Supplementary Material (ESI) for Soft Matter

Lane formation in oppositely charged colloidal mixtures - supplementary information

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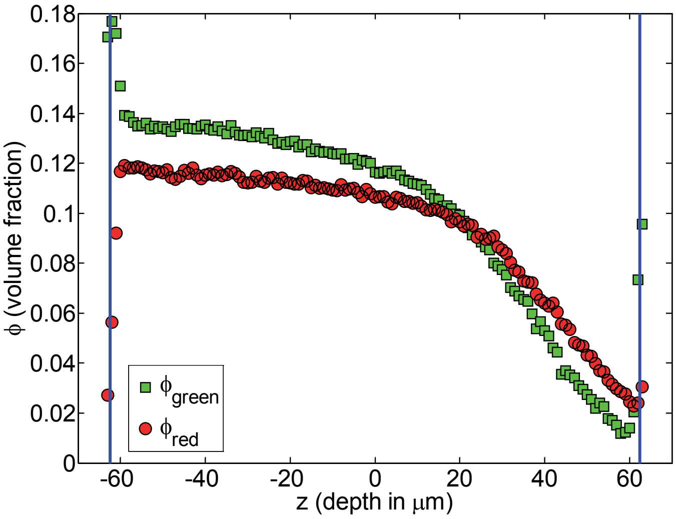
EFFECTS OF SEDIMENTATION ON THE LOCAL VOLUME FRACTION

In the experiments, we found a small degree of sedimentation at long times. To illustrate this effect, we measured the volume fraction at different depths in the channel using 3D particle tracking (Supplementary Fig. 1). The experiments that are described in the main paper were all carried out in the lower region of the capillary ($z < -20$ μm) where the volume fraction was nearly constant (Supplementary Fig. 1).



Supplementary Figure 1: Volume fraction as function of capillary channel depth. Experimental data: the volume fraction ϕ as a function of depth z in the capillary in our experiments for the green and red particles. The center of the capillary is located at $z = 0$. The blue vertical lines indicate the location of the glass walls. The peaks near the glass walls are due to the adsorption of particles on it.

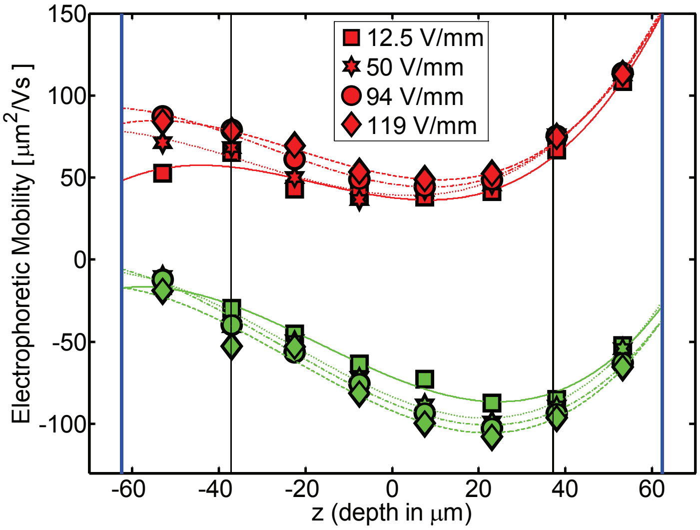
MEASURING THE ELECTROPHORETIC MOBILITY

When an electric field is applied in a closed capillary the ions near the glass walls start to move and drag the fluid with them, causing an electro-osmotic plug flow (EOF) throughout the channel. For incompressible fluids this causes a parabolic Poiseuille back-flow (PF) that counteracts the electro-osmotic flow. Using the Komagata linearization for diluted suspensions in a rectangular capillary we obtain the so-called stationary planes, where both flows cancel each other and the electrophoretic mobility should be measured. These layers are located at [1]:

$$\frac{z_{\mathrm{stat}}}{h} = \sqrt{\frac{1}{3} + 4\left(\frac{2}{\pi}\right)^5 \frac{1}{k}}, \tag{1}$$

where k is the ratio between the major and minor cross-section of the capillary, h is the distance between the center of the channel and the walls and z_{stat} is the distance from the center of the channel to either one of the stationary layers.

