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# Dynamic Behavior of PMMA-PHSA Hard Spheres Suspensions under External Electric Field

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**Summary:** The dynamic behavior of PMMA-PHSA hard spheres suspended in distinct organic solvents and under an external electric field with different intensities was evaluated by means of dynamic light scattering (DLS) relaxation rates. The study was carried out using a homebuilt copper capacitor with a black finish mate. The experimental data showed that it is possible to modify considerably the diffusion constant of the PMMA particles when an organic solvent having a relative high dielectric constant is used. The effect was attributed mainly due to an interaction between the external electric field applied with the solvent moieties.

**Keywords:** dielectric properties; dynamic behavior; dynamic light scattering; electric field; PMMA-PHSA hard spheres

## Introduction

Knowledge about dynamics of complex colloidal systems has been increasing in interest in the last decades due to their applications in different fields such as drug delivery as well as for fundamental understandings. Dynamic processes in solution or suspension can be studied by different techniques, being one of the most used the polarized dynamic light scattering (DLS). Conversely, essentially due to difficulties in the instrumental arrangements and data treatment, influences of external forces in dynamic behaviors of such systems are still rare explored in the best of our knowledge. In the literature, just a few experimental works dealing with solutions under external electric field were found[1–3] besides theoretical contributions.[4–6] Therefore, our research group addresses some importance to this topic and started to study influences of external electric fields in the dynamic behavior of structured particles in order to shed some light in the origin of the experimental effects observed.

In this contribution, polymer hard spheres are taken as a model system. The particles used were made of poly(methylmethacrylate) (PMMA) grafted with a thin layer of poly(12-hydroxy stearic acid) (PHSA). The last one avoids aggregation due to van der Waals forces. PMMA-PHSA particles have been extensively used as a colloidal model system of hard spheres by Pusey et al.,[7–9] to refer just a few of the relevant contributions made by the authors in this field of knowledge.

Here in, PMMA-PHSA hard spheres were suspended in dimethylformamide (DMF), tetradydrofuran (THF) and decalin which have distinct dielectric constants. The dynamic properties of the particles were studied under an external electric field having different intensities (up to 125 V mm$^{-1}$). The discussion is based on

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determinations of relaxation rates. According to the literature, PMMA-PHSA hard spheres behave as a completely disordered fluid under a volume fraction of 49.4% in *cis*-decalin.[10] Taking this information into account and since the only technique used in this work was ordinary DLS, the experiments were performed in the dilute regime (as explained in the experimental section) with the samples completely transparent in order to avoid multiple scattering.

## Experimental Section

### Sample Preparation

The organic solvents used (DMF, THF and decalin) were of analytical grade purchased from Aldrich. They were selected due to their distinct dielectric constants (given in Table 1).

From a PMMA-PHSA particles stock suspension in *cis*-decalin, 0.1 ml was dropped into 30 ml of organic solvent. The dilute samples were completely clear and transparent. Afterwards, the suspensions were added to an optical glass couvette containing the apparatus used to apply the external electric field. During the measurements the hard-spheres were stable and no aggregation or changes in their size were observed.

### Electric Field Application

A DC external electric field was applied to the suspensions using a homebuilt capacitor schematically represented in Figure 1. As shown (Figure 1), the electric field is pointing out perpendicular to the beam light making possible to monitor the scattered light in a wild angle range. The capacitor was constructed using polyacetal remnant as support for two parallel circular copper plates used as electrodes with a black finish to avoid undesirable light reflections. The electrode separation was choose as 4 mm. External DC electric fields were applied using a high power voltage supply Ortec® model 456. During the experiments, the temperature of the suspensions, the applied voltage and the current density are carefully monitored. The inset in Figure 1 shows a simply circuit used in our experiments to monitor the current that flows in the circuit and the voltage applied.

### Dynamic Light Scattering Measurements

The measurements were done at room temperature (20 °C ± 1) using a Brookhaven Instruments standard setup (BI200M goniometer, BI9000AT digital correlator) with a Coherent He-Ne Laser ($\lambda = 632.8$ nm) as light source. The scattering volume was minimized using a 0.4 mm aperture and an interference filter before the entrance of the photomultiplier. The polarized homodyne intensity autocorrelation functions g2 ($\tau$), were obtained using a multi-$\tau$ mode correlator with 224 channels. The sample cell containing the apparatus was placed in the index-matching liquid decahydronaphthalene (Aldrich) and the scattered light was analyzed in the angular range of 45°–135°. The calibration routine showed that in this range any kind of undesirable reflections due to the presence of the copper plates can be detected. Autocorrelation functions were analyzed by inverse Laplace transformation in order to obtain the distribution of the relaxation times using the Repes routine incorporated in the Gendist commercial software package.

