

Fast and precise measurements of particle charge with optical trapping electrophoresis

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ABSTRACT

We subject micrometer-sized, optically trapped colloidal particles in a non-polar liquid to a sinusoidally varying electric field, and measure their resulting movement. From this movement, we calculate the electrophoretic mobility and charge of the particle in the liquid. The use of high frequencies of the electric field (well above the corner frequency of the optical tweezers) allows us to estimate the electrical charge of colloidal particles with an accuracy of the order of the electron charge in a time interval of only 10 ms. This technique can be used to provide valuable information about the dynamics of the poorly understood processes that lead to the charge on colloidal particles in non-polar liquids.

Keywords: Optical tweezers, electrophoresis, colloids, elementary charge

1. INTRODUCTION

Since their invention in the seventies, optical tweezers have become a valuable tool in a multitude of research fields. They are used for the manipulation and study of objects on the nanometer and micrometer scales, ranging from single molecules¹, over colloidal particles², to living cells³. One of the most interesting applications of optical tweezers comes from their ability to locally detect very small forces exerted on an object⁴. This principle has been used for instance to investigate the visco-elastic properties of DNA-molecules⁵, the workings of molecular motors⁶, the mechanical properties of biological cells⁷ and the hydrodynamic flow around colloidal particles⁸. However, relatively little is known about applications of optical tweezers to measure electrical forces, despite their importance, for instance, for the electrical properties of colloidal suspensions.

Charged colloids with particle charges ranging from just a few to thousands of elementary charges have been studied intensively in recent years. Their large number of applications makes them interesting for a wide range of research fields. In soft condensed matter colloidal crystals of oppositely charged particles are used to model atomic systems⁹. In biophysics enzymatic reactions at particle surfaces are studied by measuring the charge on the particle¹⁰. Particle charge is important in colloid and interface science for the fundamental study of interparticle interactions¹¹. Finally, industrial processes and technologies, such as electrophoretic deposition and electrophoretic displays are based on the movement of charged particles in an electric field¹². A number of techniques exists to characterize charged colloids, such as acoustophoresis¹³, dynamic and electrophoretic light scattering¹⁴ and phase analysis light scattering¹⁵. These methods provide average properties of many particles or over a certain duration of time, but no information is obtained on individual particles. This complicates the interpretation of the results, because the size and charge of particles in a solution is usually polydisperse.

Recently the charge on single colloidal particles has been studied by optical tracking electrophoresis techniques, giving detailed information on individual particles and the distribution of particle charges¹⁶. In these techniques, usually the movement of the particle as a response to applied electrical voltages is observed with a microscope setup, and

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recorded with a CCD camera. This method enables to study multiple particles at the same time, but serious limitations arise from the fact that the particles to be studied are moving freely as a result of Brownian fluctuations or hydrodynamic flow, superimposed on the movement as a result of the electric field. Because of these reasons, the particles often move out of focus or out of the field of view of the microscope.

We overcome these problems by combining optical trapping and electrophoresis measurements. The particle to be studied is confined to a small region of space by the optical trap, while its movement (in this region) as a result of an externally applied electric voltage is measured. An additional advantage of the fact that the freedom of movement of the particle is limited is that much faster position detection techniques with a more limited range, can be used instead of CCD cameras. Previous publications on optical trapping electrophoresis¹⁷ used relatively low driving frequencies, which limits the electrical force that can be applied without pulling the particle out of the optical trap. Therefore also the accuracy and the possible speed of the charge measurements were limited. Unlike other publications, in this work we use high frequency optical trapping electrophoresis with multiple electrophoretic mobility measurements to obtain the number of elementary charges on colloidal particles in a nonpolar liquid and the dynamics of the change of this charge. We show that this method allows monitoring the single events of the charging reactions on the surface of the particle, by detecting changes of a single electron charge. This approach provides new possibilities for the characterization of colloidal particles, the (dynamic) study of charging processes, the monitoring of chemical and electrochemical reactions, and the detection of (bio)molecules bound to functionalized particles.

