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Aditya S. Khair, Denise E. Posluszny, and Lynn M. Walker

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# Coupling electrokinetics and rheology: Electrophoresis in non-Newtonian fluids

Aditya S. Khair, Denise E. Posluszny & Lynn Walker

*Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh PA 15213*

We present a theoretical scheme to calculate the electrophoretic motion of charged colloidal particles immersed in complex (non-Newtonian) fluids possessing shear-rate dependent viscosities. We demonstrate that this non-Newtonian rheology leads to an explicit shape- and size-dependence of the electrophoretic velocity of a uniformly charged particle in the thin-Debye-layer regime, in contrast to electrophoresis in Newtonian fluids. This dependence is caused by non-Newtonian stresses in the bulk (electroneutral) fluid outside the Debye layer, whose magnitude is naturally characterized in an electrophoretic Deborah number.

## I. INTRODUCTION

Electrokinetic phenomena arise as electric fields or hydrodynamic flows drive the ionic clouds that screen charged surfaces in viscous electrolytes out of equilibrium [1, 2]. The field has a rich history dating back two centuries [3]; today, electrokinetics plays an important role in colloid science [4], environmental remediation [5], biomechanics [6], and micro- and nano-fluidics [7, 8].

Surfaces immersed in electrolytes typically acquire an electrical charge, which is screened by counter-ions in solution, over a distance characterized by the Debye length  $\lambda_D$  (e.g.  $\lambda_D \approx 10\text{nm}$  for monovalent salts at milli-molar concentration and room temperature). An external electric field acts on the net charge in this “Debye layer” to drive an electro-osmotic flow, whose magnitude  $u_{\text{EOF}}$  is given by the Helmholtz-Smoluchowski (HS) formula  $u_{\text{EOF}} \sim -\varepsilon\zeta E/\eta$ . Here,  $\varepsilon$  and  $\eta$  are the permittivity and viscosity of the electrolyte, respectively, and  $\zeta$  is the electric (zeta) potential of the surface.

The HS formula assumes that the electrolyte is Newtonian, i.e. its deviatoric mechanical stress  $\boldsymbol{\tau}$  is proportional to the rate of strain  $\mathbf{e}$ ,  $\boldsymbol{\tau} = 2\eta\mathbf{e}$ , with a viscosity  $\eta$  that is independent of flow type and shear rate. However, in microfluidic devices and capillary electrophoresis, for example, electric fields are routinely used to drive electrokinetic transport in fluids whose rheology does not follow Newton’s ideal: e.g. polymer solutions [9–13] or biofluids [14–16]. Indeed, there has been significant recent interest in electro-osmotic flows of such complex, or non-Newtonian, fluids [17–30]. For example, a simple non-Newtonian constitutive relation is the power-law fluid, which possesses a shear-rate dependent viscosity  $\eta_{\text{PL}} = m\dot{\gamma}^{n-1}$ , where  $m$  is a constant,  $n$  is the power-law index, and  $\dot{\gamma} = \sqrt{\frac{1}{2}\mathbf{e}:\mathbf{e}}$  is the shear rate. For  $n < 1$  the fluid is shear-thinning (typical of polymer solutions),  $n > 1$  corresponds to shear thickening, and  $n = 1$  is Newtonian. The characteristic electro-osmotic flow velocity of a power law fluid is  $u_{\text{EOF}}^{\text{PL}} \sim n(-\varepsilon\zeta E/m)^{1/n}(\lambda_D)^{1-1/n}$ , in the Debye-Huckel limit  $\zeta \lesssim 25\text{mV}$  [11, 21]. (At larger zeta potentials, nonlinear screening results in a more complicated expression [26].) This result suggests that non-Newtonian rheology leads to electro-osmotic flows that are nonlinear in the applied field and zeta poten-

tial, a marked departure from electro-osmosis in Newtonian fluids. Pressure-driven streaming potentials and currents in complex fluids have also been investigated [31–35]. In these studies non-Newtonian effects result from a non-linear dependence of the mechanical (Cauchy) stress on the rate of strain. This is distinct from the visco-electric effect [36], electro-rheological fluids [37], the electro-viscous effect [38], and charge-induced thickening [39]: in the first two cases non-Newtonian rheology originates from an explicit dependence of the Cauchy stress on the electric field, in the third it arises from the deformation of Debye layers in applied flows, and in the fourth it is due to a local increase in viscosity due to ion crowding in the Debye layer at large  $\zeta$ .

Electrophoresis is the motion of a freely suspended charged colloid animated by an electric field. Smoluchowski calculated that a spherical particle with a uniform  $\zeta$  potential and thin Debye layer translates at an electrophoretic velocity  $U_{\text{EP}} = \varepsilon\zeta E/\eta$  (without rotating). Morrison [40] proved that this result is independent of particle size, shape, and even concentration, provided all the particles have equal  $\zeta$  and surface currents in the Debye layer (characterized by the Dukhin number,  $Du$  [1]) are negligible. This remarkable finding has been experimentally verified for concentrated suspensions of red blood cells [41]. Morrison’s proof also has profound implications for particulate separations: e.g. in capillary electrophoresis of DNA, strands of different length (but uniform  $\zeta$ ) move at equal velocities in bulk electrolyte [42], thus requiring a gel matrix or molecular “drag-tags” [43] to affect separation. Given the recent intense interest in electro-osmosis of complex fluids, it is natural to ask how electrophoresis is affected by non-Newtonian rheology. In particular, does non-Newtonian rheology endow the electrophoretic velocity with a size and shape dependence, thereby “breaking” Morrison’s result?

