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Transient Electrophoresis of a Cylindrical Colloidal Particle

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Abstract: We develop the theory of transient electrophoresis of a weakly charged, infinitely long cylindrical colloidal particle under an application of a transverse or tangential step electric field. Transient electrophoretic mobility approaches steady electrophoretic mobility with time. We derive closed-form expressions for the transient electrophoretic mobility of a cylinder without involving numerical inverse Laplace transformations and the corresponding time-dependent transient Henry functions. The transient electrophoretic mobility of an arbitrarily oriented cylinder is also derived. It is shown that in contrast to the case of steady electrophoresis, the transient Henry function of an arbitrarily oriented cylinder at a finite time is significantly smaller than that of a sphere with the same radius and mass density as the cylinder so that a cylinder requires a much longer time to reach its steady mobility than the corresponding sphere.

Keywords: transient electrophoresis; transient electrophoretic mobility; cylindrical colloidal particle; Henry function

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Citation: Ohshima, H. Transient Electrophoresis of a Cylindrical Colloidal Particle. *Fluids* **2022**, *7*, 342. https://doi.org/10.3390/fluids7110342

Academic Editor: Mehrdad Massoudi

Received: 10 October 2022
Accepted: 28 October 2022
Published: 29 October 2022

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1. Introduction

Transient electrophoresis is the time-dependent unsteady response of a charged colloidal particle in an electrolyte solution to an applied step electric field [1–19]. It is often required to determine the time necessary for the velocity of a particle to approach its steady value when an electric field is applied to the particle. This information is of practical importance in the efficient design of systems for measurements of steady-state electrophoresis. Morrison [1,2] and later Ivory [3,4] initiated the theory of transient electrophoresis of a spherical or cylindrical particle. The theory of transient electrophoresis has been advanced significantly by Keh and his coworkers [5–7,9,10,14–16].

Li and Keh [14], in particular, derived the general expression for the Laplace transform of the transient electrophoretic mobility of a weakly charged infinitely long cylinder with arbitrary double-layer thickness in an applied transverse or tangential step electric field and calculated the transient electrophoretic mobility of the particle by using the numerical inverse Laplace transformation method. This method, however, requires tedious numerical calculation and it is not very convenient for practical purposes.

In a previous paper [18], we have shown that the fundamental electrokinetic equations describing the transient electrophoresis of a spherical colloidal particle are quite similar to those for the dynamic electrophoresis of the spherical particle in an applied oscillating electric field [20]. Indeed, it has been shown that there is a simple correspondence between the Laplace transform of the transient electrophoretic mobility and the dynamic electrophoretic mobility of a charged particle in an electrolyte solution [18]. As in the case of a spherical particle, it will be shown that there is the same correspondence relation between the Laplace transform of the transient electrophoretic mobility of a cylinder and its dynamic electrophoretic mobility [21].

The purpose of the present paper is to develop further the theory of transient electrophoresis of a weakly charged infinitely long cylinder in an applied transverse or tangential step electric field and derive closed-form expressions for the transient electrophoretic mobility of the cylinder without involving numerical inverse Laplace transformations.

2. Theory

Let us consider an infinitely long, cylindrical colloidal particle of mass density ρ_p, radius a, and zeta potential ζ in an aqueous electrolyte solution of mass density ρ_o, viscosity η, and relative permittivity ε_r. The electrolyte consists of N ionic species of valence z_i, bulk concentration (number density) n_i^∞, and drag coefficient λ_i ($i = 1, 2, \ldots, N$). We suppose that a step electric field $\boldsymbol{E}(t)$ is suddenly applied transversely or tangentially to the cylinder at time $t = 0$, viz.,

$$\boldsymbol{E}(t) = \begin{cases} 0, & t = 0 \\ \boldsymbol{E}_o, & t > 0 \end{cases} \tag{1}$$