The principle of our experiments is similar to the famous oil-drop experiment of Millikan almost hundred years ago¹⁸ in which the elementary charge was determined using oil drops in an electric field in air. Finding the elementary charge in a liquid is much harder, because the viscosity is much higher than that of air, which reduces the motion of weakly charged particles in an electric field to a value which is below the sensitivity of most measurement systems or which can not be separated from Brownian motion. In addition, the charge on particles in air changes only occasionally (a few times per minute), while in liquids (even nonpolar liquids) the particle is always interacting and exchanging charges with its environment (a few times per second for nonpolar liquids). This reduces the time available to obtain a single measurement of the momentary charge on the particle. Therefore, the main goal of this work is not to obtain accurate values of the elementary charge (for which much better techniques are available), but to provide a method to detect the single events of electrochemical reactions, and to use the known value of the electron charge for calibration purposes.

2. MATERIALS AND METHODS

2.1 Nonpolar colloidal suspension and electrophoretic device

In this study we use PMMA particles with radius 498 nm, sterically stabilized by chemically grafted poly-12-hydroxystearic acid (PHSA), obtained from Andrew Schofield and synthesized following known procedures¹⁹. The particles are dispersed in the non-polar solvent n-dodecane (Rectapur, VWR) at volume fractions below 0.001. Because of the low dielectric constant ($\epsilon=2$) and the large Bjerrum length (28 nm) of n-dodecane, separated charges are rare²⁰. As a result the charge of the PMMA particles in dodecane is low: A study by Roberts et al¹⁷ on similar mixtures reports a distribution of particle charges between $-20e$ and $10e$, with e the elementary charge. This is more than a hundred times smaller than the charge on similar particles in water ($\epsilon=80$)²¹. Due to the low charge concentration, electro-osmosis can be neglected. The mixture of nonpolar liquid and colloidal particles is inserted into a custom-made electrophoretic device with two electrodes separated by a distance $d=500\ \mu\text{m}$.

2.2 Optical trapping setup and calibration

We use a standard optical tweezers setup to trap a PMMA particle in the middle of the channel between the two electrodes, about $30\ \mu\text{m}$ above the bottom glass plate, and forward-scattering detection of a second laser beam to monitor the position of the trapped particle. Figure 1 shows a schematic representation of the setup. The basis of the optical trapping setup is a self-built inverted microscope, with Kohler illumination and a CCD camera to capture the microscope image. A 100 mW, 985 nm laser beam is expanded so that it overfills the entrance aperture of a 100x, 1.4 NA objective lens. The position of the focus of the trapping beam can be controlled with a mirror which at a conjugate plane of the entrance pupil of the objective lens. Because of the high gradient of the light intensity at the focus, particles with relative dielectric constants higher than that of the surrounding medium, such as PMMA particles in dodecane, are attracted

towards the focus of the laser beam. A second, 633 nm laser beam is also focused on the trapped particle, and its forward scattered light is collected by a condenser lens and imaged on a position sensitive detector (PSD).

The optical tweezers act like a Hookean spring between the trapped particle and a point in space close to the focus of the trapping beam. In this work we are only interested in a single spatial dimension (coordinate x), which is perpendicular to the long axis of the channel and to the laser beam, and parallel with the glass plates. The force F_t of the optical tweezers on the particle in this direction is:

$$F_t = -k_t x, \quad (1)$$

with k_t the trap stiffness and $x=0$ the position of the center of the trap.

The PSD yields a voltage V_{PSD} which is proportional with the x -position of the particle:

$$\Delta x = \rho_{\text{PSD}} \Delta V_{\text{PSD}}, \quad (2)$$

with ρ_{PSD} the proportionality constant. Since the detector acts as a low pass filter with bandwidth f_{PSD} , equation (2) is only valid for low frequencies. The data from the position sensitive detector are recorded at a rate of 20 kS/s.

