Electromigration of microspheres in ferroelectric smectic liquid crystals

I. Dierking,* P. Cass, K. Syres, R. Cresswell, and S. Morton
School of Physics and Astronomy, University of Manchester, Schuster Building, Oxford Road, Manchester M13 9PL, United Kingdom
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When an electric field is applied to microspheres which are dispersed in a ferroelectric smectic liquid crystal, particle translation along the smectic layer plane, i.e., in a direction nearly perpendicular to that of the director, can be observed. Under certain electric field conditions the translation is shown to be linear in time. We have determined the stability regime of linear particle displacement in the parameter space of amplitude and frequency for various applied wave forms. This regime enlarges for increasing electric field amplitude and frequency, with a threshold behavior observed for small parameters. The upper stability boundary is related to the reciprocal ferroelectric switching time. The microspheres translational velocity is independent of the applied electric field amplitude, but increases linearly with applied frequency. The microsphere velocity also increases with increasing temperature, which is indicative of the respective decrease in liquid crystal viscosity. Possible mechanisms of electric-field-induced particle motion are discussed.

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I. INTRODUCTION

The electric-field-induced motion of particles dispersed in a fluid medium is known as electrophoresis, and has been a long standing topic in research, covering both rotational and translational motion. A rich number of applications, ranging from analytical chemistry and biology [1] all the way to modern display technologies [2], are evidence of its scientific importance. First investigations were carried out more than a century ago by Weiler [3], who reported a field induced translation of chininsulfate particles in turpentine oil, and by Quincke [4], who reported rotational motion of solid particles in a liquid subjected to dc fields. Only very much later first theoretical models were developed to describe the Quincke rotation [5,6], as well as translational electrophoretic motion [7–13], the latter being the main topic of interest. All of these models were restricted to isotropic liquids, although discussing different properties of applied electric fields or particle geometry: static [7] and alternating [8] electric fields, spheroidal [9] and slender particles [10,11], or particles with a nonuniform charge distribution [12,13].

In contrast, very little work has been reported for electric field induced particle motion in anisotropic fluids, such as liquid crystals. Furthermore, the reported behavior is mostly of qualitative nature, lacking a systematic approach. This is somewhat surprising, because the motion of microspheres in liquid crystals could lead to novel techniques in microrheology [14–16], i.e., the determination of the anisotropy of the viscosity on a microscopic scale [17]. This would be a significant advancement over the classic macroscopic liquid crystal viscosity measurements on nematic phases of Kneppe and Schneider [18] more than two decades ago. It could also provide a valuable tool to experimentally verify the very recently reported results on viscosity measurements of smectic phases in free-standing liquid crystal films [19]. Also recent publications on laser trapping of colloidal particles and their motion in anisotropic media [20–22] are related, for example through the elastically mediated interaction between an optically distorted liquid crystal director field and the dispersed colloidal particle.

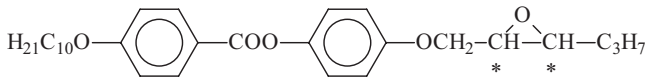
Up to now, experimental reports of micron-sized particles dispersed in liquid crystal matrices often focus on the regime of relatively large particle volume fractions, leading to largely enhanced mechanical properties [23,24]. Studies of the motion of individual microspheres, migrating in an anisotropic liquid crystalline environment under the influence of electric fields have so far been mostly of nonsystematic nature. For the isotropic and cholesteric (chiral nematic) phases, particles were reported to move along circular trajectories [25], while linear motion along the layer plane was observed for smectic liquid crystals [16,25]. A comprehensive experimental account of microsphere translation in nematic liquid crystals was given in Ref. [26], discussing stability regions of linear particle motion and the respective velocity dependence on field amplitude and frequency.

It should be stressed that in all the reported cases of microsphere electromigration in liquid crystals, the macroscopic translational motion of particles takes place in a plane perpendicular to the applied electric field direction. This is different from conventional electrophoresis, where the particle's velocity vector $\mathbf{v}$ is directed along the applied electric field $\mathbf{E}$, $\mathbf{v}=\mu\mathbf{E}$, with μ being the electrophoretic mobility. The dynamics of microsphere motion in anisotropic fluids is rather complicated, displaying a wealth of modes, such as rotation and translation, but also irregular particle movement, all depending on applied external conditions. No theoretical model to describe such behavior is available to date; even the cause of translational motion perpendicular to the applied field direction seems to be unclear. In this paper we report systematic experimental investigations of microsphere translational electromigration in ferroelectric smectic liquid crystals.

