as nanowires (3,4), viruses (5-7), latex spheres (8,9) and macromolecules (10,11). The dielectrophoretic force exerted on a particle can be positive (attractive) or negative (repulsive) depending on whether the particle is more or less polarisable than the medium; if the particle is exposed to an alternating (AC) electric field, then the magnitude and direction of the force will vary as a function of frequency according to the interplay of the charges both within and surrounding the particle. For example, figure 1 shows a planar electrode array with a cross-shaped gap, energised by AC potentials with opposite polarity on adjacent electrodes and covered with a weak KCl solution containing fluorescently-labelled latex spheres of diameter 220nm. Where the spheres are more polarisable than the medium they are attracted to regions of high electric field (between adjacent electrodes), where they are less polarisable they collect in the electric field null at the centre of the array. These collections usually appear within a second or two of applying the field.

Since the feasibility of dielectrophoretic manipulation of nano-scale particles was demonstrated using microstructured electrodes to collect protein molecules (10), a number of applications have been found for the technique. These have included the separation of virus particles on an electrode array (9), the alignment of nanowires into functional nano-scale semiconductor devices (3,4), and the trapping of single DNA molecules in order to

study its electrical properties (11). However, the latter examples of nano-manipulation using dielectrophoretic forces have been limited to the static (DC) case. The extension of the technique to the use of AC fields offers great potential for the isolation of specific objects – such as nanotubes of a given size or electrical conductivity – from a heterogeneous solution of nanotubes with varying lengths, which offers great potential for the application of dielectrophoresis in practical semiconductor fabrication using nanotubes or nanowires.

Homogeneous nanoparticles suspended in a dielectric medium undergo a single interfacial relaxation process at a frequency related to the properties of the particle and medium. If the dispersion process causes the net polarisability of the particle to change from being greater than that of the medium to being less than that of the medium, then the dielectrophoretic force will change sign. The characteristic frequency at which this change occurs is commonly referred to as the *crossover* frequency. Analysis of the crossover frequency as a function of medium conductivity can be used to characterise the dielectric properties of a particle, and is at present the principal method of dielectrophoretic analysis of sub-micrometre particles such as latex beads (8-11) and viruses (5-7).

Homogeneous dielectric particles experience one Maxwell-Wagner interfacial polarisation, the frequency of which is dictated by the relationship between the complex permittivities of body and surrounding medium expressed by the real part of the Claussius-Mossotti factor, $Re[K(\omega)]$:

$$Re[K(\omega)] = Re \left[\frac{\varepsilon_p^* - \varepsilon_m^*}{\varepsilon_p^* + 2\varepsilon_m^*} \right] \quad [1]$$

where ε_m^* and ε_p^* are the complex permittivities of the medium and particle respectively and a general complex permittivity is given by $\varepsilon^* = \varepsilon - j\sigma/\omega$, with ω the angular frequency of the applied field. It is frequency-variant, and dictates both the magnitude and sign of the dielectrophoretic force. However, it has been observed that for colloidal particles, there are a number of deviations from this behaviour, which have been attributed to movement of charge in the diffuse (12,13) and Stern (14) layers of the electrical double layer.

For colloidal particles, the presence of an ionic cloud of counterions (the electrical double layer) plays a significant role in the dielectric response of charged particles in solution (15). Previous work (5-7,16) has showed that in solutions of lower conductivity (less than approximately 10mS/m) the dielectrophoretic behaviour of sub-micrometre particles is dominated by the effects of charge movement across the particle surface. It has been demonstrated that the surface conductance can be modelled as two separate components: a conductance due to the movement of charge in the diffuse double layer (counterions loosely associated with the particle) and another due to charge movement in the Stern layer (counterions and water molecules adsorbed onto the particle surface). Studies into the diffusion of ions in the electrical double layer (12,13) have shown that the movement of ions through the Debye layer cause an observed increase in effective particle conductivity which is dependent on the bulk ionic strength (and hence the Debye length) by adding an additional surface conductance component. Similarly, electrorotation studies (14) have

shown that a surface conductivity due to tangential charge movement through the Stern layer contributes another additional term to the net polarisability of the particle, such that the net equivalent conductivity of the particle is given by

$$\sigma_p = \sigma_{pbulk} + \frac{2K_s^i}{r} + \frac{2K_s^d}{r} \quad [2]$$

where σ_{pbulk} is the bulk conductivity of the particle with radius r , and the effective conductances due to the movement of charge in the diffuse double layer Stern layer are represented by K_s^d and K_s^i respectively.

However, in solutions of higher ionic strength, in which the particle is anticipated to be less polarisable than the medium and therefore to be repelled from high electric fields at all frequencies, attraction has still been observed for latex beads and virus particles. Similarly, studies of the frequency-dependent force exerted on virus particles and latex beads in low ionic strength media have shown large increases in particle polarisability in the same frequency window as the anomalous crossover in high ionic strength media (e.g. 12, 17). Whilst the extensions to classical theory presented in equation 2 successfully account for the dielectrophoretic behaviour of particles below the threshold medium conditions where the particle is more polarisable than the medium at low frequencies, there is an anomalous condition in media of high ionic strength. Particles are observed to undergo positive dielectrophoresis at lower frequencies, with observed crossovers in the range 100kHz-1MHz. The crossover frequency is typically constant for particles of one

type, but has been observed to scale with particle radius for particles with similar surface chemistry (12), and with surface conductance for particles with similar size (16).