The three quantities k_t , ρ_{PSD} and f_{PSD} can be obtained by analyzing the power spectral density of the detector signal under influence of Brownian fluctuations, using a well established procedure²². These fluctuations are the result of random collisions of solvent molecules, which cause a force F_B on the particle:

$$F_B(t) = \sqrt{2k_B T \gamma} \xi(t), \quad (3)$$

where k_B is Boltzmann's constant, T is the absolute temperature, γ is the friction coefficient of the particle in the liquid, and $\xi(t)$ is white Gaussian noise with amplitude 1.

Before every measurement shown in this work, we performed a calibration measurement during which no voltage was applied to the electrodes. We used the method and Matlab program from Refs. 23 and 24 to obtain a fit of the theoretical power spectral density to the calibration data^{22,23}. The values obtained varied around $k_t=8$ pN/ μm , $\rho_{\text{PSD}}=430$ nm/V and $f_{\text{PSD}}=22$ kHz.

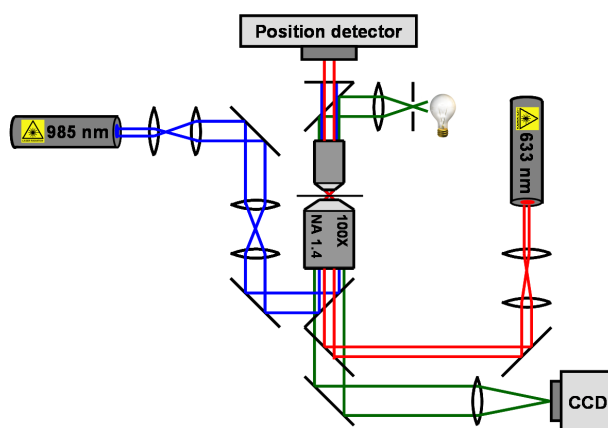


Figure 1. (Color online) Schematic representation of the optical part of the measurement setup. The 985 nm laser used for trapping is drawn in blue, the 633 nm laser used for position detection is shown in red, and the green light for imaging is drawn in green.

2.3 Optical trapping electrophoresis

After performing the calibration measurement, we apply a sinusoidal voltage $V(t)$ with amplitude 1000 V and frequency 1 kHz between the electrodes. The solvent n-dodecane behaves as a dielectric, so the electric field strength $E(t)$ can be calculated as:

$$E(t) = \frac{V(t)}{d}. \quad (4)$$

Since the distance d between the electrodes is 0.5 mm, the amplitude of the electric field is 2 MV/m. If a particle carries a charge Zq_e , with Z its valency and q_e the elementary charge, it feels an electrical force F_e :

$$F_e(t) = Zq_e E(t). \quad (5)$$

Because of this periodical force, the particle oscillates with high velocity. The high driving frequency limits the amplitude of these oscillations, so that the particle stays in the optical trap. From an analysis of the oscillations the charge on the particle can be estimated.

3. RESULTS AND DISCUSSION

3.1 Position and velocity

We measured the variation in the position x of four different optically trapped PMMA particles under influence of an applied electric field and Brownian motion during 25 s. A representative time interval of these measurements is shown in figure 2(a).