***Table 1.***
Physical parameters of the organic solvents used.[11]

| Solvent | Viscosity (mPa s) | Refractive index | Dielectric Constant |
|---|---|---|---|
| DMF | 0.92 | 1.431 | 38.25 |
| THF | 0.55 | 1.407 | 7.52 |
| decalin | 2.61* | 1.475 | 2.17 |

* Value determined using an Ostwald viscosimeter at 20 °C.

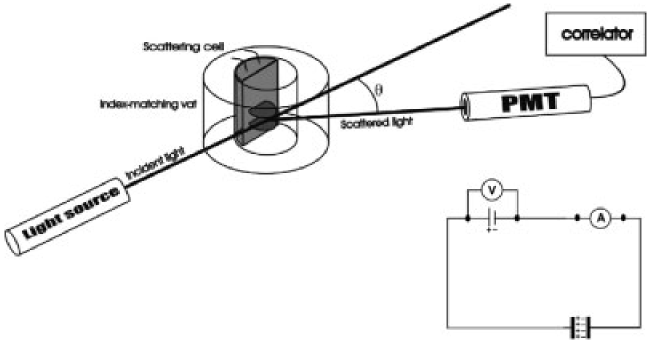

***Figure 1.***
View of scattering cell configuration; PMT is a photomultiplier tube to light scattering detection. The inset shows a circuit used to monitor the current and applied voltage.

## Results and Discussion

### Preliminary Characterization

In order to analyze the DLS correlation functions, it may be considered that the hard spheres are moving in a continuous medium by Brownian motion. The relaxation rates (Γ) obtained by analysis of the autocorrelation functions are related to the apparent diffusion coefficient of the particles ($D_{\text{app}}$) through the scattering vector (q), as given in equation 1.

$$D_{\text{app}} = \frac{\Gamma}{q^2} \tag{1}$$

The scattering vector is defined by the equation 2, taking the refractive index of the solvent ($n$) and the scattering angle ($\theta$) into account.

$$q = \frac{4\pi n}{\lambda} sen\left(\frac{\theta}{2}\right) \tag{2}$$

Having the apparent diffusion coefficients, the well-known Stokes-Einstein relation is used to evaluate the hydrodynamic radius ($R_{\text{h}}$) of the particles (equation 3), which is a suitable approximation since they are spherical.

$$D_{\text{app}} = \frac{k_{\text{B}} T}{6\pi\eta R_{\text{h}}} \tag{3}$$

Where $k_B$ is the Boltzmann constant, $T$ is the temperature and $\eta$ is the viscosity of the solvent. Figure 2 shows the normalized intensity autocorrelation functions measured at scattering angle of 90° for PMMA-PHSA hard spheres suspended in different solvents. The distribution of the relaxation times determined using the Repes routine software is given in the inset. All systems are described by a single relaxation mode and a narrow size distribution as expected.

The Hydrodynamic Radius of the particles determined in different solvents according to equation 3 is given in Table 2. They were in the range of 136–140 nm, attesting the stability of the hard spheres during the course of the experiments.

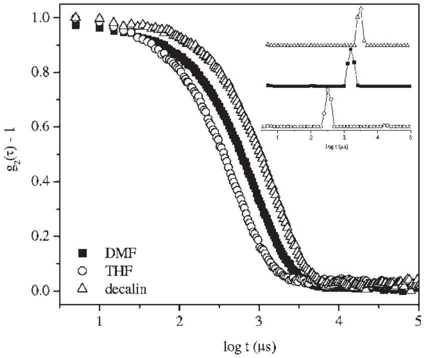

***Figure 2.***
Autocorrelation functions measured at scattering angle of 90° for PMMA-PHSA hard spheres suspended in different solvents and distribution of the relaxation times determined using the Repes routine (inset).

