Supporting Information for

Electrokinetic Vortices and Traveling Waves in Non-dilute Colloidal Dispersions

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S1. Electroviscous velocity in a traveling wave

The electroviscous velocity $U_{ev}$ results from a balance of electric body forces and viscous forces in the Navier-Stokes equations and is given as,

$$ U_{ev} = \frac{f_E d^2}{\eta_m}. $$

(1)

where $f_E$ is the electric body force, $d$ is the length scale over which velocity gradients changes occur, and $\eta_m$ is the dynamic viscosity of the medium. The electric body force in a liquid is given by

$$ f_E = \rho_e \varepsilon_0 \vec{E} - \frac{\varepsilon_0}{2} \vec{E} \cdot \nabla \varepsilon + \frac{1}{2} \nabla \left( \rho_e \varepsilon_0 \frac{\partial \varepsilon}{\partial \rho_e} \vec{E} \cdot \vec{E} \right). $$

(2)

The first term accounts for electrostatic forces on free charge. The second term is a polarization force due to electric fields coupled with gradients in permittivity, while the third term denotes the body force that may develop due to density differences that may occur due to the deformations of the dielectric, i.e. suspension. Assuming that the particles are hard, rigid spheres, that the fluid is incompressible and that the particle has nearly the density of the background solution, the last term can be assumed to be negligible and is hence neglected. Using Gauss’ law,

$$ \varepsilon_0 \nabla \cdot (\varepsilon \vec{E}) = \rho_e $$

(3)

we can write the charge density as

$$ \rho_e = \varepsilon_0 \varepsilon \nabla \cdot \vec{E} + \varepsilon_0 \vec{E} \cdot \nabla \varepsilon. $$

(4)

Neglecting temporal changes in charge density, the conservation equation for current can be written as,

$$ \nabla \cdot (\sigma \vec{E}) = 0, $$

(5)
which can be expressed as,

\[ \nabla \cdot \vec{E} = -\vec{E} \cdot \frac{\nabla \sigma}{\sigma}. \tag{6} \]

Now, the generation of charge density is expressed in terms of gradients in electrical conductivity and permittivity in the direction of the electric field

\[ \rho_e = -\varepsilon_0 \varepsilon \vec{E} \cdot \frac{\nabla \sigma}{\sigma} + \varepsilon_0 \varepsilon \vec{E} \cdot \nabla \varepsilon. \tag{7} \]

Following Chen et al. (2005), we write all variables in (7) as the sum \( \alpha = \alpha_b + \xi \alpha' \) where subscript \( b \) denotes the base state (particles are evenly distributed in the channel), the prime denotes a perturbation and \( \xi \) is a smallness parameter. \(^3\) We assume electroneutrality in the base state such that \( \rho_o = \varepsilon_0 E_b \cdot (\nabla \sigma_b / \sigma_b) + \varepsilon_0 E_b \cdot \nabla \varepsilon_b \) is zero. Noting that gradients of base state properties are zero, and neglecting \( \xi^2 \) terms we find that

\[ \rho'_e \sim -\varepsilon_0 \varepsilon_b \vec{E}_b \cdot \frac{\nabla \sigma'}{\sigma_b} + \varepsilon_0 \varepsilon_b \vec{E}_b \cdot \nabla \varepsilon'. \tag{8} \]

In this work, gradients in permittivity might occur from gradients in volume fraction between a traveling wave’s peak and valley. Thus, we scale gradients in the permittivity perturbation as

\[ \nabla \varepsilon' \sim \frac{\varepsilon_h - \varepsilon_l}{\lambda / 2} = \frac{2 \varepsilon_l}{\lambda} (\beta - 1) \tag{9} \]

where subscripts \( h \) and \( l \) correspond to high and low volume fraction regions, \( \lambda \) is a wave length \( \lambda = 2\pi / \kappa \) and \( \beta = \varepsilon_h / \varepsilon_l \). The base value of permittivity is approximated as

\[ \varepsilon_b \sim \frac{\varepsilon_h + \varepsilon_l}{2} = \frac{\varepsilon_l}{2} (\beta + 1). \tag{10} \]
Perturbation conductivity gradients resulting from volume fraction variations along a traveling wave are scaled as 
\[
\frac{\nabla \sigma' - \sigma}{\sigma_b} \sim \frac{2(\sigma_2 - \sigma_i)}{\lambda / 2(\sigma + \sigma_i)} = \frac{4(\gamma - 1)}{\lambda (\gamma + 1)}
\]
where \(\gamma = \sigma_2 / \sigma_i\).

Now, expression (8) for the perturbation charge density is 
\[
\rho_e' \sim -\frac{2\varepsilon_0 \varepsilon_i}{\lambda} (\beta + 1) \left(\frac{\gamma - 1}{\gamma + 1}\right) E_b + \frac{2\varepsilon_i}{\lambda} (\beta - 1) E_b,
\]
and the electric body force is 
\[
f_E \sim -\frac{2\varepsilon_0 \varepsilon_i}{\lambda} (\beta + 1) \left(\frac{\gamma - 1}{\gamma + 1}\right) E_b^2 + \frac{2\varepsilon_i}{\lambda} (\beta - 1) E_b^2.
\]