## II. MODEL DEVELOPMENT

Here, we present a theoretical approach for calculating electrophoretic motion in non-Newtonian fluids. It appears that the only previous studies in this area are from Hsu and co-workers [45–55] who computed the electrophoresis of spherical and rod-shaped particles in shear-

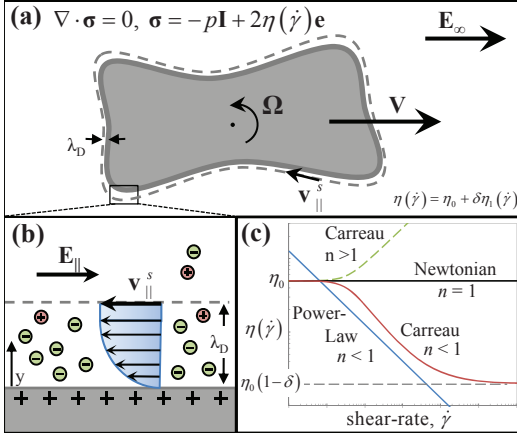


FIG. 1. (Color online) Electrophoresis of a uniformly charged particle under an electric field  $\mathbf{E}_\infty$  in a non-Newtonian fluid with stress  $\boldsymbol{\sigma}$ . (a) Particle motion at rectilinear velocity  $\mathbf{V}$  and angular velocity  $\boldsymbol{\Omega}$ , arising from electro-osmotic slip  $\mathbf{v}_\parallel^s$  in the thin Debye layer (b). (c) Power-law and Carreau models for the non-Newtonian viscosity  $\eta(\dot{\gamma})$  (1).

thinning Carreau fluids using numerical methods. In contradistinction, our approach applies to particles of any shape in fluids whose viscosity can be shear-thickening or -thinning (or even both). Specifically, we consider weakly generalized Newtonian fluids with a shear-rate dependent viscosity [57]

$$\eta(\dot{\gamma}) = \eta_0 + \delta\eta_1(\dot{\gamma}), \quad (1)$$

where  $\eta_0$  is a “base” Newtonian viscosity,  $\eta_1$  is a non-Newtonian (shear-rate dependent) “correction,” and  $\delta(< 1)$  is a generic small parameter.

We consider a uniformly-charged colloidal particle in a binary symmetric electrolyte (figure 1). The particle can be of any shape, but we invoke the thin-Debye-layer limit, whereby  $\lambda_D$  is much smaller than the local radii of curvature of the particle. Furthermore, we neglect surface currents in the Debye layer ( $Du \ll 1$ ). Given the disparity between  $\lambda_D$  and the particle size, it is judicious to analyze the transport processes in the Debye layer and electroneutral bulk separately. The particle appears locally flat on the scale of  $\lambda_D$ , and the momentum equation at zero Reynolds number reduces to a balance of tangential electrical and viscous stresses [4]

$$\frac{\partial}{\partial y} \left( \eta(\dot{\gamma}) \frac{\partial \mathbf{v}_\parallel}{\partial y} \right) = \varepsilon \frac{\partial^2 \phi}{\partial y^2} \mathbf{E}_\parallel, \quad (2)$$

where  $y$  is a Cartesian coordinate normal to the local surface,  $\mathbf{v}_\parallel$  and  $\mathbf{E}_\parallel$  are the tangential velocity and electric fields, respectively, and  $\phi$  is the electric potential. Inserting (1) into (2) the “slip” velocity at the boundary between the Debye layer and bulk ( $y \rightarrow \infty$ ) is to  $O(\delta)$

$$\mathbf{v}_\parallel^s = -\frac{\varepsilon\zeta}{\eta_0} \mathbf{E}_\parallel + \delta \frac{\varepsilon}{\eta_0} \mathbf{E}_\parallel \int_0^\infty \frac{\eta_1(\dot{\gamma}_0)}{\eta_0} \frac{d\phi}{dy} dy, \quad (3)$$

where the first term is the familiar Helmholtz-Smoluchowski slip, and the second is due to non-Newtonian rheology, with the viscosity  $\eta_1$  evaluated using the Newtonian  $O(\delta^0)$  shear rate  $\dot{\gamma}_0$ .