II. EXPERIMENT

The liquid crystal employed in the investigations was 4-[(S,S)-2,3 epoxyhexyloxy]-phenyl-4-(decyloxy)-benzoate, abbreviated as W46:

*Author to whom correspondence should be addressed. ingo.dierking@manchester.ac.uk



purchased from Displaytech and used as supplied. Its phase sequence determined by polarizing microscopy on slow cooling is given by: Iso. 96 N^* 82.5 SmC^* 60 SmI^*, with also higher ordered phases observed, which are not of relevance to this study. All measurements were carried out in the SmC^* phase.

Monodisperse glass spheres of diameter $D=3$ and 4 μm were added in very small concentrations to the liquid crystal, prior to the capillary filling of commercial sandwich cells (E.H.C., Japan). Cells were of thickness $d=10$ μm, with planar aligning, unidirectionally rubbed polyimide layers on top of the transparent ITO electrodes. The spheres were not treated for any special alignment conditions. As the employed liquid crystal orients planar on untreated glass plates, we also assume planar alignment on the dispersed microspheres. No characteristic defects in the close vicinity of dispersed particles could be observed or resolved by polarizing microscopy. The sample geometry is schematically shown in Fig. 1, with the side view [Fig. 1(a)] illustrating the "bookshelf-geometry" of the smectic layers, i.e., smectic layers being perpendicular to the confining substrates. Figure 1(b) schematically shows the top view of the employed ferroelectric liquid crystal (FLC) sample cells, as observed in the experiments. The director, i.e., the average direction of the long molecular axis, is tilted with respect to the layer normal by the tilt angle Θ, which is a temperature dependent quantity, reaching maximum angles of approximately 20° for this specific compound. Due to the ferroelectric properties of this material, i.e., the exhibition of a spontaneous polarization, the director, which also represents the optical axis, can be reoriented by application of electric fields of different polarity. This is indicated in Fig. 1(b), illustrating the molecule's reorientation from $+\Theta$ to $-\Theta$ during ferroelectric switching on application of ac electric fields. The direction of microsphere electromigration is along that of the smectic layers, not along the director **n**, as observed for nematic liquid crystals [26]. Particle motion is confined to the smectic layer plane, but can occur in either direction.

For the experimental investigations, electric fields were applied at varying field amplitude and frequency by a function generator (TTi TG1010) in combination with an in house built high voltage linear amplifier. Temperature dependent measurements were carried out using a Linkham hot stage (TMS91) providing a temperature stability better than 0.1 K. The motion of microspheres was monitored by polarizing microscopy (Nikon Optiphot-pol), equipped with a digital imaging system (JVC KY-F1030), recording digital images at a resolution of 1280×960 pixels at a time resolution of one image per second. The spatial resolution of recorded images corresponds to an area of 520×390 μm^2. Subsequent image analysis was carried out with software IMAGETOOL3.0, developed at the University of Texas Health Science Center, San Antonio. At all times, care was taken to only monitor the motion of microspheres which were well separated from others in order to minimize the influence from possible flow fields created by other particles. Also, microsphere pinning at possible defects or contaminating particles, was avoided.

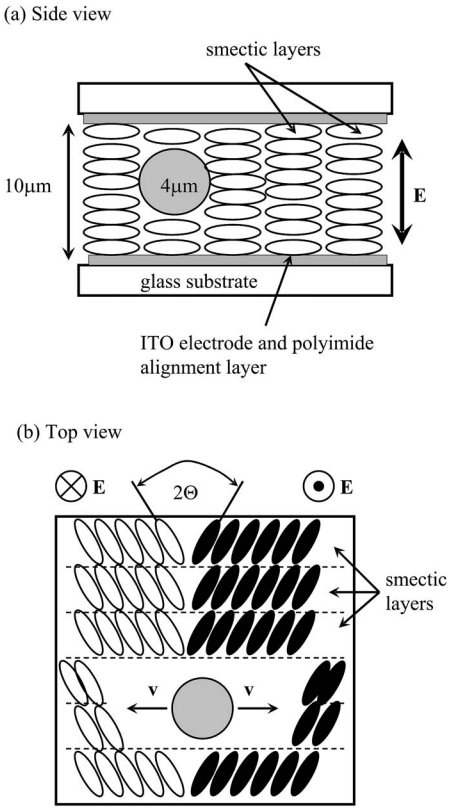


FIG. 1. Schematic illustration of the experimental geometry. (a) Side view of the cell where smectic layers are oriented in the "bookshelf-geometry" between two substrates with planar boundary conditions, separated by a distance of 10 μm. Particles of diameter $D=3-4$ μm are dispersed within the ferroelectric liquid crystal matrix. Electric fields are applied perpendicular to the substrate plane. (b) Top view of the cell, indicating the two director orientations of the FLC in response to the applied electric ac field. The observed microsphere translation occurs along the smectic layer plane.