where $\boldsymbol{E}_o$ is constant and the particle starts to move with an electrophoretic velocity $\boldsymbol{U}(t)$ in the direction parallel to $\boldsymbol{E}_o$ (Figure 1). The transient electrophoretic mobility $\mu(t)$ of the particle is defined by $\boldsymbol{U}(t) = \mu(t)\boldsymbol{E}(t) = \mu(t)\boldsymbol{E}_o$. The origin of the cylindrical coordinate system (r, θ, z) is held fixed at the center of the particle. We treat the case where (i) the liquid can be regarded as incompressible, (ii) the applied electric field $\boldsymbol{E}(t)$ is weak so that terms involving the square of the liquid velocity in the Navier–Stokes equation can be neglected and the particle velocity $\boldsymbol{U}(t)$ is proportional to $\boldsymbol{E}(t)$, and (iii) the relative permittivity of the particle ε_p is much smaller than that of the electrolyte solution ε_r ($\varepsilon_p \ll \varepsilon_r$).

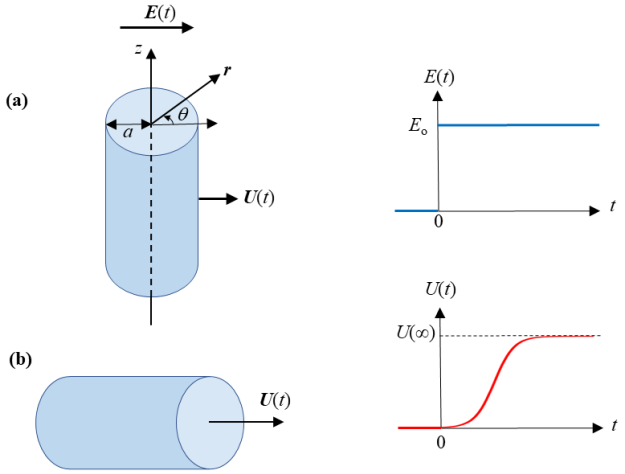


Figure 1. Cylindrical colloidal particle of radius a and zeta potential ζ moving with a transient velocity $\boldsymbol{U}(t)$ in an applied step electric field $\boldsymbol{E}(t)$. The electric field $\boldsymbol{E}(t)$ is perpendicular to the cylinder axis (**a**) or parallel to it (**b**). $U(\infty)$ is the magnitude of $\boldsymbol{U}(\infty)$ at $t = \infty$.

2.1. Cylinder in a Transverse Field

We first treat the case where $\boldsymbol{E}(t)$ is perpendicular to the cylinder axis (Figure 1a). The fundamental electrokinetic equations for the liquid flow velocity $\boldsymbol{u}(\boldsymbol{r}, t)$ at position $\boldsymbol{r}(r, \theta, z)$ and time t and the velocity $\boldsymbol{v}_i(\boldsymbol{r}, t)$ of i th ionic species are given by

$$\rho_o \frac{\partial}{\partial t}\{\boldsymbol{u}(\boldsymbol{r}, t) + \boldsymbol{U}(t)\} + \eta \nabla \times \nabla \times \boldsymbol{u}(\boldsymbol{r}, t) + \nabla p(\boldsymbol{r}, t) + \rho_{el}(\boldsymbol{r}, t)\nabla\psi(\boldsymbol{r}, t) = \boldsymbol{0} \tag{2}$$

$$\nabla \cdot \boldsymbol{u}(\boldsymbol{r}, t) = 0 \tag{3}$$

$$\boldsymbol{v}_i(\boldsymbol{r}, t) = \boldsymbol{u}(\boldsymbol{r}, t) - \frac{1}{\lambda_i}\nabla\mu_i(\boldsymbol{r}, t) \tag{4}$$

$$\frac{\partial n_i(\boldsymbol{r}, t)}{\partial t} + \nabla \cdot \{n_i(\boldsymbol{r}, t)\boldsymbol{v}_i(\boldsymbol{r}, t)\} = 0 \tag{5}$$

$$\pi a^2 \rho_p \frac{d\boldsymbol{U}(t)}{dt} = \boldsymbol{F}_H(t) + \boldsymbol{F}_E(t) \tag{6}$$