For our capillaries, $z = \pm\ 36.3\ \mu$m ($k \approx 100$). For depths other than $z_{\rm stat}$, the measured mobility is a superposition of the local fluid flow (EOF+PF) and the electrophoretic motion of the particles. Generally, in the case where particles are homogeneously distributed along z, the mobility profile is parabolic and symmetric around the center of the capillary (z = 0). We measured the electrophoretic mobility $\mu = v/E$ for different points along the z-axis and various field strengths for both particle species (Supplementary Fig. 2). Since the particle volume fractions were a function of z, the mobility profile was not exactly symmetric. In theory, the density inhomogeneities could have influenced the macroscopic fluid flows and have slightly shifted the position of the stationary layers.



Supplementary Figure 2: Mobilities measured in the capillary channel. Experimental data: electrophoretic mobilities at different depths in the channel for the green and red particles. Mobility data obtained at different field strengths are shown. Blue vertical lines represent the glass walls, black vertical lines depict the positions of the theoretical stationary planes. The center of the capillary is located at $z = 0$.

ESTIMATING THE PARTICLE CHARGES

To the best of our knowledge, there is currently no theoretical framework that allows us to precisely calculate the particle charges directly from the electrophoretic mobilities in concentrated binary systems of oppositely charged particles. For the systems we use, we have observed that the particles are affecting each other and the particle charges depend on the local density of both species. Therefore, it was hard to accurately determine the charges inside the binary mixture by independently measuring the mobilities of the one-component systems containing only green or red particles. For these reasons, we estimated the particle charges from the electrophoretic mobilities in the binary system, using theory for one-component systems. We used the measured electrophoretic mobility profile at a field strength of $|E| = 119$ V/mm (see Supplementary Fig. 2) to obtain values for the electrophoretic mobility at the stationary planes. First, the ζ-potential is found using [1]:

$$\zeta = \frac{3\eta\mu}{2\epsilon_{\rm m}\epsilon_0 f(\kappa\sigma)}, \tag{2}$$

where μ is the electrophoretic mobility, η is the viscosity, $\epsilon_{\rm m}$ is the relative permittivity of the medium, ϵ_0 the permittivity of vacuum, and $f(\kappa\sigma)$ the Henry function. From the ζ-potential, the charge was found using [1]:

$$Q = 2\pi\epsilon_{\rm m}\epsilon_0\sigma(1 + \frac{\kappa\sigma}{2})\zeta, \tag{3}$$

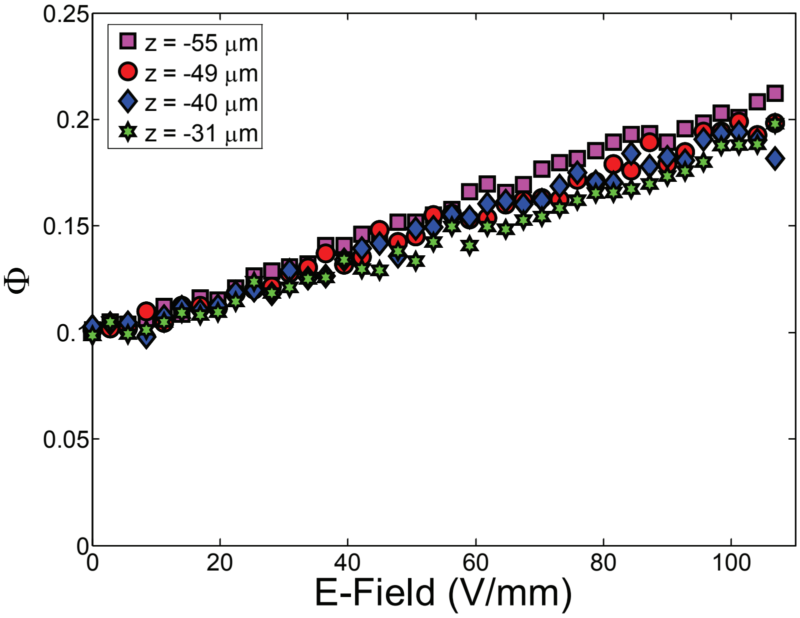
where $Q = Ze$ is the charge, Z is the charge number and e is the elementary charge. In addition, we used calculations of Carrique *et al.* [2] correcting for the effects of overlapping double layers in one-component systems. In these calculations, the non-linearized Poisson-Boltzmann equation is solved and the electrostatic potential between the particles is calculated, using the Kuwabara cell model. The charge is then obtained by applying Gauss's law on the surface of the colloid, $Q = -4\pi\epsilon_{\rm m}\epsilon_0 a^2 \left[\frac{\partial\Psi}{\partial r}\right]_{r=a}$, where $\epsilon_{\rm m}$ is the relative dielectric constant of the solvent medium. The resulting estimates are listed in Table I.