In order to describe the low-frequency dispersion it is suggested here that this behaviour is due to the dielectric polarisation and dispersion in the Stern layer. This can be modelled by adding an additional dispersion following the Debye model of the form $1/(1+j\omega\tau_e)$ where τ_e is the relaxation frequency of the additional dispersion. Unlike the diffuse layer, the Stern layer is of fixed size and charge, these being dictated by the surface charge density of the particle. Hence, the frequency of the dielectric dispersion would be expected to be stable over a range of medium conductivities; this is observed in the experimental data published on the subject (5,6,12,16-18). Furthermore, the dispersion frequency has been observed to vary linearly with predicted surface conductance K_s^i for latex beads with functionalised surfaces (12) and *herpes simplex* viruses in a variety of biophysical states (18). The frequency of the anomalous dispersion has also been observed to vary linearly with bead diameter in a range of electrolytes.

Previous attempts to model the full dielectrophoretic response of latex beads (e.g. 16) explored the possibility that a Debye-type relaxation may be responsible for the anomalous dielectrophoretic effect in high-conductivity media, but considered the dispersion process as being related solely to ionic diffusion through the double layer. An accurate fit to all published data is a dispersion having relaxation time related to the effective resistor-capacitor (i.e. lossy dielectric) nature of the electrical double layer. This can be derived from the well-known expression for the time constant for a resistor-capacitor circuit:

$$\tau_0 = RC \quad [3]$$

where R and C are the values of resistance and capacitance respectively. Taking the equations for resistance and capacitance for a cuboid of material of cross-sectional area A and thickness d ;

$$\left. \begin{aligned} R &= \frac{1}{\sigma} \frac{A}{d} \\ C &= \varepsilon \frac{A}{d} \end{aligned} \right\} \quad [4]$$

By combining equations 4 into equation 3 and eliminating, and letting the permittivity of the Stern layer as being $\varepsilon_0 \varepsilon_s$, and the conductivity as being $\sigma = K_s^i / a$ where a is the diameter of the particle, then we find:

$$\tau_e = \frac{\varepsilon_o \varepsilon_s a}{K_s^i} \quad [5]$$

When compared to published data for latex beads and viruses, it has been found that the above model provides an accurate fit if the value of the relative permittivity of the medium is approximately five to six times lower than that for the bulk medium. Since the Stern layer consists of bound ions and water molecules held in specific orientations by electrostatic interactions with the charged particle surface, it is suggested here that this factor is not unreasonable; a value of 10 has been suggested for the relative permittivity of the metal-electrolyte interface elsewhere (19). As an example, the experimentally obtained

frequency-dependent dielectrophoretic behaviour of 216nm-diameter latex beads suspended in KCl solutions of varying conductivity, including data previously published in this journal (12; Hughes and Green, in press), is shown in figure 2. Superimposed on this is a best-fit line derived using the above equations and values $K_s^i=0.9\text{nS}$, $\zeta=-100\text{mV}$, $\epsilon_s=14\epsilon_0$. The relative permittivities of the particle and medium 2.55 and 78; the internal conductivity of the beads was considered to be negligible. As can be seen, the model accurately predicts the behaviour both below and above the decade transition in crossover frequency at 40-50mS/m. The model also accurately predicts the behaviour of latex beads of various sizes and functionalities published in the literature (12,16) and virus particles in various conditions (18). It is interesting to note that the dispersion indicates that the total capacitance of the double layer is dominated by the capacitance of the Stern layer. However, we may anticipate that at very high conductivities, the Debye relaxation frequency may diminish due to the diminution of the diffuse layer thickness, and corresponding reduction in diffuse layer capacitance.

This result is significant in that it completes the understanding of the principal processes of charge movement affecting the dielectrophoretic manipulation of colloidal particles in AC fields. It therefore describes the terms under which particles may be engineered so as to allow for on-chip self-assembly according to applied frequency and suspending medium. There remains further anomalous behaviour to be understood, including the peak in crossover frequency observed in the crossover spectrum just before the “drop” in crossover frequency at higher conductivities, which will necessitate further study.

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Figures

Figure 1. Fluorescence micrographs showing positive and negative dielectrophoresis of 216nm diameter latex spheres in solution. Left: particles are attracted to regions of high electric field (positive dielectrophoresis). Right: particles are repelled from regions of high electric field and trapped in a field null at the centre of the array (negative dielectrophoresis). The collections occurred over a period of approximately 5 seconds with applied potentials of $20V_{pk-pk.}$, and frequencies of 1MHz and 10MHz respectively. The transition frequency between these modes of behaviour is called the crossover frequency, and is related to the dielectric properties of particle and medium. Scale bar: $20\mu m$.

Figure 2. Experimental DEP crossover spectra (dots) for 216nm diameter latex beads suspended in KCl solutions of varying conductivity, with best fit line according to the model described in the text. The best-fit values for the model indicate a surface conductance K_s^i of 1nS and zeta potential ζ of 100mV, with an assumed internal permittivity of $2.25\epsilon_0$ and internal conductivity assumed to be less than 1mS/m.