where e is the elementary electric charge, k is the Boltzmann constant, T is the absolute temperature, ε_o is the permittivity of a vacuum, $p(\boldsymbol{r}, t)$ is the pressure, $\rho_{el}(\boldsymbol{r}, t)$ is the charge

density, $\psi(\boldsymbol{r}, t)$ is the electric potential, $\boldsymbol{F}_{\mathrm{H}}(t)$ and $\boldsymbol{F}_{\mathrm{E}}(t)$ are, respectively, the hydrodynamic and electric forces acting on the cylinder. Equations (2) and (3) are the Navier–Stokes equation and the equation of continuity for an incompressible flow (condition (i)). The term involving the particle velocity $\boldsymbol{U}$ (t) in Equation (2) arises from the fact that the particle has been chosen as the frame of reference for the coordinate system. Equation (4) states that the flow $\boldsymbol{v}_i(\boldsymbol{r}, t)$ of the i th ionic species is caused by the liquid flow $\boldsymbol{u}(\boldsymbol{r}, t)$ and the gradient of the electrochemical potential $\mu_i(\boldsymbol{r}, t)$. Equation (5) is the continuity equation for the i th ionic species. Equation (6) is the equation of the motion of the cylinder per unit length.

The initial and boundary conditions for $\boldsymbol{u}(\boldsymbol{r}, t)$ and $\boldsymbol{v}_i(\boldsymbol{r}, t)$ are given by

$$\boldsymbol{u}(\boldsymbol{r}, t) = \boldsymbol{0} \quad \text{at } t = 0 \tag{7}$$

$$\boldsymbol{u}(\boldsymbol{r}, t) = \boldsymbol{0} \quad \text{at } r = a \tag{8}$$

$$\boldsymbol{u}(\boldsymbol{r}, t) \to -\boldsymbol{U}(\boldsymbol{r}, t) \text{ as } r \to \infty \tag{9}$$

$$\boldsymbol{v}_i(\boldsymbol{r}, \boldsymbol{t}) \cdot \hat{\boldsymbol{n}} = 0 \text{ at } r = a \tag{10}$$

where $\hat{\boldsymbol{n}}$ is the unit normal outward from the particle surface. Equation (8) states that the slipping plane (at which $\boldsymbol{u}(\boldsymbol{r}, t) = \boldsymbol{0}$) is located on the particle surface. Equation (10) follows from the condition that electrolyte ions cannot penetrate the particle surface.

For a weak field $\boldsymbol{E}(t)$, the deviations of $n_j(\boldsymbol{r}, t)$, $\psi(\boldsymbol{r}, t)$, and $\mu_j(\boldsymbol{r}, t)$ from their equilibrium values (i.e., those in the absence of $\boldsymbol{E}(t)$) due to the applied field $\boldsymbol{E}(t)$ are small so that we may write

$$n_i(\boldsymbol{r}, \boldsymbol{t}) = n_i^{(0)}(r) + \delta n_i(\boldsymbol{r}, \boldsymbol{t}) \tag{11}$$

$$\psi(\boldsymbol{r}, \boldsymbol{t}) = \psi^{(0)}(r) + \delta\psi(\boldsymbol{r}, \boldsymbol{t}) \tag{12}$$

$$\mu_i(\boldsymbol{r}, \boldsymbol{t}) = \mu_i^{(0)} + \delta\mu_i(\boldsymbol{r}, \boldsymbol{t}) \tag{13}$$

where the quantities with superscript (0) refer to those at equilibrium, the quantities, with δ referring to the deviations from the corresponding equilibrium values, and $\mu_i^{(0)}$ is a constant independent of r. It is assumed that the equilibrium concentration $n_i^{(0)}(r)$ obeys the Boltzmann distribution and the equilibrium electric potential satisfies the Poisson-Boltzmann equation, viz.,