***Table 2.***
Relaxation rates ($\Gamma$) and Hydrodynamic Radius ($R_h$) determined for PMMA-PHSA hard spheres in different organic solvents.

| Solvent | $\Gamma$ (ms$^{-1}$) | $R_h$ (nm) |
|---|---|---|
| DMF | 0.64 | 140 |
| THF | 1.18 | 137 |
| decalin | 0.35 | 136 |

## Behavior under Electric Field

Figure 3 shows typical normalized intensity autocorrelation functions measured for PMMA-PHSA hard spheres suspended in THF in the absence and under an applied electric field of 125 V mm$^{-1}$ (A). Figure 3B depicts the relaxation rates $\Gamma$ (ms$^{-1}$) obtained by data analysis against the square of the scattering vector ($q^2$) in the same conditions. In absence of electric field, the behavior of $\Gamma$ *vs.* $q^2$ indicates that PMMA particles are moving by diffusional dynamics. On the other hand, when an electric field is applied, whereas the linear relation between $\Gamma$ and $q^2$ is maintained, the dynamics begins to be governed by the equation $\Gamma = \Gamma_E + D_E q^2$. $\Gamma_E$ and $D_E$ are respectively the relaxation rate obtained by linear regression at $\theta = 0°$ and the diffusion constant of the PMMA particles under distinct electric fields.

The values of $D_E$=0 (in absence of electric field) and $D_E$=125 are equal to 2.6 and $18.9 \times 10^{-11}$ cm$^2$ s$^{-1}$. Its meaning that, in THF, when an external voltage is applied through the solution, a displacement of $\Gamma$ in

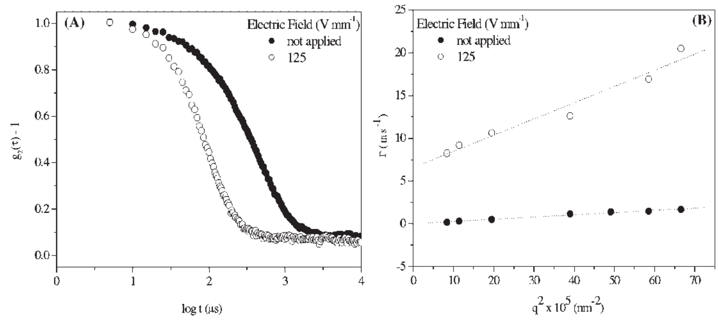

***Figure 3.***
Autocorrelation functions measured at scattering angle of 90° for PMMA-PHSA hard spheres suspended in THF in the absence of electric field and for an applied electric field of 125 V mm$^{-1}$ (A) and decay rate constants $\Gamma$ (ms$^{-1}$) obtain square of the scattering vector ($q^2$) in the same conditions (B).

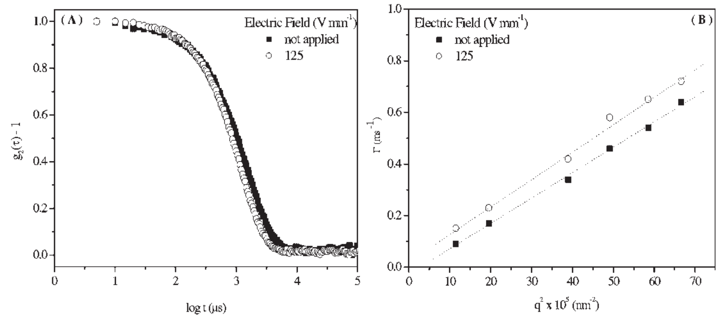

***Figure 4.***
Autocorrelation functions measured at scattering angle of 90° for PMMA-PHSA hard spheres suspended in decalin in the absence of electric field and for an applied electric field of 125 V mm$^{-1}$ (A). Decay rate constants $\Gamma$ (ms$^{-1}$) obtained by data analysis against the square of the scattering vector ($q^2$) at the same conditions (B).

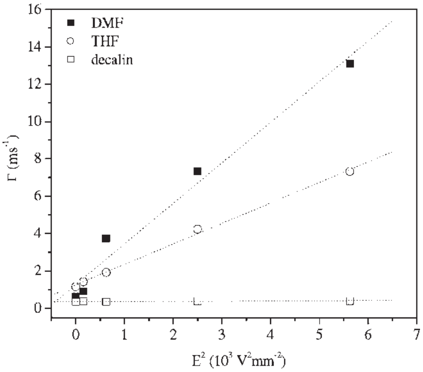

***Figure 5.***
Relaxation rates $\Gamma$ ($\mathrm{ms}^{-1}$) determined from the autocorrelation functions measured at a scattering angle $\theta = 90^\circ$ plotted against the square of the electric field applied for PMMA-PHSA suspended in different organic solvents.

