Measurement of elementary charges on colloidal particles

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I. Introduction

The elementary charge e is a fundamental physical constant with a measured value of approximately $1.602176487(40) \times 10^{-19}$C. It is the smallest measurable value of the electric charge in stable matter, despite many recent attempts to measure fractional charges such as 1/3e and 2/3e [1]. Almost 100 years ago, Robert Millikan carried out the first measurement of the value of e by observing the motion of charged oil drops in air under the influence of an electric field [2]. Here, a demonstration is given of the first measurement of the elementary charge on solid particles in a liquid (see also [3], [4], [5]). Finding the elementary charge in a liquid is much harder than in air because of the higher viscosity. This reduces the motion of weakly charged particles in an electric field to a value which may be below the sensitivity of most measurement systems.

II. Experimental Results

For the charge measurement, optical tracking of isolated particles in a liquid is used [6]. The position of spherical silica particles with radius $1.05 \pm 0.05 \mu$m in pure dodecane is measured as a function of time, while a square wave voltage is applied (see Fig. 1).

The motion in the x-direction, which is the direction of the electric field, shows a roughly triangular shape, while in the y-direction, perpendicular to the field, the motion is governed by random Brownian motion. The electrophoretic mobility μ is calculated in each half period of the square wave as $\Delta x/(\Delta t E)$.

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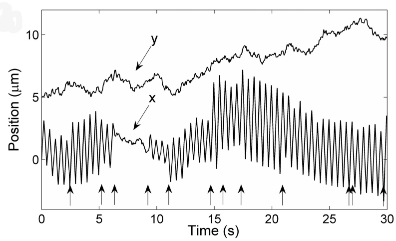

Figure 1. The particle position in the x- and y-direction, during the application of a square wave voltage.

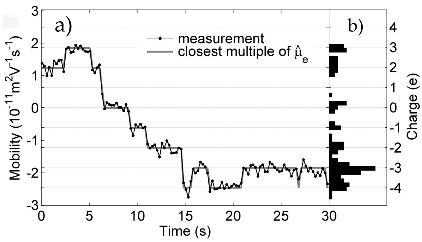

Figure 2. a) The electrophoretic mobility and b) histogram of the mobility.

As can be seen in Fig. 2a, the mobility does not change in a continuous way, but rather in discrete steps with amplitude μ_e, the elementary mobility corresponding to a change in the particle charge with e. With the Stokes-Einstein relation we can estimate $\mu_e = e/6\pi\eta R \approx 6 \times 10^{-12} \mathrm{m}^2\mathrm{V}^{-1}\mathrm{s}^{-1}$, with the particle radius $R = 1.05\mu$m and viscosity

$\eta = 1.38 \times 10^{-3}$Pas, which agrees well with the distance between the peaks in the histogram of the mobility in Fig. 2b and which confirms that the elementary charge is resolved.

III. Statistical Analysis

An estimated value of μ_e is obtained by analysis of the function $R^2(\mu)$:

$$R^2(\mu) = \sum_{i=1}^{M} (\mu_i - [\mu_i/\mu])^2, \qquad (1)$$

with M the number of mobility measurements (see Fig. 3) and μ_i the measured values of the mobility. For random values of the mobility, $R^2(\mu)$ has the expected value $M\mu^2/12$. If the mobility values are clustered around multiples of μ_e, $R^2(\mu_e)$ is expected to be much smaller than $M\mu_e^2/12$. Therefore, an estimation $\hat{\mu}_e$ corresponds to a local minimum in $R^2(\mu)$. For this experiment with $M = 120$, we find $\hat{\mu}_e = (6.18 \pm 0.05) \times 10^{-12}\text{m}^2\text{V}^{-1}\text{s}^{-1}$.

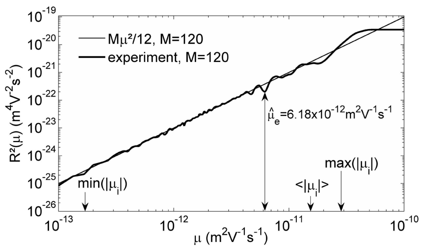

Figure 3. $R^2(\mu)$ is shown for the experiment in Fig. 1, with M=120.

Once $\hat{\mu}_e$ is known, accurate estimations can be made of the particle radius $\hat{R} = e/6\pi\eta\hat{\mu}_e$ and the diffusion constant $\hat{D} = \hat{\mu}_e kT/e$ using the Stokes-Einstein relation. Or, using $R = 1.05\mu$m, an estimation for the elementary charge is found: $\hat{e} = 6\pi\eta R\hat{\mu}_e$. The value $\hat{e}$ for 10 particles is $(1.64 \pm 0.05) \times 10^{-19}$C. Each measured mobility μ_i corresponds to an estimation of the number of elementary charges $\tilde{Z}_i = \mu_i/\hat{\mu}_e$. Fig. 4 shows a histogram of $\tilde{Z}_i$ with clearly visible peaks at multiples of the elementary charge e.

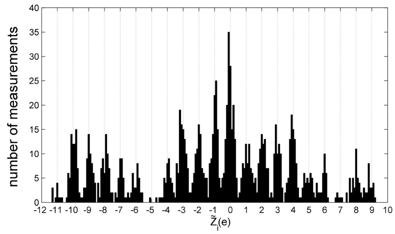

Figure 4. High resolution histogram of $\tilde{Z}_i$ for 1200 measurements on 10 particles.

IV. Conclusions

In conclusion, we have demonstrated that the number of elementary charges, the particle size and changes of the charge with multiples of the elementary charge can be measured on weakly charged particles in a non-polar liquid. This method can be used for the characterization of weakly charged colloids, detection of single biomolecule binding events on the particle surface and for studying fundamental electrokinetic phenomena.

Acknowledgments

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