Parameter	green (lower)	green (higher)	red (lower)	red (higher)
ϕ	0.12	0.06	0.14	0.06
μ	$-42\ \mu$m^2/Vs	$-98\ \mu$m^2/Vs	78 μm^2/Vs	69 μm^2/Vs
ζ (Ref. [2])	-4.87 mV	-8.79 mV	8.48 mV	6.19 mV
ζ (Eq. 2)	-3.12 mV	-7.36 mV	5.83 mV	5.18 mV
Ze (Ref. [2])	-41e	-74e	57e	41e
Ze (Eq. 3)	-27e	-63e	38e	34e

TABLE I: Estimates of the charges and ζ-potentials based on electrophoresis measurements. We used the electrophoretic mobility profile μ that was measured at 119 V/mm, the listed mobility values at the stationary layers were obtained by interpolation of the measured data points. For each parameter, the values are shown for both particle species (green or red) and for the two stationary layers (lower or higher). The diameters $\sigma = 2a$ of the green and red particles are $\sigma_{\rm green} = 1.06\ \mu$m and $\sigma_{\rm red} = 0.91\ \mu$m respectively. For our calculations, we used $\kappa^{-1} = 170$ nm.

From Table I, it can be seen that by correcting for the volume fraction, the charge estimates were higher than when we performed our calculations at infinite dilution. For the charge numbers Z_i used in the simulations, we fitted Brownian Dynamics data and found optimal quantitative agreement between the experiments and computer simulations when we used charges of -42e for the green particles, and 67e for the red particles, which is slightly higher in magnitude than the estimates by electrophoresis on the lower stationary plane in Table I. However, qualitative agreement between the experiments and the computer simulations was observed for all charges between -20e and -80e for the green particles and 20e and 80e for the red particles. Therefore, we conclude that for this system, and field strengths between 10 and 110 V/mm, lane formation was not sensitive to the balance of the charges. This again illustrates that the attractive electrostatic forces are in this case of minor importance compared to the electric driving force, and that the collisions between the oppositely charged colloids drive the laning.

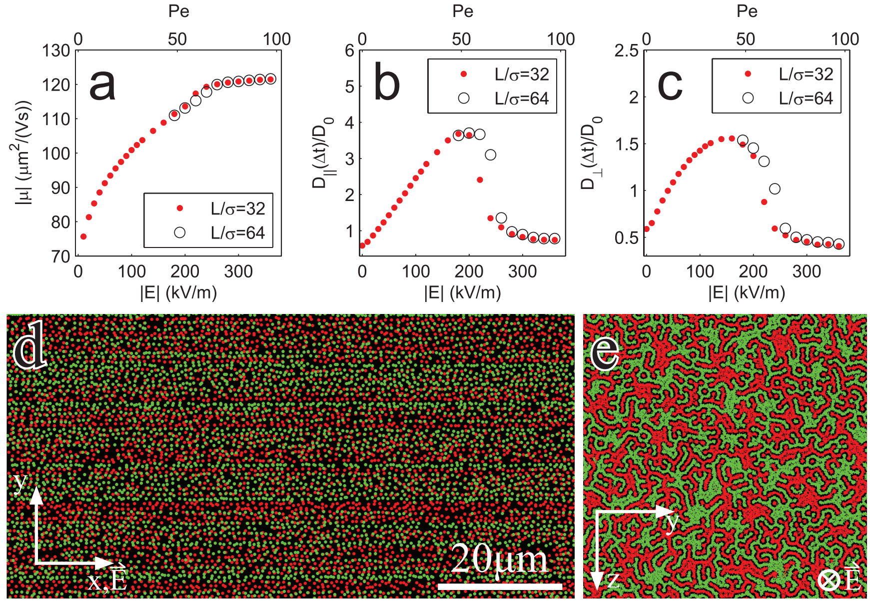
THE EFFECT OF MACROSCOPIC FLUID FLOWS ON LANE FORMATION



Supplementary Figure 3: Effect of electro-osmosis on lane order. Experimental data: the order parameter $\Phi(E)$ was measured at different depths in the channel for experiments where the field strength was gradually increased and decreased. The experiment was carried out in a different capillary but with a volume fraction profile $\phi(z)$ that was similar to Supplementary Fig. 1 (with nearly constant $\phi(z)$ in the lower region of the channel). The results show that in our system, electro-osmosis did not have an important effect on the lane formation.