III. RESULTS AND DISCUSSION

Figure 2 depicts a series of texture photographs taken during the period of electric field application, tracking the induced particle motion (indicated by a black arrow) of a $D=3$ μm microsphere. The smectic layer plane is indicated by

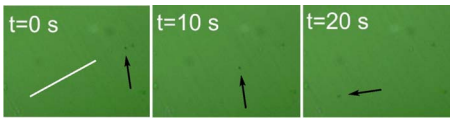


FIG. 2. (Color online) Exemplary time series of texture photographs during particle translations, with black arrows indicating the position of an isolated $D=3$ μm microsphere. Particle motion is linear in time and proceeds within the smectic layer plane, which is indicated by the white line in the left part of the figure. (Displayed image size is 130 μm$\times$100 μm).

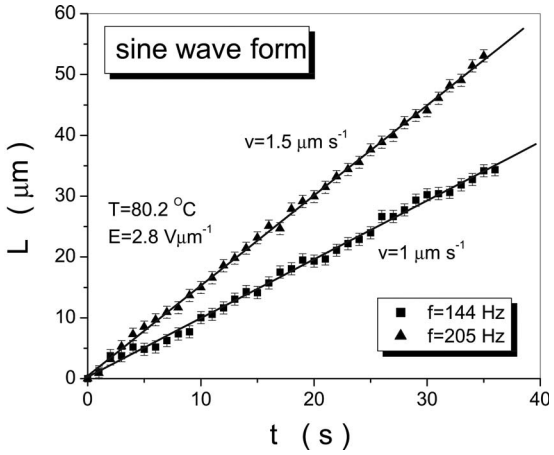


FIG. 3. Exemplary demonstration of linear microsphere motion confined within the smectic layer plane of a particle of $D=4$ μm diameter for different frequencies of the applied sine wave form electric field.

a white line in the left part of the figure. The particle clearly moves on a straight line trajectory. Figure 3 exemplary translates the spatial-temporal information of such microsphere image series, demonstrating linear particle motion for a $D=4$ μm diameter microsphere at constant applied electric field amplitude and temperature, for two different frequencies. The microsphere translates within the smectic layer plane by a constant distance per unit time, which allows a straightforward evaluation of the migration velocity, which increases with increasing frequency.

Nevertheless, such linear translation dynamics is confined to a specific parameter regime. We have thus determined the stability regions for linear microsphere motion within the ferroelectric liquid crystalline SmC* phase. The results are shown in Figs. 4(a)–4(c) for different applied wave forms, sinusoidal [Fig. 4(a)], triangular [Fig. 4(b)], and square wave electric field excitation [Fig. 4(c)], respectively. In all cases the stability regime of linear microsphere motion increases significantly with increasing electric field amplitude and frequency. It is worthwhile to point out that there is not only an upper parameter limit, beyond which particle motion ceases, i.e., at large frequencies and large applied electric field amplitudes, and we will revisit this question further below. There is also a lower limit of parameters where linear particle motion is observed. This occurs at low frequencies and small applied electric field amplitudes. Below this parameter curve, only random motion of the dispersed particles is observed. The distinction between the upper and lower limiting regimes as compared to linear microsphere motion is not always very pronounced, thus a logarithmic representation as in Fig. 4 is convenient to emphasize the fundamental behavior. Note that the frequency scale is in kHz, thus very different from previously reported data for nematic liquid crystals [26]. The upper stability curve is increased by approximately two orders of magnitude as compared to the nematic phase. The reasons for this behavior will be discussed below.