$$n_i^{(0)}(r) = n_i^{\infty}(r) e^{-z_i y(r)} \tag{14}$$

$$\Delta y(r) = -\kappa^2 \frac{\sum_{i=1}^{N} z_i n_i^{\infty} e^{-z_i y(r)}}{\sum_{i=1}^{N} z_i^2 n_i^{\infty}} \tag{15}$$

with

$$y(r) = \frac{e\psi^{(0)}(r)}{kT} \tag{16}$$

$$\kappa = \sqrt{\frac{e^2}{\varepsilon_{\mathrm{r}}\varepsilon_{\mathrm{o}} kT} \sum_{i=1}^{N} z_i^2 n_i^{\infty}} \tag{17}$$

where y (r) is the scaled equilibrium electric potential, κ is the Debye–Hückel parameter, and $1/\kappa$ is the Debye length.

From symmetry, we may write

$$\boldsymbol{u}(\boldsymbol{r}, t) = \left(-\frac{h(r,t)}{r} E(t) \cos\theta,\ \frac{dh(r,t)}{dr} E(t) \sin\theta,\ 0 \right) \tag{18}$$

$$\delta\mu_i(\boldsymbol{r},\ t) = -z_i e \phi_i(r, t) E(t) \cos\theta \tag{19}$$

where $E(t)$ is the magnitude of $\boldsymbol{E}(t)$, $h(r, t)$, and $\phi_i(r, t)$ are functions of r and t. By substituting Equations (11)–(13), (18), and (19) into Equations (2)–(5), we obtain the following equations for $h(r)$:

$$L\left[Lh(r,t) - \frac{1}{\nu}\frac{\partial h(r,t)}{\partial t}\right] = G(r,t) \tag{20}$$

where

$$L = \frac{d}{dr}\frac{1}{r}\frac{d}{dr}r = \frac{d^2}{dr^2} + \frac{1}{r}\frac{d}{dr} - \frac{1}{r^2} \tag{21}$$

is a differential operator, $G(r, t)$ is defined by

$$G(r,t) = -\frac{e}{\eta r}\frac{dy}{dr}\sum_{i=1}^{N} z_i^2 n_i^{\infty} e^{-z_i y}\phi_i(r,t) \tag{22}$$

and

$$\nu = \frac{\eta}{\rho_o} \tag{23}$$

is the kinematic viscosity. It follows from Equations (9) and (18) that the transverse transient electrophoretic mobility $\mu(t)$ can be obtained by

$$\mu_{\perp}(t) = \frac{U(t)}{E(t)} = \frac{U(t)}{E_o} = \lim_{r\to\infty}\frac{h(r,\ t)}{r} \tag{24}$$

We solve Equation (20) by introducing the Laplace transforms $\hat{h}(r, s)$, $\hat{G}(r, s)$, and $\hat{\mu}_{\perp}(s)$ of $h(r, t)$, $G(r, t)$, and $\mu_{\perp}(r, t)$, respectively, which are given by

$$\hat{h}(r,s) = \int_0^{\infty} h(r,t)e^{-st}dt \tag{25}$$

$$\hat{G}(r,s) = \int_0^{\infty} G(r,t)e^{-st}dt \tag{26}$$

$$\hat{\mu}_{\perp}(s) = \int_0^{\infty} \mu_{\perp}(t)e^{-st}dt \tag{27}$$

and the Laplace transform of Equation (26) is

$$\hat{\mu}_{\perp}(s) = \lim_{r\to\infty}\frac{\hat{h}(r,s)}{r} \tag{28}$$

The Laplace transform of Equation (20) thus gives

$$L\left[L\hat{h}(r,s) - \frac{s}{\nu}\hat{h}(r,s)\right] = \hat{G}(r,s) \tag{29}$$