The order parameter Φ was measured as a function of field strength $|E|$ for different depths z in the lower region of the channel (Supplementary Fig. 3). These experiments were carried out in a different capillary but with a volume fraction profile $\phi(z)$ similar to Supplementary Fig. 1. Since no large differences in $\Phi(E)$ were observed for different values of z, we conclude that the macroscopic fluid flows (EOF and PF) that were induced by electro-osmosis on the capillary walls did not have an important effect on the lane formation in our system.

LANE FORMATION AT HIGHER FIELD STRENGTHS



Supplementary Figure 4: Simulations showing the trends at higher Péclet numbers. **a,** The electrophoretic mobility increases with field strength, and finally reaches a steady plateau. **b,c,** The fluctuations parallel and perpendicular to the field axis first increase with $|E|$ and then fall off as the lanes percolate the system. The simulations were performed for two box sizes ($L/\sigma = 32$ and $L/\sigma = 64$), showing similar results. **d,e,** Typical simulation snapshots for $|E| = 360$ V/mm. **d,** Top-view on a slice out of the 3D system, showing that the lanes percolate the system parallel to the field axis. **e,** A cross-section perpendicular to the field axis. The lanes form a network consisting of lane-branches.

Dzubiella *et al.* performed computer simulations for like-charged particles driven in opposite directions [3]. It was demonstrated in these simulations that for higher driving fields there exists a sharp transition towards the full lane state, with lanes spanning the size of the simulation box. In our computer simulations with oppositely charged particles a similar transition was observed (Supplementary Fig. 4). We also studied our system experimentally at higher driving fields and observed that individual lanes merged and extended in both the direction parallel and perpendicular to the electric field (Supplementary Fig. 5). Since the experimental system was finite (no periodic boundary conditions), the particles became depleted in time at these high driving fields due to accumulation at the electrodes, limiting the possibility to observe the steady-state behavior observed in the simulations.

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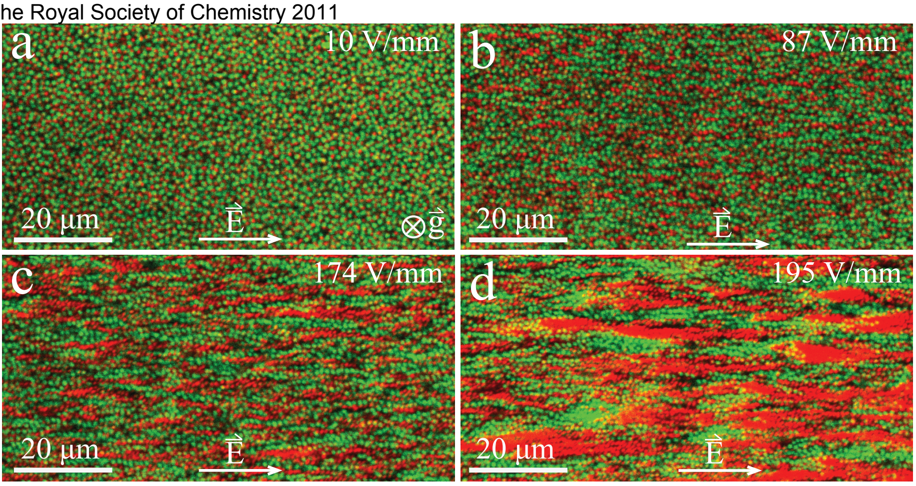

Supplementary Figure 5: Typical confocal images for the binary system of oppositely charged particles at different field strengths just after the field had been turned on. **a,** $|E| = 10$ V/mm, **b,** $|E| = 87$ V/mm, **c,** $|E| = 174$ V/mm, and **d,** $|E| = 195$ V/mm. Going to higher field strengths, the lanes grow in the field direction (a,b). For fields higher than 110 V/mm (c,d), different lanes merged and extended in both the directions parallel and perpendicular to the electric field.