The slip velocity (3) provides the required matching condition on the fluid flow outside the Debye layer. The bulk fluid is electroneutral and conservation of momentum requires  $\nabla \cdot \boldsymbol{\sigma} = 0$ , where the hydrodynamic stress  $\boldsymbol{\sigma} = -p\mathbf{I} + 2\eta(\dot{\gamma})\mathbf{e}$ , with  $p$  the pressure,  $\mathbf{I}$  the isotropic tensor,  $\mathbf{e} = \frac{1}{2}(\nabla\mathbf{v} + (\nabla\mathbf{v})^T)$  the rate of strain, and  $\mathbf{v}$  the velocity field. Additionally, the fluid is incompressible  $\nabla \cdot \mathbf{v} = 0$ . We invoke the weakly non-Newtonian limit (1) by expanding the velocity and pressure as  $\{\mathbf{v}, p\} = \{\mathbf{v}_0, p_0\} + \delta\{\mathbf{v}_1, p_1\} + O(\delta^2)$ . At  $O(1)$  the familiar problem of electrophoresis in a Newtonian fluid is recovered, namely  $\nabla^2 \mathbf{v}_0 = \nabla p_0$  and  $\nabla \cdot \mathbf{v}_0 = 0$ , subject to  $\mathbf{v}_0 \rightarrow 0$  as  $|\mathbf{r}| \rightarrow \infty$  and the slip condition  $\mathbf{v}_0 = \mathbf{V}_0 + \boldsymbol{\Omega}_0 \wedge \mathbf{r} + \mathbf{v}_\parallel^{s,0}$  on the particle surface. Here,  $\mathbf{v}_\parallel^{s,0} = -\varepsilon\zeta\mathbf{E}_\parallel/\eta_0$  is the Newtonian contribution to the slip velocity in (3), and  $\mathbf{V}_0$  and  $\boldsymbol{\Omega}_0$  are the rectilinear and angular velocities of the particle, respectively. Finally, we require that the hydrodynamic force and torque on the surface enclosing the particle and Debye layer vanishes. The  $O(1)$  problem admits the well-known irrotational flow solution  $\mathbf{v}_0 = -\varepsilon\zeta\mathbf{E}/\eta_0$ , and  $\mathbf{V}_0 = \varepsilon\zeta\mathbf{E}_\infty/\eta_0$  and  $\boldsymbol{\Omega}_0 = 0$ , which is valid for any particle shape [40, 61, 62].

Non-Newtonian effects emerge at  $O(\delta)$ , for which

$$\eta_0 \nabla^2 \mathbf{v}_1 - \nabla p_1 = 2\nabla \cdot [\eta_1(\dot{\gamma}_0)\mathbf{e}_0], \quad \nabla \cdot \mathbf{v}_1 = 0, \quad (4)$$

subject to  $\mathbf{v}_1 \rightarrow 0$  as  $|\mathbf{r}| \rightarrow \infty$  and  $\mathbf{v}_1 = \mathbf{V}_1 + \boldsymbol{\Omega}_1 \wedge \mathbf{r} + \mathbf{v}_\parallel^{s,1}$  on the particle surface, where the  $O(\delta)$  slip velocity  $\mathbf{v}_\parallel^{s,1}$  is the second term in (3). Here,  $\mathbf{V}_1$  and  $\boldsymbol{\Omega}_1$  are the non-Newtonian contributions to the rectilinear and angular velocities of the particle, respectively. At  $O(\delta)$  the flow satisfies the inhomogeneous Stokes equations with a “non-Newtonian body force”  $2\nabla \cdot [\eta_1(\dot{\gamma}_0)\mathbf{e}_0]$  arising from gradients in the Newtonian velocity field. In principle, one can obtain the  $O(\delta)$  particle motion,  $\mathbf{V}_1$  and  $\boldsymbol{\Omega}_1$ , by solving (4) subject to zero force and torque on the particle. However, for even the simplest non-Newtonian model of  $\eta(\dot{\gamma})$  the forcing term in (4) necessitates numerical evaluation of the velocity  $\mathbf{v}_1$  and pressure  $p_1$  fields. Remarkably, one does not need these fields to compute the  $O(\delta)$  particle motion. Instead, we employ the Lorentz reciprocal theorem, which has been used to calculate particle dynamics in weakly non-Newtonian fluids under external forces [56–58] and imposed fluid flows [59, 60].

Let  $\mathbf{v}_{\text{aux}}$  and  $\boldsymbol{\sigma}_{\text{aux}}$  be the velocity field and stress tensor, respectively, belonging to an “auxiliary” Stokes flow around the particle. Evidently,

$$\int_V \mathbf{v}_{\text{aux}} \cdot (\nabla \cdot \boldsymbol{\sigma}_1) dV = \int_V \mathbf{v}_1 \cdot (\nabla \cdot \boldsymbol{\sigma}_{\text{aux}}) dV \quad (5)$$

where the integral is over the fluid volume outside the Debye layer and  $\boldsymbol{\sigma}_1 = -p_1\mathbf{I} + 2\eta_0\mathbf{e}_1 + 2\eta_1(\dot{\gamma}_0)\mathbf{e}_0$  is the

$O(\delta)$  stress. Manipulation of (5) yields

$$\mathbf{V}_1 \cdot \mathbf{F}_{\text{aux}} + \boldsymbol{\Omega}_1 \cdot \mathbf{L}_{\text{aux}} = \int_S \mathbf{v}_{||}^{s,1} \cdot (\boldsymbol{\sigma}_{\text{aux}} \cdot \mathbf{n}) dS + 2 \int_V \eta_1(\dot{\gamma}_0) \mathbf{e}_0 : \nabla \mathbf{v}_{\text{aux}} dV, \quad (6)$$

where  $\mathbf{F}_{\text{aux}}$  and  $\mathbf{L}_{\text{aux}}$  are the force and torque on the particle in the auxiliary problem, which we are free to choose, thereby providing the requisite number of equations to determine  $\mathbf{V}_1$  and  $\boldsymbol{\Omega}_1$ . In (6) the first integral is over the surface  $S$  enclosing the particle and Debye layer and represents the contribution due to non-Newtonian electro-osmosis in the Debye layer. The second integral arises from non-Newtonian stresses in the bulk. Finally, note that (6) is valid for a particle of arbitrary shape.