Increasing the electric field amplitude at constant applied frequency and also keeping the temperature constant, indicates that the particle motion in ferroelectric SmC* liquid

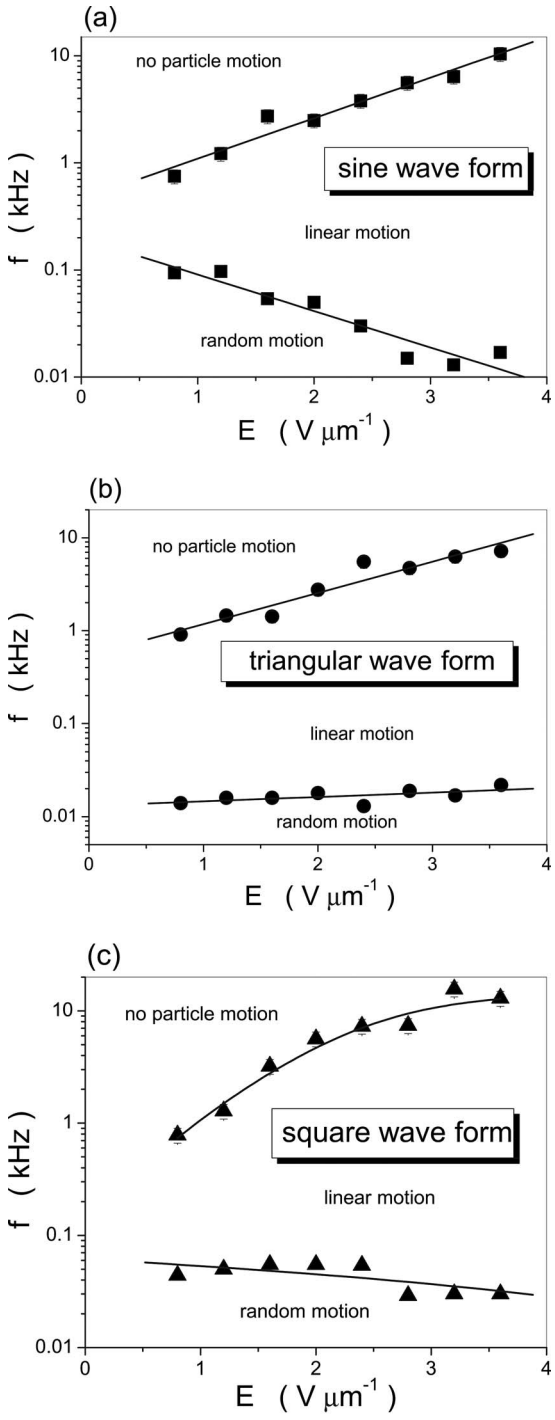


FIG. 4. Stability regimes of linear microsphere motion in the electric field amplitude—frequency space for different applied wave forms, (a) sine, (b) triangular, and (c) square wave applied electric field. In all cases the stability regime of linear particle motion increases largely with increasing field amplitude and frequency. Solid lines are a guide to the eye.

crystals is independent of the applied electric field amplitude. We have tested this behavior for both $D=3$ and 4 μm microsphere diameters, as well as several varied electric field frequencies. In all cases the microsphere velocity was effectively independent of electric field amplitude. The respective

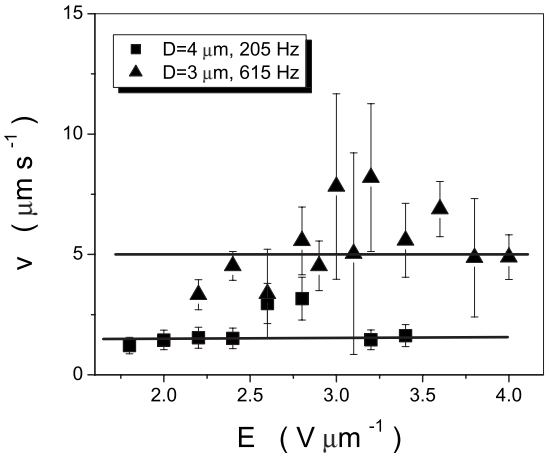


FIG. 5. Microsphere velocity as a function of applied electric field amplitude for $D=4$ μm particles at $f=205$ Hz (squares) and $D=3$ μm particles at $f=615$ Hz. Microspheres motion is on the average independent of the applied electric field amplitude, considering the abnormally large variation of velocities around fields of approximately $E=3$ V μm^{-1}. Solid lines are indicating the average of the respective particle velocities.

experimental behavior is exemplary demonstrated in Fig. 5 for different particle sizes and applied electric field frequencies.