Finally, the electroviscous velocity is given by 
\[
U_{ev} \sim -\frac{\lambda}{2\eta_m} \varepsilon_0 \varepsilon_i (\beta + 1) \left(\frac{\gamma - 1}{\gamma + 1}\right) E_b^2 + \frac{\lambda}{4\eta_m} \varepsilon_0 \varepsilon_i (\beta - 1) E_b^2.
\]

To estimate the electroviscous velocity we require values electrical permittivity and conductivity for the range of volume fractions of interest here. Carrique et al. provides numerical estimates of electric permittivity for solutions with high concentration of spheres. For particles with a zeta potential of approximately -100mV, in concentrations of 5% and 10% (low and high concentrations) and extrapolating to \(\kappa a \sim 30\), we find that \(\varepsilon_{2b}\) and \(\varepsilon_{2i}\) are approximately 244 and 235 (\(\beta = 1.038\)), respectively. Posner reports measurements on the conductivity of colloids as a function of particle volume fraction for various \(\kappa a\) values. Extrapolating their data to \(\phi = 5\%\) and 10\% we find \(\sigma_2\) and \(\sigma_i\) to be 0.049 and 0.026 S m\(^{-1}\) (\(\gamma = 1.6\)), respectively. The calculated electroviscous velocity for our system is approximately 0.01 \(\mu\)m s\(^{-1}\) increasing only slightly if \(\gamma\) and \(\beta\) approach 2 independently. In order to attain experimentally obtained traveling wave velocities (of \(~ 40 \mu\)m s\(^{-1}\)) we’d require values of \(\gamma\) and \(\beta\)
of $O(100)$ (700 and 1500). Volume fraction gradients that result in such conductivity and permittivity variations are unobtainable in our system, hence, electroviscous effects appear to be unlikely candidates for the generation and sustenance of traveling waves.

**S2. Dielectrophoretic velocity due to particle-particle dipolar attraction**

Particles become polarized under the application of an electric field. Each particle generates its own dipole which can interact with neighboring dipoles resulting in attractive forces between particles. The dielectrophoretic force produced by a neighboring particle is

$$F_{dp} = \frac{24\pi \varepsilon \varepsilon_0 R^6 E_0^2}{\delta^4} \left( \frac{2Du - 1}{2Du + 2} \right)^2 \delta^4,$$

(15)

In low Reynolds number flow, a particle moving with velocity $U$ will experience a (Stokes) drag force $F_D$ given by

$$F_D = 6\pi \eta m RU$$

(16)

If we consider that a particle will attain velocity $U$ due to the balance between particle-particle attraction and Stokes drag, we can estimate it as

$$U_{dp} \sim \frac{4\varepsilon \varepsilon_0 R^6 E_0^2}{\eta m \delta^4} \left( \frac{2Du - 1}{2Du + 2} \right)^2 \delta^4,$$

(17)

For two particles with a distance of $10R$ the velocity is approximately 0.01 $\mu$m/s and decreases rapidly (as $\sim \delta^{-4}$) with interparticle distance. A maximum dielectrophoretic velocity of approximately 10 $\mu$m s$^{-1}$ is achieved for a minimum interparticle distance $R \sim 2$. 
S3. Dielectrophoretic velocity due to volume fraction gradients

The dielectrophoretic force on a particle that is much smaller than spatial electric field variations can be expressed as

\[ F_{dp} = 2\pi \varepsilon_m \varepsilon_0 R^3 \text{Re} \left[ K(\omega) \nabla \left( \bar{E} \cdot \bar{E} \right) \right] \]  

(18)

where \( \text{Re} \left[ K(\omega) \right] \) is the real part of the Clausius-Mossotti function. For an insulating particle exposed to an ac electric field where \( 1/\omega >> \tau_{MW} \), the Clausius-Mossotti function can be expressed as

\[ \text{Re}[K(\omega)] = \frac{2Du - 1}{2Du + 2}. \]  

(19)

Spatial variations of electric field might be caused by gradients in conductivity produced by gradients in volume fraction. In one dimension, we assume the total electric field \( E_x \) is a linear function with slope \( \Delta E / \ell \) and y-intercept \( E_0 \). The gradient in (18) becomes

\[ \frac{d}{dx} \left( E_x^2 \right) = 2 \frac{\Delta E}{\ell} E_0. \]  

(20)

Perturbations in electric field (\( \Delta E \)) may be scaled as

\[ \Delta E \sim E_0 \frac{\gamma - 1}{\gamma + 1}. \]  

(21)

The dielectrophoretic force is then

\[ F_{dp} \sim \frac{8\pi \varepsilon_m \varepsilon_0 R^3}{\lambda} \left( \frac{2Du - 1}{2Du + 2} \right) \left( \frac{\gamma - 1}{\gamma + 1} \right) E_0^2 \]  

(22)

and the resulting velocity is

\[ U_\phi \sim \frac{4 \varepsilon_m \varepsilon_0 R^2}{3 \lambda \eta_m} \left( \frac{2Du - 1}{2Du + 2} \right) \left( \frac{\gamma - 1}{\gamma + 1} \right) E_0^2 \]  

(23)
The dielectrophoretic velocity is 0.4 $\mu$m s$^{-1}$ for the $Du$ and $\gamma$ is this work. A maximum velocity of approximately 6 $\mu$m s$^{-1}$ can be achieved in the limit of infinite $Du$ and $\gamma$.

References


(2) Stratton, J. A. Electromagnetic Theory; McGraw-Hill, 1941.