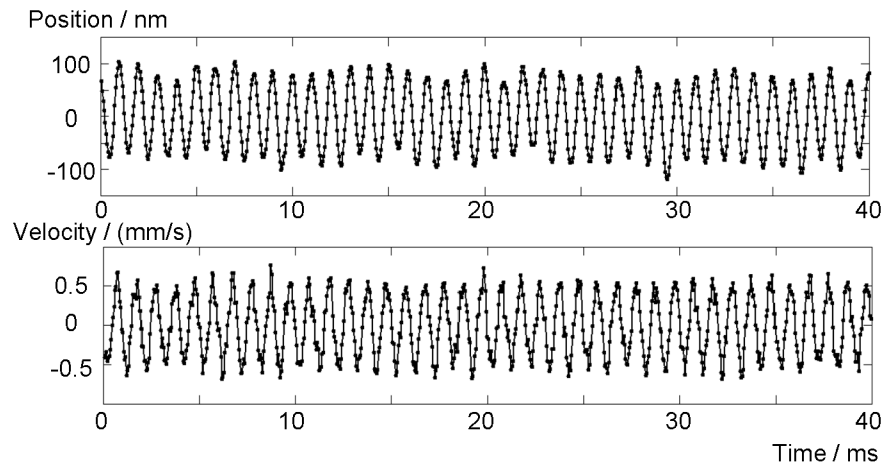


Figure 2. Example of the measured position and velocity of a trapped particle in an electric field, as a function of time.

From these measurements, the velocity $v = \dot{x}$ of the particle can be obtained. Figure 2(b) shows the velocity for the same time interval as in figure 2(a).

Neglecting inertial effects, all forces acting on the particle have to be balanced:

$$F_t + F_B + F_e + F_f = 0, \quad (6)$$

Where $F_f(t) = -\gamma v(t)$ is the friction force.

We will assume in the following that the force of the optical trap can be neglected compared to the viscous force for the used modulation frequency. This assumption is justified by the measurements: the amplitude of the displacement due to the electric field is of the order of 100 nm (figure 2a), so we find a trapping force in the order of 1 pN; the amplitude of the velocity is about 1 mm/s (figure 2b) and the friction constant of our mixture is $\gamma = 12.6$ nN s/m, so we find that the viscous force is about 10 pN. This is in agreement with the fact that the corner frequency $f_c = k_t / (2\pi\gamma)$ of the optical trap (101 Hz) is much lower than the frequency (1 kHz) of the external voltage. At the driving frequency, the particle therefore behaves approximately as if there is no optical trap, but at low frequencies the optical trap prevents the particle from moving away. With this assumption we can rewrite equation (6) as:

$$v = \frac{Zq_e}{\gamma} E(t) + \sqrt{\frac{2k_B T}{\gamma}} \xi(t). \quad (7)$$

3.2 Estimation of the particle charge

Equation (7) states that the velocity of the particle is the result of two phenomena: a deterministic motion in the electric field and a random Brownian motion. The charge Zq_e can be estimated from the measured velocities. For that purpose we write equation (7) as:

$$Zq_e = \frac{\gamma v}{E} \pm \frac{1}{E} \sqrt{2k_B T \gamma}, \quad (8)$$

where the second term on the right hand side has to be interpreted as the standard deviation on our estimation of the charge, which is the first term on the right hand side. This is true when we estimate the charge from one single measurement. We used an average of $N=800$ measurements of the velocity to obtain one charge measurement (corresponding to 40 ms, or a sampling frequency of the charge of 25 S/s). This reduces the standard deviation, which is inversely proportional to the number of points. Our estimation of the charge, and the standard error on this value, is then:

$$Zq_e = \gamma \left\langle \frac{v}{E} \right\rangle \pm \frac{1}{E} \sqrt{\frac{2k_B T \gamma}{N}}. \quad (9)$$

Figure 3 shows the estimations of the particle charge obtained in this way, for four different particles. In the next paragraph we will show that the estimated charges are clustered around integer multiples of the elementary charge, which are indicated by the horizontal line segments in figure 3. The discrete values become visible because the value $N=800$ is chosen in such a way that the standard error becomes lower than the elementary charge.