In contrast, the microsphere velocity increases approximately in a linear fashion as the applied electric field frequency is increased, as demonstrated in Fig. 6. for the $D=4$ μm microspheres. A consistent behavior is obtained for the microspheres of somewhat smaller diameter of $D=3$ μm. From the experimental results it can be deduced that within the accessible parameter space, i.e., below the regime of electroconvection and dielectric breakdown, particle motion in ferroelectric liquid crystals is enhanced linearly by increasing the frequency of the applied electric ac field, but is approximately independent of electric field amplitude.

In order to correlate the experimentally observed behavior of particle translation dynamics to collective liquid crystal-

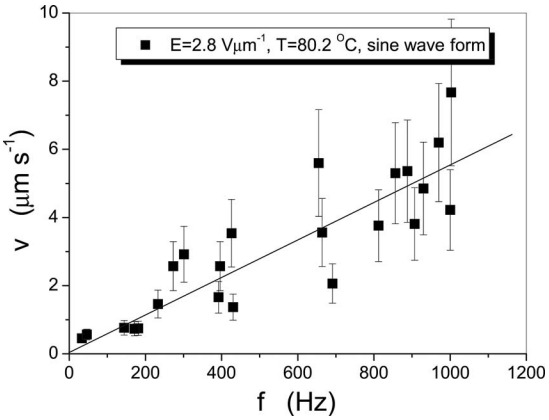


FIG. 6. Frequency dependence of the microsphere velocity for the $D=4$ μm particles. Despite relatively large scattering, the data clearly indicates a (linear) increase of the particle velocity with frequency of the applied electric field.

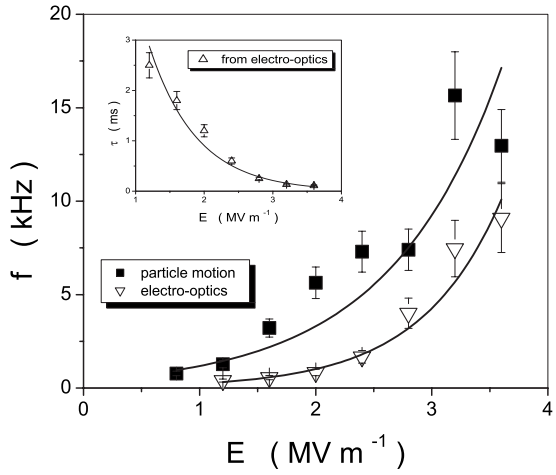


FIG. 7. Comparison between $D=4$ μm microsphere dynamics and ferroelectric liquid crystal director switching at applied square wave electric field. The inset of the figure depicts the saturated director switching times τ of the FLC reorientation as a function of applied electric field. This translates into a characteristic frequency $f=1/\tau$, shown as open down triangles in the main graph. The latter compares well with the upper stability limit for linear particle motion [solid squares, compare to Fig. 4(c)], especially, when taking into account that particles may also be propelled at larger frequencies beyond the regime of saturated director switching.

line molecular reorientation, electro-optic response times were recorded as a function of applied electric field [inset of Fig. 7, $\tau(E)$, open up triangles]. The corresponding characteristic frequency of the director reorientation, $f=1/\tau$ (open down triangles), compares well to the number of electric field reversals per unit time in particle motion (closed squares), as demonstrated in Fig. 7. The fact that the values from particle motion in FLCs are somewhat larger in experimental systems as compared to those obtained from optical director reorientation times (down triangles), is due to the difference between saturated and nonsaturated ferroelectric switching. The presented electro-optic switching times τ or relaxation frequencies $1/\tau$ (open symbols in Fig. 7) were obtained for saturated director switching. The maximum particle velocity (closed squares) can of course be somewhat larger than the inverse of the saturated ferroelectric switching time, as microspheres can also be propelled via nonsaturated director reorientation.

Lastly, the microsphere's translational behavior within an anisotropic fluid will depend on temperature, i.e., on the viscosity of the surrounding matrix. This is evidenced in Fig. 8, depicting the velocity of a $D=4$ μm microsphere as a function of temperature. As the temperature increases, the viscosity decreases, thus the microsphere velocity increases accordingly.