By solving Equation (29) and using Equation (28), we obtain the following general expression for $\hat{\mu}_{\perp}(s)$:

$$\hat{\mu}_{\perp}(s) = \frac{\nu\int_a^{\infty}\left[\left(\frac{r^2}{a^2}-1\right)\sqrt{\frac{s}{\nu}}aK_0\left(\sqrt{\frac{s}{\nu}}a\right) - 2\left\{K_1\left(\sqrt{\frac{s}{\nu}}a\right) - \frac{r}{a}K_1\left(\sqrt{\frac{s}{\nu}}r\right)\right\}\right]\hat{G}(r,s)dr}{4s\left\{K_1\left(\sqrt{\frac{s}{\nu}}a\right) + \beta_{\perp}\sqrt{\frac{s}{\nu}}aK_0\left(\sqrt{\frac{s}{\nu}}a\right)\right\}} \tag{30}$$

where $K_n(z)$ is the n th order modified Bessel function of the second kind.

Now consider the low ζ potential case. In this case, it can be shown that (see Ref. [21])

$$\phi_i(r,t) = r + \frac{a^2}{r} \tag{31}$$

and Equation (22) becomes

$$G(r,t) = -\frac{\varepsilon_r \varepsilon_o \kappa^2}{\eta}\left(1+\frac{a^2}{r^2}\right)\frac{d\psi^{(0)}(r)}{dr} \tag{32}$$

The Laplace transform $\hat{G}(r,s)$ of $G(r,t)$ is given by

$$\hat{G}(r,s) = \frac{G(r,t)}{s} = -\frac{\varepsilon_r \varepsilon_o \kappa^2}{\eta s}\left(1+\frac{a^2}{r^2}\right)\frac{d\psi^{(0)}(r)}{dr} \tag{33}$$

where the equilibrium electric potential $\psi^{(0)}(r)$ for the low ζ potential case is given by

$$\psi^{(0)}(r) = \zeta\frac{K_0(\kappa r)}{K_0(\kappa a)} \tag{34}$$

which is obtained from the linearized Poisson-Boltzmann equation $\Delta\psi^{(0)}(r) = \kappa^2\psi^{(0)}(r)$ (see Equation (15)). By substituting Equation (34) into Equation (30), we obtain

$$\hat{\mu}_\perp(s) = -\frac{\varepsilon_r \varepsilon_o \kappa^2 \nu \int_a^\infty \left[\left(\frac{r^2}{a^2}-1\right)\sqrt{\frac{s}{\nu}}aK_0\left(\sqrt{\frac{s}{\nu}}a\right) - 2\left\{K_1\left(\sqrt{\frac{s}{\nu}}a\right) - \frac{r}{a}K_1\left(\sqrt{\frac{s}{\nu}}r\right)\right\}\right]\left(1+\frac{a^2}{r^2}\right)\frac{d\psi^{(0)}(r)}{dr}dr}{4\eta s^2\left\{K_1\left(\sqrt{\frac{s}{\nu}}a\right) + \beta_\perp\sqrt{\frac{s}{\nu}}aK_0\left(\sqrt{\frac{s}{\nu}}a\right)\right\}} \tag{35}$$

which agrees with Li and Keh's result [14]. Li and Keh [14] obtained the transient electrophoretic mobility $\mu_\perp(t)$ by using the numerical inverse Laplace transform of Equation (35). This method, however, involves tedious numerical calculations and is not very convenient for practical uses. In order to avoid this difficulty, we employ the same approximation method as used for the static electrophoresis problem [22]. We first note that the integrand in Equation (35) has a sharp maximum around $r = a + \delta/\kappa$, δ being a factor of order unity. This is because the electrical double layer (of the thickness $1/\kappa$) around the cylinder is confined in the narrow region between $r = a$ and $r \approx a + 1/\kappa$. Since the factor $(1 + a^2/r^2)$ in the integrand of Equation (35) varies slowly with r as compared with the other factors, one may approximately replace r in the factor $(1 + a^2/r^2)$ by $r = a + \delta/\kappa$ and take it out before the integral sign. That is, we make the following approximate replacement of the difficult factor $(1 + a^2/r^2)$ by an r-independent constant factor:

$$1+\frac{a^2}{r^2} \approx 1+\frac{1}{\left(1+\frac{\delta}{\kappa a}\right)^2} \tag{36}$$