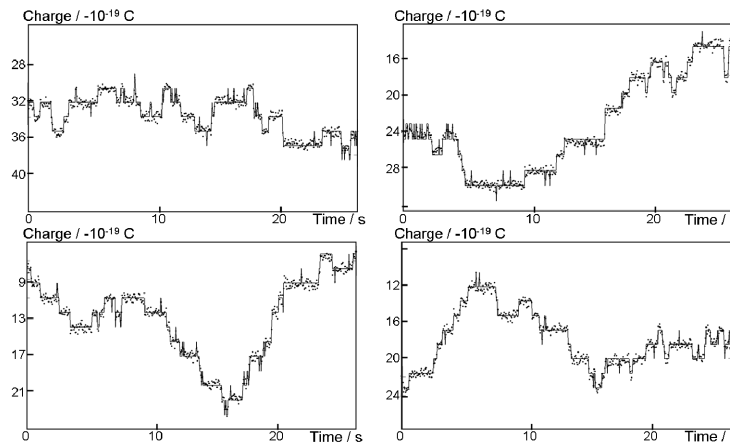


Figure 3. Variation of the electrical charge on four different particles as a function of time. The data are concentrated around integer multiples of a certain value.

3.3 Detection of elementary charging events

As seen in figure 3, the measured values concentrate around integer multiples of a certain value. This becomes more visible in the histograms of the experimental values, shown in figure 4 for each particle. It is obvious that these histograms show evenly spaced peaks. We have developed an algorithm to verify that the peaks appear for integer multiples of a certain value and to estimate the elementary charge from this spacing¹⁶.

We want to find a value \hat{q}_e for the elementary charge q_e which minimizes the sum of the squared differences between the measurements Q_i and the closest multiples $Z_i \hat{q}_e$. The index i corresponds to the different measurements of the charge, and runs (for each bead) from one to $i_{\max}=625$. The (integer) valency of the closest multiple is equal to $Z_i = [Q_i / \hat{q}_e]$, where the square brackets denote rounding to the closest integer value. The function R^2 yields the sum of the squared errors with respect to the closest multiple of a charge q :

$$R^2(q) = \sum_{i=1}^{i_{\max}} \left(Q_i - \left[\frac{Q_i}{q} \right] q \right)^2. \quad (10)$$

For uniformly distributed measurement points Q_i , it can be verified that this function is equal to $i_{\max} q^2 / 12$. A value of R^2 smaller than this means that the data are to some extent concentrated around integer multiples of q . In a good approximation, the best estimation \hat{q}_e can be found as the value where the function $R^2(q)$ reaches its minimum:

$$R'^2(q) = \frac{\sum_{i=1}^{i_{\max}} \left(Q_i - \left[\frac{Q_i}{q} \right] q \right)^2}{i_{\max} q^2 / 12}. \quad (11)$$

We calculated this function for the four different measurement sets, and the results are shown on figure 5. In each case, we find a local minimum close to the known value of the elementary charge $q_e = 1.602 \times 10^{-19}$. This justifies our conclusion that we are indeed detecting variations of single elementary charges.