To date, there is no model or even a qualitative explanation for the dynamics of microsphere motion perpendicular to the applied electric field direction, as it is observed in different liquid crystal phases. This needs to be related to some kind of collective flow transferred from the switching liquid crystal onto the dispersed microsphere. This is the case for colloids in nematic liquid crystals [26], as well as in

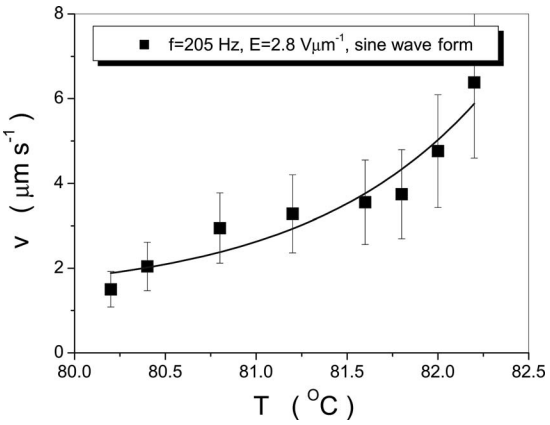


FIG. 8. Temperature dependence of the $D=4$ μm microsphere velocity at a fixed electric field amplitude of $E=2.8$ V μm^{-1} and frequency $f=205$ Hz. The observed increase in microsphere velocity can be attributed to the decrease in liquid crystal viscosity by increasing the temperature.

smectic liquid crystals, as studied in this investigation. For both phases the motion of the dispersed colloidal particles is directed along the direction of the main director displacement. In the nematic phase particle motion is observed perpendicular to the applied electric field direction, but parallel to the director. Nevertheless, particle displacement also seems to be related to the ionic content contained within the sample [26]. In the case of electromigration in fluid smectic phases, the motion is directed within the smectic layer plane, i.e., perpendicular to the applied electric field direction, but also mainly perpendicular to the liquid crystal director. Nevertheless, the direction of microsphere motion still coincides with the direction of the main director displacement. The latter occurs practically in the plane of the substrate, being related to electroclinic or ferroelectric switching in nature, i.e., corresponding to the SmA^* or SmC^* phase, respectively. It is thus indicative that the particle motion occurs along the main direction of the collective director displacement. The stability regions for linear particle motion also suggest that the observed particle translation is directly related to a collective reorientation of the director field, in both the nematic [26], as well as the fluid smectic case, which is discussed in this investigation. A question which is not answered is, why do the particles move in a certain direction when the electric field is applied. That is, why do particles in one instance on electric field application move to the left along the smectic layer plane, while at another instance they move to the right? (Only on very rare occasions do we observe the reversal of particle motion without interrupting the application of the symmetric electric field). The selection of collective particle migration direction appears to be stochastic, which is in accordance with the symmetric boundary conditions. However, it is not clear why all ensemble particles in a specific experimental run move in the same direction. This behavior appears to be very sensitive to the applied external conditions and may be related to bifurcation phenomena.

The actual physical mechanism underlying the colloidal particle motion in fluid (ferroelectric) smectic liquid crystals, may be related to a process introduced as "mass pumping" [27], similar to backflow effects, as reported for nematic liquid crystals. That is, an alteration of the director field induces a flow field, which in turn influences the director field orientation in a ferroelectric liquid crystal [28]. The pumping mechanism indeed takes place in a direction which promotes flow parallel to the smectic layers, while permeation flow across smectic layers is more or less prohibited [27]. Nevertheless, mass pumping only occurs in one direction which is determined by the chirality of the ferroelectric liquid crystal system. Further, material displacement was reported to be nonlinear in nature [27], while the particle motion observed in this study is linear (Fig. 3) within a certain regime of electric field amplitude and frequency parameters (Fig. 4). It thus appears that mass pumping of a ferroelectric liquid crystal may be closely related to the reported phenomenon of microsphere electromigration, but it does not seem to capture the whole underlying physical processes of the here reported particle migration phenomena. We believe that a full theoretical interpretation and model of electromigration of particles in anisotropic liquid crystal phases still presents a considerable challenge.

CONCLUSIONS

The motion of single, micron-sized glass spheres in a ferroelectric liquid crystal was investigated systematically. The dispersed microspheres exhibit translational motion confined to the smectic layer plane. The motion is linear within certain parameter regimes of electric field amplitude and frequency. These stability regimes were determined for different applied wave forms and it is suggested that they are related to saturated director switching in the ferroelectric SmC^* phase. Particle motion is independent of the amplitude of the applied electric field, but increases linearly with field frequency. At constant field amplitude and frequency the velocity of microspheres increases with temperature, due to a decrease in viscosity of the liquid crystal. The described electromigration of microspheres is almost certainly caused by flow effects, possibly due to mass pumping.

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