Single Particle Optical Electrophoresis

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Abstract

Described here is Single Particle Optical Electrophoresis, a novel method to measure charge in colloidal systems. We use an electrophoretic cell in combination with an optical tweezers setup to measure the motion of a single colloidal particle in an oscillating electric field with sub-nanometre precision. This method allows us to measure extremely low charges with a resolution of less than an electron, to investigate the field and frequency dependence of the mobility and to look at the charge distribution within a system.

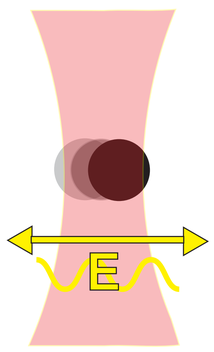
We have studied the charging behaviour of an undyed PMMA and dodecane system with three different additives: PHSA, a polymer that has no effect on the mean particle charge, AOT, a surfactant that charges the particles negatively and Zirconyl 2-Ethylhexanoate, a surfactant that charges the particles positively. This system also allows us to provide a practical demonstration of the behaviour of a Brownian oscillator in a time-dependent external field. We give theoretical expressions derived from the Langevin equation for the motion, and illustrate these with results from the PHSA system where the magnitude of the applied field has been varied.

1. The Experiment

1. An oscillating electric field is applied to a charged particle held in an optical trap.

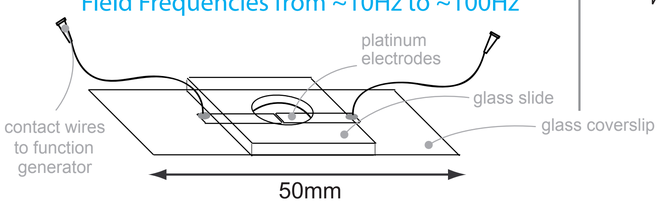
Particle: Undyed PMMA
Radius 610nm

Trap Stiffness ~ 5 fN nm^{-1}

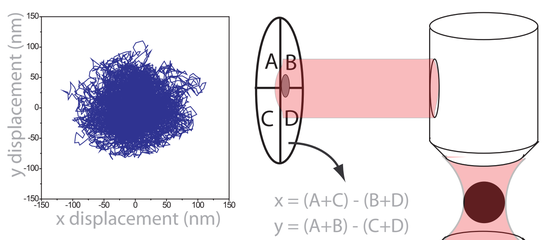


2. The electric field is applied using a function generator, via the electrodes in the electrophoretic cell

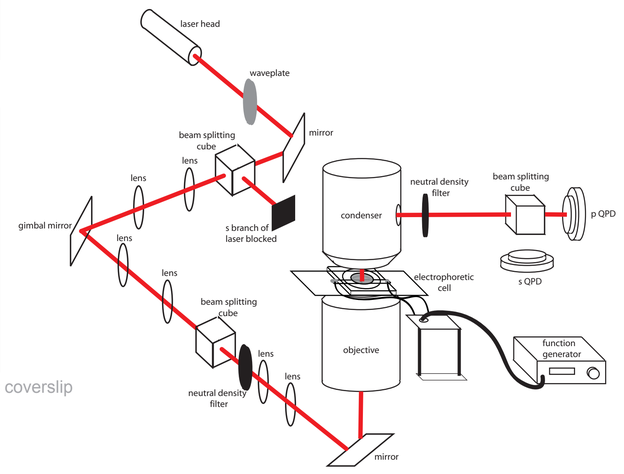
Electrode Separation ~ 128 μm
Max Field Magnitude ~ 80 kV m^{-1}
Field Frequencies from ~10Hz to ~100Hz



3.