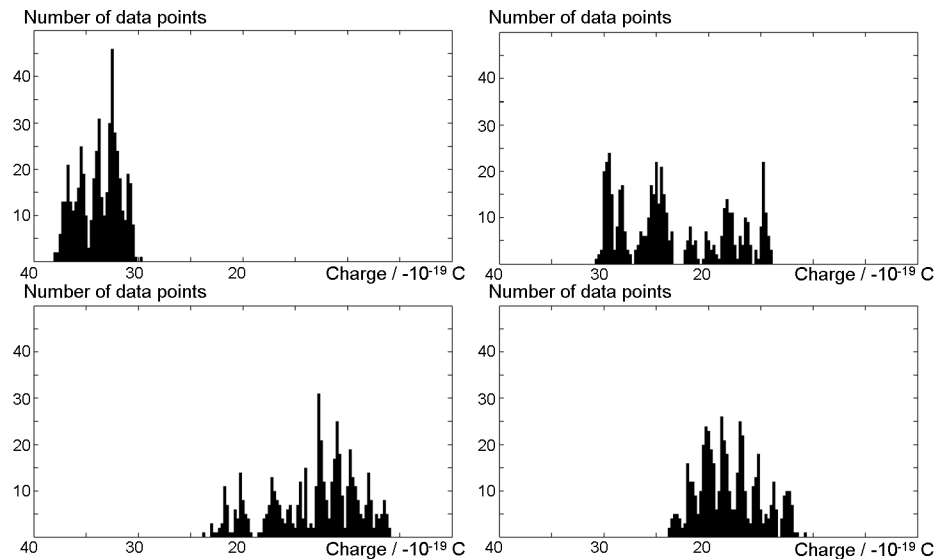


Figure 4. Histogram of the measured charge for four different beads. Peaks can be seen at integer multiples of a certain value.

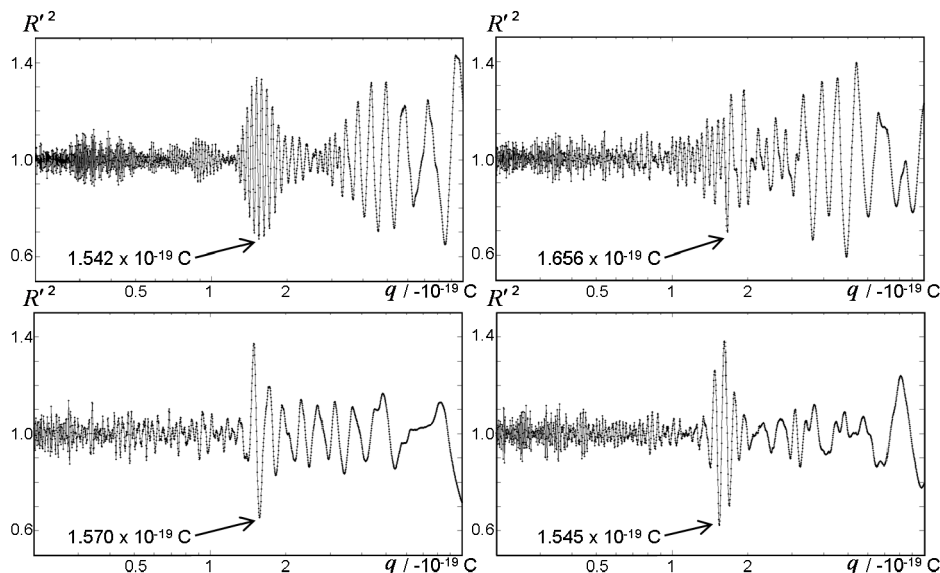


Figure 5. The function according to equation (11) for four different beads. The function reaches a (local) minimum when the relative difference between the measurement points and their closest integer multiple of the variable q is minimal.

4. CONCLUSIONS

We have shown that, using optical trapping electrophoresis, the charge on PMMA particles in n-dodecane can be measured accurately enough to resolve the elementary charge, and fast enough to see changes corresponding to elementary charges. The function of the optical tweezers in this setup is firstly to keep the particle in focus and in the field of view of the microscope during the measurements time, and secondly to allow the use of fast and accurate position detection based on forward light scattering. The high accuracy is reached mainly because of the high electric field. This high field is made possible by the use of a high frequency for the driving voltage, so that the particle is not pulled out of the optical trap because of the strong electrical force.

We were able to obtain accurate values for the elementary charge. There are of course much more accurate methods to determine the elementary charge, and we can use the known value to obtain other quantities with high precision. Instead of considering the bead size as known and determining the elementary charge, we can just as well consider the elementary charge known, and determine the bead size (or the viscosity, the electric field, ...) with very high accuracy.

The main motivation of this method lies in the study of the dynamics of the physical and chemical processes responsible for charging colloidal particles. In nonpolar liquids such as in our work, these processes are not well understood today. Since we can monitor the single events of the charging processes, we expect that a lot of new information about these phenomena can become available.

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