### III. RESULTS

In this study, (6) is applied to a spherical particle of radius  $R$ , for which  $\mathbf{v}_0 = \frac{\varepsilon\zeta}{2\eta_0}(R/r)^3(3\hat{\mathbf{r}}\hat{\mathbf{r}} - \mathbf{I}) \cdot \mathbf{E}_\infty$ , where  $r = |\mathbf{r}|$ ,  $\hat{\mathbf{r}} = \mathbf{r}/r$ , and  $\mathbf{r}$  is the position vector [61]. We select the auxiliary flow to be that produced by a torque-free sphere translating under an imposed force  $\mathbf{F}_{\text{aux}}$ . Hence, (6) reduces to

$$\mathbf{V}_1 = \frac{\varepsilon\zeta}{\eta_0} \left( \mathbf{I} \int_0^\infty \frac{\eta_1(\dot{\gamma}_0)}{\eta_0} e^{-\hat{y}} d\hat{y} + \frac{3}{4\pi} \int_V \frac{\eta_1(\dot{\gamma}_0)}{\eta_0} \mathbf{F} d\hat{V} \right) \cdot \mathbf{E}_\infty. \quad (7)$$

In deriving (7) we have used  $\phi = \zeta e^{-\hat{y}}$  in the Debye-Huckel limit ( $\hat{y} = y/\lambda_D$ ),  $d\hat{V} = dV/R^3$ , and  $\mathbf{F} = (3\hat{r}^{-6} - 2\hat{r}^{-8})\hat{\mathbf{r}}\hat{\mathbf{r}} - \hat{r}^{-8}\mathbf{I}$ , where  $\hat{r} = r/R$ . The first and second dimensionless integrals in (7) are the contributions from the Debye layer and bulk, respectively.

We first consider a power-law viscosity correction  $\eta_1(\dot{\gamma}_0) = m\dot{\gamma}_0^{n-1}$ . By symmetry,  $\mathbf{V}_1$  is colinear with the applied field, hence let  $\mathbf{V}_1 = (V_{1,D} + V_{1,B})V_0\hat{\mathbf{E}}_\infty$ , where  $V_0 = \varepsilon\zeta E_\infty/\eta_0$ ,  $\mathbf{E}_\infty = E_\infty\hat{\mathbf{E}}_\infty$ , and  $V_{1,D}$  and  $V_{1,B}$  are the dimensionless contributions to the  $O(\delta)$  velocity from the Debye layer and bulk, respectively. Adopting a spherical coordinate system attached to the particle centroid, and taking  $\mathbf{E}_\infty$  to be along the symmetry axis, from (7) it is found

$$V_{1,D} = -\frac{1}{n} \frac{m}{\eta_0} \left( \frac{\varepsilon\zeta E_\infty}{\eta_0 \lambda_D} \right)^{n-1}, \quad (8)$$

$$V_{1,B} = \frac{3m}{2\eta_0} \left( \frac{3\varepsilon\zeta E_\infty}{2\eta_0 R} \right)^{n-1} \int_0^\pi \int_1^\infty h(\hat{r}, \theta; n) d\hat{r} d\theta, \quad (9)$$

where  $\theta$  is the polar angle and  $h(\hat{r}, \theta; n) = (\sqrt{1 + 2\cos^2\theta/\hat{r}^4})^{n-1} [(3\hat{r}^{-6} - 2\hat{r}^{-8})\cos^2\theta - \hat{r}^{-8}] \sin\theta$ . As expected,  $V_{1,D}$  and  $V_{1,B}$  vanish for a Newtonian fluid  $n = 1$ . For a non-Newtonian fluid both contributions are non-linear in the zeta potential and applied field, reminiscent of electro-osmosis in power-law fluids [11, 21]. Moreover,  $V_{1,B} \sim R^{1-n}$ , demonstrating that the electrophoretic velocity has an explicit particle-size dependence, originating from the bulk electrolyte. However,

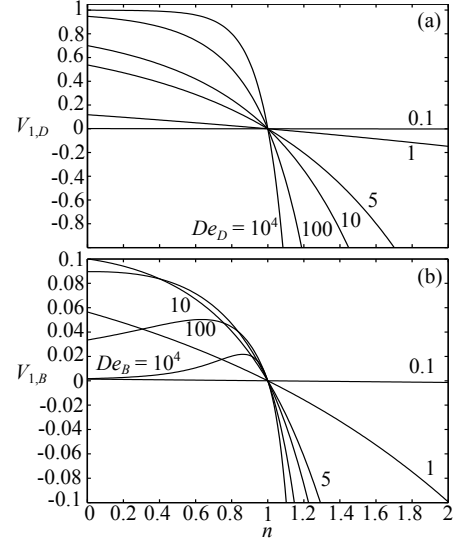


FIG. 2. Non-Newtonian Debye layer  $V_{1,D}$  (a) and bulk  $V_{1,B}$  (b) velocity contributions versus Carreau index  $n$ .