Particle motion in the trap detected to sub-nanometre precision using a Quadrant Photo Diode (QPD)



2. A Brownian Oscillator in a Time Dependent External Field - Analysis and Results

ξ = friction coefficient
ω_c = corner frequency
e = unit charge
E_0 = field strength

3 forces acting on a particle in the optical trap:

$$\xi\dot{x}(t) + \kappa_H x(t) = A\sin(\omega_p t + \Phi) + R(t)$$

- Harmonic Force: Optical trap, stiffness κ_H
- External Periodic Force: Oscillating electric field, frequency ω_p, amplitude A, initial phase Φ
- Random Force: Thermal forces at temp T

Langevin equation describing the motion of a particle in the optical trap with an external time-dependent field.

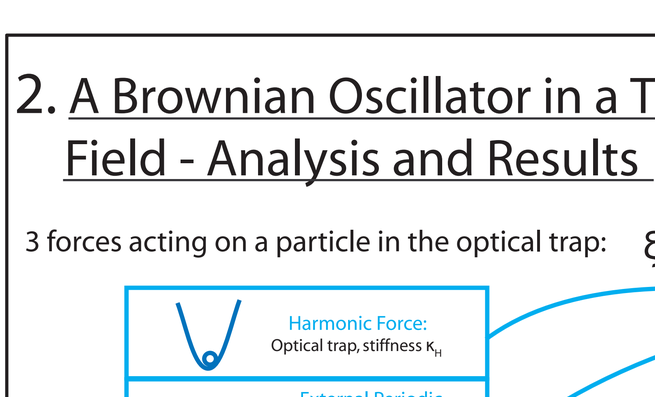
Inertial terms have been dropped as the Brownian time t_B for the particle is ~10^3 times smaller than our experimental time resolution (with 10kHz sample rate).

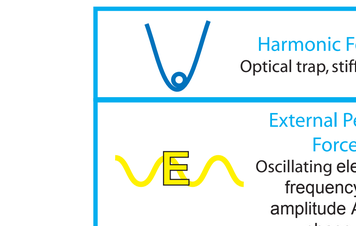
From this equation we can get expressions for the autocorrelations, power spectra and probability density functions (PDF's)

1. Autocorrelations $\gamma \approx 1$

undyed PMMA in dodecane with 0.035% wt free PHSA

$$C(\tau) = \frac{1}{1+\gamma^2}\exp(-\omega_c\tau) + \frac{\gamma^2}{1+\gamma^2}\cos\omega_p\tau$$





The autocorrelation is given by the linear superposition of the exponential decay due to thermal motion and the oscillations due to periodic motion.

We can clearly see that as the field magnitude increases, so the oscillations become increasingly dominant in the autocorrelation. We can also see the effects in the decay at short times.

Define parameter $\gamma^2 = \frac{\alpha^2}{[1 + (\omega_p/\omega_c)^2]}$

where α = ratio of periodic to thermal forces

$= \frac{A^2}{2\,k_B T\,\kappa_H}$ where $A = Z_{eff}eE_0$

so when: $\gamma \ll 1$ periodic « thermal; $\gamma \approx 1$ periodic ≈ thermal; $\gamma \gg 1$ periodic » thermal

2. Power Spectra $\gamma \approx 1$

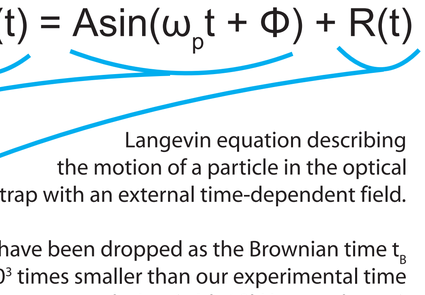
undyed PMMA in dodecane with 0.035% wt free PHSA

$$I(\Omega) = \frac{k_B T}{\pi\xi}\,\frac{1}{\Omega^2 + \omega_c^2} + \frac{k_B T\gamma^2}{2\kappa_H}\,[\partial(\Omega - \omega_p) + \partial(\Omega + \omega_p)]$$

contribution from periodic motion: peak at ω_p

contribution from thermal motion: Lorentzian curve

Using the power spectrum we can detect smaller oscillations than using the autocorrelations (see 13.7 kVm^{-1} results)

