Analysis of intensity/time series obtained in homodyne evanescent wave DLS electrophoretic experiments

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Abstract. The electrophoretic motion in monodisperse and polydisperse systems of silica microspheres was studied by evanescent wave dynamic light scattering technique with homodyne detection. Instead of the attempts to calculate average autocorrelation function, the intensity temporal profile was assessed by short-time Fourier transform followed by multivariate curve resolution. The profile contained random alternate smooth regions and oscillating regions with definite frequencies. The effect was attributed to the few number of moving particles in the narrow zone, illuminated by evanescent wave. The changes in the short-time spectrum corresponded to entry or exit of individual particles. Feasibility to evaluate the mobility of individual particles in polydisperse systems is discussed.

1. Introduction

Optical method are used to evaluate various properties of the colloid system (particle size, charge, shape; medium viscosity, concentration, electrophoretic mobility and others [1-6]. Dynamic light scattering (DLS) has been recently gaining interest as the method of assessment of electrophoretic mobility, offering express measurements and small sample sizes [7]. Several setups have been proposed to measure DLS [7-10]. While the basic principle (Doppler shift) and measurements of DLS are relatively simple, data reduction may be challenging. In electrophoretic studies, the simplification of uncorrelated movement does not apply, and generic models become complex. So more studies of feasible experimental setups and data reduction approaches are needed to create robust and simple measurement systems.

Here we describe measurements of electrophoretic mobility by evanescent wave DLS (EWDLS), also known as total internal reflection (TIR) mode [11]. Time variations of scattered light intensity were recorded, corresponding to homodyne detection. Homodyne EWDLS has several advantages over heterodyne or bulk measurements, it is more robust [12], and less sensitive to electroosmosis. However, the first principle analysis of homodyne EWDLS is complex, as particle dynamics in the illuminated submicron zone near the glass surface is far from isotropic. Moreover, the number of...
particles in the illuminated zone may be very low, so that the scattering is non-stationary. The latter mode was observed in our experiments. So we rejected the attempts to build a model of global average autocorrelation function and focused on medium- and short-term dynamics of intensity, aiming at the description of velocities of individual particles.

2. Experimental setup and data analysis

2.1. Measurement setup and samples
The measurement setup has been described in [13]. Briefly, laser beam (2.5 mW, 655 nm) was put through the TIR prism. The 1.5 mm electrophoretic capillary was organized directly on the reflecting surface of the prism. Scattered light was captured by optical fiber, positioned at 12° from the main TIR beam (solid angle ~10^{-4} sr). Intensity was measured by H10723-20 PMT (Hamamatsu) and sampled with 10 kHz rate with E 20-10 ADC board (L-CARD). One run comprised ~1 sec, 100 runs per sample were measured. The polarity of the electric field was reversed between runs to reduce accumulation of particles and electrochemical effects at the electrodes. Suspensions of 320 nm silica microspheres in distilled water (monodisperse systems) were studied at 0 V/cm and 10 V/cm. The mixtures of 320 nm and 1 μm spheres were assessed at 0 V/cm and 7 V/cm (polydisperse systems).

2.2. Data reduction and analysis
Each run was mean centered, multiplied by confined Gaussian window (α 0.1), zero filled to 2^{14} points and subject to FFT. The truncated power spectra (0-121.6 Hz) comprised the 100 × 200 data matrix. The data matrix was analyzed by principal component analysis (PCA) and multivariate curve resolution by alternate least squares (MCR-ALS) with nonnegativity constraints [14, 15]. Short-time Fourier transform [16] was implemented on mean-centered data with a moving 2^{11} point (~0.2 s) Tukey window.

3. Results and discussion
Basing on the theory of homodyne DLS of bulk electrophoretic samples, oscillations in intensity occur only for systems with skewed or multimodal mobility distribution [17,18]. However, in our electrophoretic experiment, distinct oscillations were observed even in the monodisperse system. The global average autocorrelation function had periodic term, but could not be easily modeled. The analysis of individual runs revealed distinct temporal structure with alternating smooth and oscillating regions (figure 1). Naturally, no oscillations were observed for systems with zero electric field.

![Figure 1](image.png)

Figure 1. A sample series of raw intensity profiles for EWDLS of 320 nm spheres in 10 V/cm (left) and an evolution of short-time amplitude spectrum of a single run (run #5, right).

The fundamental frequency of the oscillations for monodisperse system at 10V/cm comprised 36 Hz, corresponding to the velocity 24 μm/s, accompanied by the weak second harmonic. The
polydisperse system was more complex, producing at least 4 frequency peaks (21, 33, 28 and 47 Hz) with highly variable dynamics. We propose the following feasible explanation for the observed effects. As the layer, illuminated by the evanescent wave is thin (~400 nm) and comparable to the size of the particle, only few particles scatter light at a given moment of time, and these particles are very close to the prism surface. The presence of oscillations may evidence that some particles stick to the surface, providing zero-velocity scattered wave, which serves as an effective heterodyne. When particles enter or exit the illuminated layer, the interference mode may changes, producing the stationary and oscillating regions (like those shown in figure 1). For monodisperse particles three modes are possible: all particles stuck, all moving, and some stuck/ some moving. Only the latter case produces oscillations, while the two former produce stationary runs. The exact origin of the second harmonic in the monodisperse systems is not clear.

To reveal the number of significant contributing spectra we performed principal component analysis (PCA). By doing PCA we assumed that there is a small number of different scattering states, which are common to the runs but vary in their occurrence between the runs, and the contribution of states to the power spectrum of a run is roughly additive. The significance of the lower principle components (PC) is shown in Table 1. For zero electric field, only 2 PCA loadings resembled power spectra, which displayed no peaks. Electrophoretic data were effectively 3-component, with distinct lines in the loadings.

Table 1. Percent of total variance, explained by principal components 1-4.

| Sample                        | PC-1   | PC-2   | PC-3   | PC-4   |
|-------------------------------|--------|--------|--------|--------|
| 320 nm spheres, 0 V/cm        | 81.5%  | 7.8%   | 3.7%   | 2.0%   |
| 320 nm spheres, 10 V/cm       | 72.6%  | 11.8%  | 4.4%   | 3.0%   |
| 320 nm+1 μm spheres, 0 V/cm   | 79.5%  | 8.8%   | 3.5%   | 2.0%   |
| 320 nm+1 μm spheres, 7 V/cm   | 72.8%  | 16.7%  | 2.6%   | 2.5%   |

Figure 2. Bilinear decomposition of data matrices into nonnegative spectra by MCR-ALS, left – normalized spectra, right – weights of decomposition (‘concentrations’). Numbers over the spectra indicate formal positions of maxima.

The data matrix was successfully decomposed into weighted sum of 3 nonnegative spectra by MCR-ALS (figure 2). MCR-ALS estimates may be not unique [15], so the displayed spectra should be
treated with care. The results generally agree to our assumption. In monodisperse system there were three different modes: stationary state (no peaks), moving state (36+72 Hz), and slowly moving state (~5 Hz interference). In polydisperse system there were a stationary response (static particles), a single-frequency response (possibly a shift of a large slow particle), and a multi-frequency response (a triple interference between static, fast and slow particles). The relation of frequencies of these lines could not be easily guessed from this single experiment. It should be noted, that MCR-ALS may have underestimated the number of states and multi-frequency response is actually a combination of several states. More experiments and specific models are required to assign the frequencies.

We believe that short-time analysis of intensity profiles, possibly improved by more accurate data processing like wavelet transform [19] or model-constrained curve resolution, may yield the mobility characteristics of individual particles, complementing analysis of average autocorrelation curves.

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