$h \sim \hat{r}^{-4n}$  at large distances,  $\hat{r} \gg 1$ ; hence, the integral in (9) diverges at  $n = \frac{1}{4}$ . This is unsurprising in hindsight, since the power-law model for shear-thinning fluids ( $n < 1$ ) has the *unphysical* feature of an unbounded viscosity as  $\dot{\gamma} \rightarrow 0$  (figure 1(c)). Hence,  $\eta_1$  diverges at low shear rates (large distances) for  $n < 1$ , clearly invalidating the premise that non-Newtonian effects are a correction to the base viscosity  $\eta_0$  (1). (Note, a similar calculation for sedimentation in a power-law fluid would yield a divergence at  $n = \frac{1}{2}$ , cf. [57].)

Therefore, we now consider a bounded viscosity correction of the Carreau type

$$\eta_1(\dot{\gamma}) = \eta_0 \left[ (1 + (\tau\dot{\gamma})^2)^{\frac{n-1}{2}} - 1 \right], \quad (10)$$

where  $\tau$  is a fluid timescale. For  $n < 1$  the viscosity thins from a zero-shear Newtonian plateau to another plateau at large shear rates, whereas for  $n > 1$  the viscosity grows monotonically with shear rate (figure 1(c)). Substituting (10) into (7) yields

$$V_{1,D} = 1 - \int_0^\infty (1 + De_D^2 e^{-2\hat{y}})^{\frac{n-1}{2}} e^{-\hat{y}} d\hat{y}, \quad (11)$$

$$V_{1,B} = \frac{3}{2} \int_0^\pi \int_1^\infty \left[ 1 + \left( \frac{3}{2} De_B \right)^2 \frac{1 + 2\cos^2\theta}{\hat{r}^8} \right]^{\frac{n-1}{2}} ((3\hat{r}^{-6} - 2\hat{r}^{-8})\cos^2\theta - \hat{r}^{-8}) \sin\theta d\hat{r} d\theta, \quad (12)$$

where  $De_D = \tau V_0/\lambda_D$  and  $De_B = \tau V_0/R$  are Deborah numbers for the fluid in the Debye layer and bulk respectively. The Deborah number is the ratio of the fluid timescale  $\tau$  to the flow timescale,  $\lambda_D/V_0$  for the Debye layer and  $R/V_0$  for the bulk, and characterizes the importance of non-Newtonian rheology. The particle size ( $R$ ) dependence enters through the bulk Deborah number  $De_B$ .

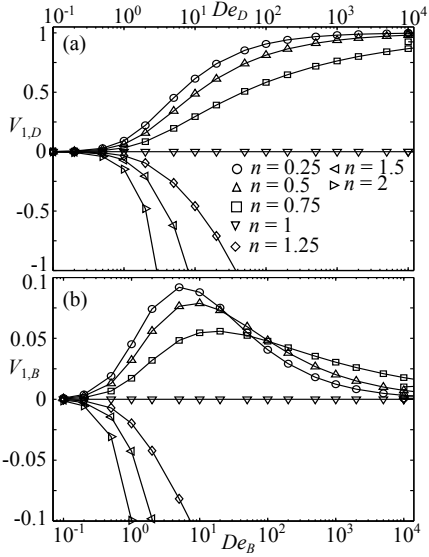


FIG. 3. Non-Newtonian bulk  $V_{1,B}$  (a) and Debye layer  $V_{1,D}$  (b) velocity contributions versus appropriate Deborah numbers. The lines are to guide the eye.

Figure 2 plots the bulk and Debye layer contributions to the velocity as a function of  $n$  at various Deborah numbers. Importantly, the bulk contribution no longer diverges for  $n < 1$ , as the Carreau model has a finite zero-shear rate viscosity. Both contributions are positive(negative) for  $n < 1(> 1)$ , corresponding to an increase(decrease) in the particle velocity in a shear-thinning(thickening) fluid, which is intuitively sensible.

Figure 3 plots the two contributions as a function of appropriate Deborah number for various  $n$ . At small Deborah numbers the fluid approaches its Newtonian zero shear-rate viscosity  $\eta_0$  and hence  $V_{1,D}$  and  $V_{1,B}$  vanish as  $V_{1,D} \sim \frac{1-n}{6} De_D^2$  and  $V_{1,B} \sim \frac{9(1-n)}{65} De_B^2$  to leading order as  $De_D \rightarrow 0$  and  $De_B \rightarrow 0$ , respectively. (The two contributions also vanish in the trivial Newtonian case  $n = 1$ ). For  $n > 1$  the monotonic shear-thickening of the Carreau model results in both contributions being negative and decreasing with increasing Deborah numbers: i.e. the particle velocity is smaller than in a Newtonian fluid. In contrast, for  $n < 1$  the Debye layer contribution  $V_{1,D}$  is positive and increasing, corresponding to an increase in particle velocity, until a common plateau is reached at large  $De_D$ . This plateau occurs since at very large shear rates  $\eta \rightarrow \eta_0(1 - \delta)$ ; the reduced viscosity drives a faster electro-osmotic flow in the Debye layer (by a factor of  $1 + \delta + O(\delta^2)$ ), leading to a concomitant increase in  $V_{1,D}$ . The bulk contribution  $V_{1,B}$  for  $n < 1$  goes through a maximum before decaying to zero as  $De_D \rightarrow \infty$ . This is expected as  $V_{1,D}$  is driven by non-Newtonian stresses in the bulk, which vanish as  $De_D \rightarrow \infty$ , where the Carreau fluid attains a high-shear rate Newtonian plateau.