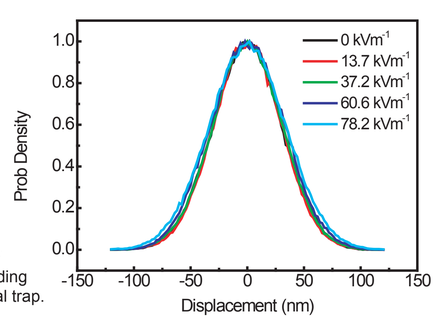


3. PDF's

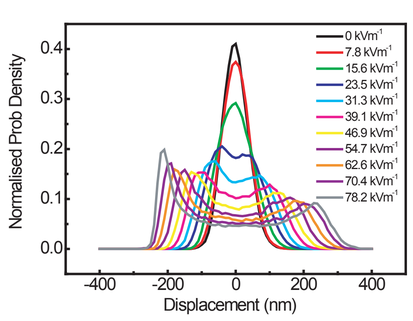
The PDF is the least sensitive method for detecting changes in the motion of a particle in the optical trap due to the applied field. This is because the PDF is not given by a linear superposition of contributions from the thermal and periodic motion but an average of both.

At low γ values we hardly see any change in the width of the PDF, but in a more highly charged system with higher γ values the effect is striking. As the field magnitude is increased the PDF becomes bimodal, with the particle spending most of its time at the edges of the optical trap.

$\gamma \approx 1$ undyed PMMA in dodecane with 0.035% wt free PHSA



Max $\gamma \approx 8$ undyed PMMA in dodecane with 100mM AOT



3. Charging Results

For particles in a nonaqueous medium to bear any charge, ions in solution must be stabilised. Surfactant or polymer additives form micelles in nonaqueous solvents which can perform this function, thus allowing the system to charge.

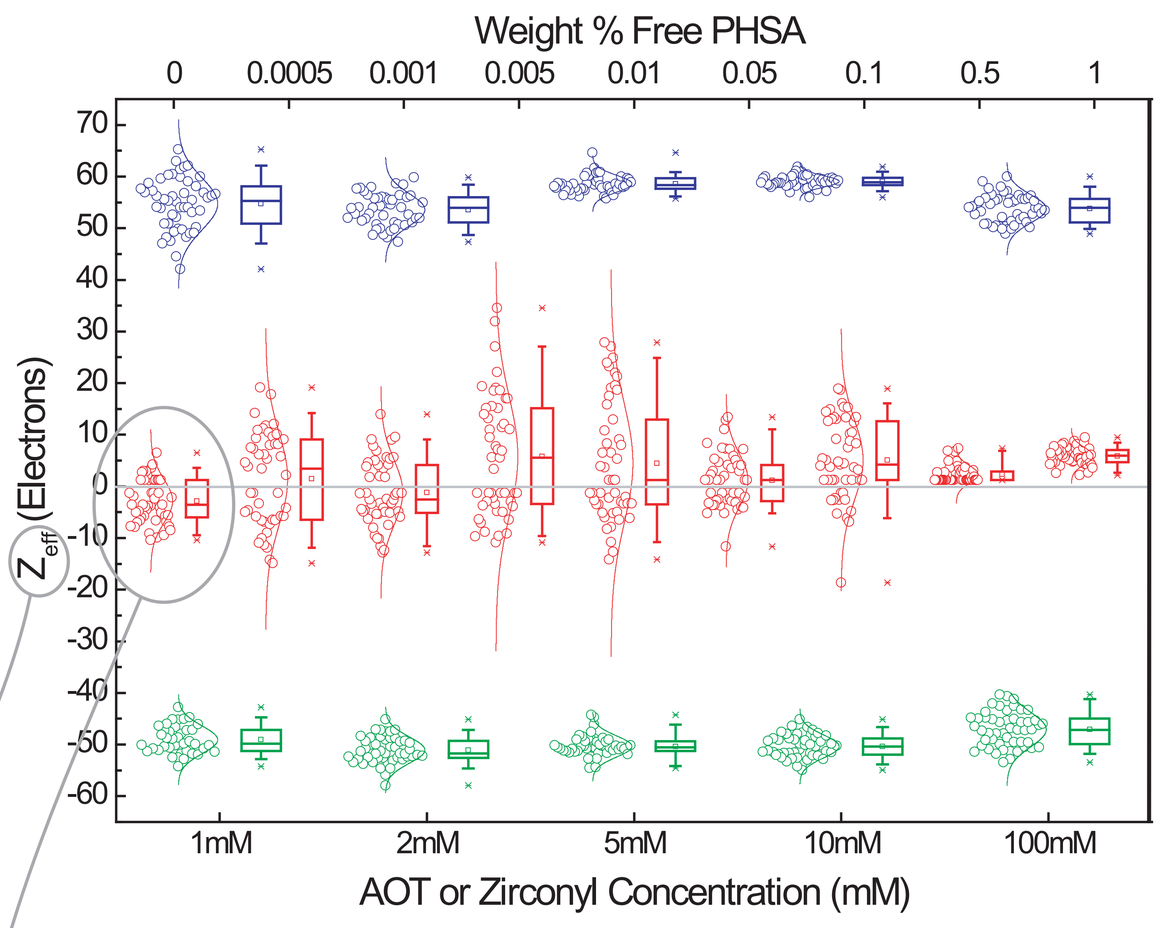
We have investigated the charging behaviour of three different micelle-forming additives in samples of undyed PMMA particles in dodecane: Zirconyl 2-Ethylhexanoate (Zirconyl), Polyhyrdoxystearic acid (PHSA) and AOT.