the direction of higher values occurs (Figure 3B) meaning a higher diffusion constant. Furthermore, the relaxation rate obeys a linear positive behavior against the square of the applied electric field (see Figure 5)

In DMF, the PMMA-PHSA hard spheres diffuse apparently in a same way as in THF. As a rule, the autocorrelation curves and the $\Gamma$ *vs.* $q^2$ plots have the same profiles. Nevertheless, the increase in the diffusion constant of the particles is higher in DMF than in THF for a same applied electric field. This is related to the higher dielectric constant of the first one.

Figure 4 shows normalized intensity autocorrelation functions and $\Gamma$ *vs.* $q^2$ plots for PMMA-PHSA hard spheres suspended in decalin at the same conditions of that recorded in THF. As can be seen in this case, the increment in the diffusion constant (slope of $\Gamma$ *vs.* q2 plots) is much smaller than the increment observed in THF. The values of $D_E$=0 and $D_E$=125 for these cases were calculated as being 0.98 and $1.06 \times 10^{-11}$ $\mathrm{cm}^2\ \mathrm{s}^{-1}$. Also, the increment in $\Gamma$ is proportional to the square of the electric field, however, with a much smaller slope.

These results suggest that the dielectric properties of the systems are the main factor affecting the diffusion constant of the PMMA particles. The diffusion constant of PMMA-PHSA hard spheres is significantly affected by the external electric field when they are suspended in a solvent with a dielectric constant higher than the hard spheres (THF and DMF). The average dielectric constant of the main component of the particles (PMMA) is equal to 3.6[12]. In other words, the intensities of the applied electric fields were not enough to induce any pronounced change in the diffusion constant of the particles suspended in decalin due to low dielectric contrast ($\Delta\varepsilon$) between the solvent and the main particle component. On the other hand, when suspended in DMF and THF, the dynamic behavior of the particles is significantly affected. This improvement in the relaxation rates can be attributed to the polarity of the solvent molecules. It is believed that a simple polarization model[13] may be used to estimate the relative importance of the electric force produced by the external electric field in the motion of the PMMA particles. When the dielectric contrast between the hard spheres and the solvent is high enough, the electric force outweighs the thermal forces (Brownian motion), and thus, it starts to be considerably important in the motion of the particles. In fact, two experimental evidences corroborate our supposition. First, the linear behavior the $\Gamma$ vs. $E^2$ and the increase in its angular coefficient in the order decalin < THF < DMF (Figure 5) which is the same order of the increase in the dielectric contrast. Further, in previous results, we observed that the dynamic behavior of relative apolar particles with a diameter roughly 5 nm is not affect by electric fields of same magnitude when dissolved in the same solvents used in this work, since the relevancy of the electric force is dependent of the diameter of the particles considering the polarization model mentioned above.

The increment observed in the diffusion constant of the hard spheres may be attributed to the dipole moment acquired by the hard spheres when they are surrounded by solvent molecules having a high dielectric constant. The electric force produced by the electric field may accelerate the hard spheres that are solvated by solvent molecules. In the samples containing decalin, the dielectric contrast between the hard spheres and solvent is low and the electric force does not have influence in the movement of the particles. In this case, the thermal force is the only one governing the motion of them.

Finally, it is important to mention that this work is still in progress. Our research group is interested on the influence of external forces in solutions and suspensions of macromolecular systems. In the present studies we are dealing with the influence of shape and size as well as of the polarity of polymeric samples in the dynamic behavior under external electric field of diblock and triblock copolymers containing polystyrene.

## Conclusion

The results evidenced by polarized dynamic light scattering revealed that the electric field can have a pronounced influence on the dynamic motion of PMMA-PHSA hard spheres suspensions. This effect is clearly observed when the PMMA particles are suspended in solvents having a relative high dielectric constant. A significantly increase in the relaxation rates was monitored when an electric field is applied through suspensions of THF or DMF. Also the increase is proportional to the square of the electric field applied. This effect was attributed to the polarity of the solvent molecules in the neighborhood of the PMMA particles, promoting a considerable dipole moment for them. Consequently, it accelerates the particles and the diffusion constant is improved. In the case of the decalin suspension, the effect is much smaller due to the low dielectric contrast between the particles and solvent moieties.

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