Figure 4(a) shows that for  $n < 1$  the maximum in  $V_{1,B}$  ( $V_{1,B}^{\max}$ , say) is of  $O(0.1)$  and also plots the bulk Deborah number,  $De_B^{\max}$ , at which the maximum occurs. Hence

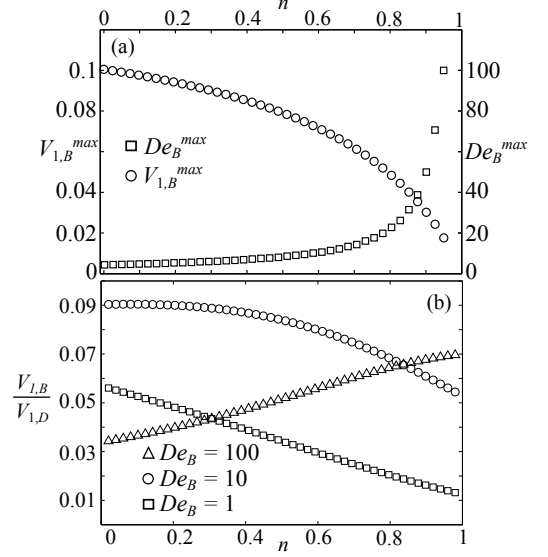


FIG. 4. (a) Maximum of the bulk velocity contribution,  $V_{1,B}^{\max}$  (circles), versus  $n$  for shear thinning fluids,  $n < 1$ . Also shown is the bulk Deborah number,  $De_B^{\max}$  (squares), at which the maximum occurs. (b) Ratio of bulk to Debye layer velocity contributions  $V_{1,B}/V_{1,D}$  versus  $n$ , at  $De_D = 10^3$  and  $De_B = 1, 10$ , and  $100$ .

$\delta V_{1,B} \sim O(10^{-1}\delta)$  for  $De_B^{\max}$ . Note that  $\tau$  can be on the order of seconds; hence taking  $\tau = 1$ s,  $\lambda_D = 10$ nm,  $R = 1\mu$ m, and  $V_0 = 10\mu$ m/s yields  $De_D \sim O(10^3)$  and  $De_B \sim O(10)$  (which is close to  $De_B^{\max}$ ). This suggests that appreciable Deborah numbers can be attained in experiments. Furthermore, figure 4(b) plots the ratio  $V_{1,B}/V_{1,D}$  versus  $n$ , at  $De_D = 10^3$  and  $De_B = 1, 10$ , and  $100$ . The ratio is  $O(10^{-1})$ , from which it is concluded that  $V_{1,B}$  and  $V_{1,D}$  are comparable at these realistic conditions. Note, the difference between  $De_D$  and  $De_B$  (namely,  $De_B/De_D = \lambda_D/R$ ) is due to the disparity in  $\lambda_D$  and  $R$ ; physically, the shear rate in the Debye layer is  $O(R/\lambda_D)$  larger than the bulk.

#### IV. CONCLUDING REMARKS

We have developed a general framework to compute the electrophoretic velocity of a colloidal particle (of any shape) suspended in a non-Newtonian fluid whose viscosity is a function of shear rate. We find that non-Newtonian rheology endows the velocity with an explicit dependence on particle size, in contrast to electrophoresis in a Newtonian fluid. We anticipate our work will be valuable to capillary electrophoresis and microfluidics, wherein electric fields are routinely used to transport particles in non-Newtonian fluids. Admittedly, we do not account for physicochemical changes to the Debye layer due to the micro-structural entities (e.g. polymer molecules) comprising the complex fluid: e.g. alterations in the zeta potential due to polymer adsorption, depletion of polymers in the Debye layer, or transient polymer-particle



collisions, each of which may play a role in the Debye-scale electrokinetics. However, of equal importance, the predicted size-dependence of the electrophoretic velocity arises from non-Newtonian stresses in the *bulk* (electroneutral) electrolyte; hence, we expect this central conclusion to be robust to the aforementioned effects.