At each concentration, data was taken for 50 particles:

Zirconyl : Surfactant
Spherical micelles (d = 1.16nm)
Aggregation no. ~ 33

PHSA : Polymer
Rod-like micelles (28nm x 5.2nm)
Aggregation no. ~ 9
Used as stabiliser in systhesis for PMMA particles. Added here as free polymer

AOT : Surfactant
Spherical micelles (d ~ 1.5nm, dry)
Aggregation no. ~ 30



Zirconyl — Mean charge positive.
Charges particles positively. Charge distribution narrows at intermediate concentrations.

PHSA — Mean charge zero.
Has no effect on mean charge, but charge distribution widens substantially as the PHSA conc. is increased, then narrows again.

AOT — Mean charge negative.
Charges particles negatively. Charge distribution shows slight narrowing at intermediate concentrations.

Explanation: Charging due to micelle adsorption

Zirconyl :
- Charged micelle fraction = 1.84 x 10^{-5} from conductivity measurements
- Assume total coverage - ~4.7 x 10^6 micelles on surface
- Assume that both charged and uncharged micelles adsorb and that micelles are singly charged → gives ~ 80 electrons: close!
- Why do positive micelles adsorb preferentially?

PHSA :
- No significant adsorption → zero mean charge (from conductivity measurements on supernatent of PMMA PHSA dodecane solutions)
- Very small amount of adsorption of both negatively and positively charged micelles accounts for charging that is present and the widening of the distribution as the concentration of PHSA is increased
- Why does distribution narrow at high concentrations?

AOT :
- Charged micelle fraction = 6.91 x 10^{-6} from conductivity measurements
- Assume total coverage - ~4.7 x 10^6 micelles on surface
- Assume that both charged and uncharged micelles adsorb and that micelles are singly charged → gives ~ 35 electrons: close!
- Why do negative micelles adsorb preferentially?

0% PHSA: just undyed PMMA in dodecane. No micelles, so should be no charge, but there is! Surface charge groups present from synthesis?

4. Conclusions

- Optical electrophoresis is a very sensitive method of measuring charge in colloidal systems
- It illustrates the physical principles of the motion of a Brownian oscillator in an external field
- It offers us insights into the origins of charging
- The charging mechanisms in nonaqueous systems are very complex