The perturbation scheme adopted here dictates that the non-Newtonian contributions to the *instantaneous* electrophoretic motion are modest in magnitude. However, one is often interested in particle motion relative to another particle or boundary, over a period of time. In this case, the instantaneous deviation from Newtonian behavior calculated herein may lead to an appreciable *cumulative* effect. To illustrate this, consider two spherical particles with radii  $0.1\mu\text{m}$  and  $1\mu\text{m}$ , respectively, each with a zeta potential of  $\zeta = 25\text{mV}$  and Debye length  $\lambda_D = 10\text{nm}$ , undergoing electrophoresis in a Carreau fluid with  $\eta_0 = 0.113\text{Pa}\cdot\text{s}$  (approximately one hundred times that of water),  $n = 0.468$  and  $\tau = 11.9\text{s}$  [63]. For these parameters,  $V_0 = 1.5\mu\text{m/s}$  in an applied field of strength  $100\text{V/cm}$ , leading to  $De_D = 1785$ ,  $De_B = 178.5$  ( $0.1\mu\text{m}$  particle), and  $De_B = 17.85$  ( $1\mu\text{m}$  particle). This gives the dimensionless non-Newtonian velocity corrections:  $V_{1,D} = 0.9768$ ,  $V_{1,B} = 0.0381$  ( $0.1\mu\text{m}$  particle), and  $V_{1,B} = 0.0745$  ( $1\mu\text{m}$  particle). Thus, our theory pre-

dicts for  $\delta = 0.05$  that the particles will separate by one micron, i.e. ten (smaller) particle lengths, in approximately six minutes.

The present study suggests several future directions. For instance, our approach can be extended to non-spherical or multiple particles. In the latter case, two particles with equal  $\zeta$  move at the same velocity in a Newtonian fluid; we expect relative electrophoretic motion in a non-Newtonian fluid — do the particles attract or repel? How does this depend on the fluid rheology (thinning versus thickening)? Moreover, a shear rate dependent viscosity is but one non-Newtonian trait; complex fluids also often possess normal stress differences, which our approach can readily be adapted to account for. We will, however, leave these interesting issues for future studies.

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- [1] J. Lyklema, *Fundamentals of Interface and Colloid Science. Volume II: Solid-Liquid Interfaces* (Academic Press, San Diego CA, 1995).
  - [2] H. C. Chang and L. Y. Yeo, *Electrokinetically-Driven Microfluidics and Nanofluidics* (Cambridge University Press, Cambridge UK, 2010).
  - [3] S. Wall, Curr. Opin. Colloid Interface Sci. **15**, 119 (2010).
  - [4] W. B. Russel, D. A. Saville, and W. R. Schowalter, *Colloidal Dispersions* (Cambridge University Press, Cambridge UK, 1989).
  - [5] R. F. Probstein and R. E. Hicks, Science **260**, 498 (1993).
  - [6] B. Reynaud and T. M. Quinn, Biophys. J. **91**, 2349 (2006).
  - [7] T. M. Squires and S. R. Quake, Rev. Mod. Phys. **77**, 977 (2005).
  - [8] L. Bocquet and E. Charlaix, Chem. Soc. Rev. **39**, 1073 (2010).
  - [9] M. S. Bello, P. Debesi, R. Rezzonico, P. G. Righetti, and E. Casiraghi, Electrophoresis **15**, 623 (1994).
  - [10] F. M. Chang and H. K. Tsao, Appl. Phys. Lett. **90**, 194105 (2007).
  - [11] M. L. Olivares, L. Vera-Candioti, and C. L. A. Berli, Electrophoresis **30**, 921 (2009).
  - [12] R. M. Bryce and M. R. Freeman, Phys. Rev. E **81**, 036328 (2010).
  - [13] W. Lo, H. C. Hong, H. J. Choi, P. Lai, and C. K. Chan, Phys. Rev. E **84**, 021802 (2011).
  - [14] S. Das and S. Chakraborty, Anal. Chim. Acta **559**, 15 (2006).
  - [15] S. Chakraborty, Anal. Chim. Acta **605**, 175 (2007).
  - [16] M. Lu and J. Yang, Microvasc. Res. **78**, 14 (2009).
  - [17] W. B. Zimmerman, J. M. Rees, and T. J. Craven, Microfluid. Nanofluid. **2**, 481 (2008).
  - [18] H. M. Park and W. M. Lee, J. Colloid Interface Sci. **317**, 631 (2008).
  - [19] C. L. A. Berli and M. L. Olivares, J. Colloid Interface Sci. **320**, 582 (2008).
  - [20] H. M. Park and W. M. Lee, Lab Chip **8**, 1163 (2008).
  - [21] C. Zhao, E. Zholkovskij, J. H. Masilyah, and C. Yang, J. Colloid Interface Sci. **326**, 503 (2008).
  - [22] G. H. Tang, X. F. Li, Y. L. He, and W. Q. Tao, J. Non-Newtonian Fluid Mech. **157**, 133 (2009).
  - [23] C. Zhao and C. Yang, Appl. Math. Comput. **211**, 502 (2009).
  - [24] T. J. Craven, J. M. Rees, and W. B. Zimmerman, Microfluid. Nanofluid. **9**, 559 (2010).
  - [25] N. Vasu and S. De, Colloid Surf. A **368**, 44 (2010).
  - [26] C. Zhao and C. Yang, Electrophoresis **31**, 973 (2010).
  - [27] A. Babaie, A. Sadeghi, and M. H. Saidi, J. Non-Newtonian Fluid Mech. **166**, 792 (2011).
  - [28] M. Hadigol, R. Nosrati, A. Nourbakhsh, and M. Raisee, J. Non-Newtonian Fluid Mech. **166**, 965 (2011).
  - [29] Q. Liu, Y. Jian, and L. Yang, J. Non-Newtonian Fluid Mech. **166**, 478 (2011).
  - [30] C. Zhao and C. Yang, Biomicrofluidics **5**, 014110 (2011).
  - [31] A. M. Afonso, M. A. Alves, and F. T. Pinho, J. Non-Newtonian Fluid Mech. **159**, 50 (2009).
  - [32] C. L. A. Berli, J. Colloid Interface Sci. **349**, 446 (2010).
  - [33] C. L. A. Berli, Microfluid. Nanofluid. **8**, 197 (2010).
  - [34] J. J. Sousa, A. M. Afonso, F. T. Pinho, and M. A. Alves, Microfluid. Nanofluid. **10**, 107 (2011).
  - [35] M. Hadigol, R. Nosrati, and M. Raisee, Colloid Surf. A **374**, 142 (2011).
  - [36] R. J. Hunter, J. Colloid Interface Sci. **22**, 231 (1966).

- [37] A. P. Gast and C. F. Zukoski, *Adv. Colloid Interface Sci.* **30**, 153 (1989).
- [38] W. B. Russel, *J. Fluid Mech.* **85**, 209 (1978).
- [39] M. Z. Bazant, M. S. Kilic, B. D. Storey, and A. Ajdari, *New J. Phys.* **11**, 075016 (2009).
- [40] F. A. Morrison, *J. Colloid Interface Sci.* **34**, 210 (1970).
- [41] C. F. Zukoski and D. A. Saville, *J. Colloid Interface Sci.* **115**, 422 (1987).
- [42] J. L. Viovy, *Rev. Mod. Phys.* **72**, 813 (2000).
- [43] J. M. Savard, S. T. Grosser, and J. W. Schneider, *Electrophoresis* **29**, 2779 (2008).
- [44] E. Lee, Y. F. Huang, and J. P. Hsu, *J. Colloid Interface Sci.* **258**, 283 (2003).
- [45] J. P. Hsu, E. Lee, and Y. F. Huang, *Langmuir*, **20**, 2149 (2004).
- [46] J. P. Hsu, S. H. Hung, and H. Y. Yu, *J. Colloid Interface Sci.* **280**, 256 (2004).
- [47] E. Lee, C. S. Tsai, J. Hsu, and C. J. Chen, *Langmuir*, **20**, 7952 (2004).
- [48] E. Lee, C. T. Chen, and J. P. Hsu, *J. Colloid Interface Sci.* **282**, 857 (2005).
- [49] E. Lee, C. J. Chang, and J. P. Hsu, *J. Colloid Interface Sci.* **282**, 486 (2005).
- [50] E. Lee, C. P. Chiang, and J. P. Hsu, *Langmuir* **22**, 1911 (2006).
- [51] J. P. Hsu, L. H. Yeh, and M. H. Ku, *Colloid. Polym. Sci.* **284**, 886 (2006).
- [52] J. P. Hsu and L. H. Yeh, *Langmuir* **23**, 8637 (2007).
- [53] J. P. Hsu, L. H. Yeh, and S. J. Yeh, *J. Phys. Chem. B* **111**, 12351 (2007).
- [54] L. H. Yeh and J. P. Hsu, *Microfluid. Nanofluid.* **7**, 383 (2009).
- [55] J. P. Hsu, C. Y. Chen, L. H. Yeh, and S. Tseng, *Colloid Surface B* **69**, 8 (2009).
- [56] R. J. Phillips, *J. Fluid Mech.* **315**, 345 (1996).
- [57] T. M. Squires, *Langmuir* **24**, 1147 (2008).
- [58] A. S. Khair and T. M. Squires, *Phys. Rev. Lett.* **105**, 156001 (2010).
- [59] B. P. Ho and L. G. Leal, *J. Fluid Mech.* **76**, 783 (1976).
- [60] P. Brunn, *Rheo. Acta.* **15**, 163 (1976).
- [61] J. L. Anderson, *Ann. Rev. Fluid Mech.* **21**, 61 (1989).
- [62] Note that  $\mathbf{V}_0 = \varepsilon\zeta\mathbf{E}_\infty/\eta_0$  represents the leading order contribution to the particle velocity in a double asymptotic series in  $\epsilon = (\lambda_D/R)^2$  and  $\delta$ . The particle velocity is thus  $\mathbf{V} = V_0 [1 + \delta(V_{1,D} + V_{1,B}) + O(\epsilon) + O(\delta^2, \epsilon^2, \delta\epsilon)] \hat{\mathbf{E}}_\infty$ . However, the  $O(\epsilon)$  terms do not derive from non-Newtonian fluid properties (they are independent of  $\delta$ ) and lead to  $O(\delta\epsilon)$  non-Newtonian contributions to the particle motion. Hence, the leading order contribution to the particle velocity due to non-Newtonian rheology is captured in  $\delta(V_{1,D} + V_{1,B})$ , which we have calculated and is of order  $\delta$ .
- [63] R. Darby and S. Pivsa-Art, *Can. J. Chem. Eng.* **69**, 1395 (1991).