In the static electrophoresis [22,23], we have found that the best approximation can be achieved if δ is chosen to be $2.55/\left(1+\boldsymbol{E}^{-\kappa a}\right)$ with negligible errors. We use this choice of δ in the transient electrophoresis problem. By using this approximation, the integration in Equation (35) can be carried out analytically to give

$$\hat{\mu}_\perp(s) = \frac{\varepsilon_r \varepsilon_o \zeta}{2\eta}\left[1+\frac{1}{\left\{1+\frac{2.55}{\kappa a(1+e^{-\kappa a})}\right\}^2}\right]\frac{K_0(\kappa a)K_1\left(\sqrt{\frac{s}{\nu}}a\right) - \frac{1}{\kappa}\sqrt{\frac{s}{\nu}}K_1(\kappa a)K_0\left(\sqrt{\frac{s}{\nu}}a\right)}{s\left(1-\frac{s}{\kappa^2\nu}\right)K_0(\kappa a)\left\{K_1\left(\sqrt{\frac{s}{\nu}}a\right) + \beta_\perp\sqrt{\frac{s}{\nu}}aK_0\left(\sqrt{\frac{s}{\nu}}a\right)\right\}} \tag{37}$$

with

$$\beta_\perp = \frac{1}{4}\left(1+\frac{\rho_p}{\rho_o}\right) \tag{38}$$

We obtain $\mu_\perp(t)$ from $\hat{\mu}_\perp(s)$ by using the inverse Laplace transformation, viz.,

$$\mu_\perp(t) = \frac{1}{2\pi i}\int_{\gamma-i\infty}^{\gamma+i\infty}\hat{\mu}_\perp(s)e^{st}ds \tag{39}$$

where the integration is carried out along the vertical line Re(s) = γ in the complex plane, where γ is large so that all the singularities of $\hat{\mu}_\perp(s)$ lie to the left of the line ($\gamma - i\infty$, $\gamma + i\infty$) (Figure 2). Since $\hat{\mu}_\perp(s)$ has a branch point at the origin s = 0, we convert this line integral into a contour integral over a large circle G with a cut along the negative part of the real axis Re(s). Since the integral over the large circle Γ vanishes as its radius R tends to infinity, the line integral is replaced by real infinite integrals along CD and EF together with the contribution from the small circle about the origin s = 0 [24].

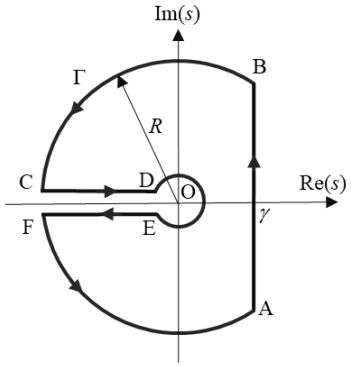


Figure 2. Contour integral on the complex plane of s.

By making the change in variables

$$s = -\frac{\nu}{a^2}\lambda^2 \tag{40}$$

We obtain from Equation (37) the following expression for $\mu_\perp(t)$:

$$\mu_\perp(t) = \frac{\varepsilon_r\varepsilon_o\zeta}{2\eta}\left[1 + \frac{1}{\left\{1 + \frac{2.55}{\kappa a(1+e^{-\kappa a})}\right\}^2}\right]\left[1 - \frac{4}{\pi^2\beta_\perp}\left\{1 + \frac{K_1(\kappa a)}{\kappa a K_0(\kappa a)\beta_\perp}\right\}\int_0^\infty \frac{\exp\left(-\frac{\nu t}{a^2}\lambda^2\right)}{\left(1 + \frac{\lambda^2}{\kappa^2 a^2}\right)\lambda\Delta_\perp(\lambda)}d\lambda\right] \tag{41}$$

with

$$\Delta_\perp(\lambda) = \left\{\lambda J_0(\lambda) - \frac{J_1(\lambda)}{\beta_\perp}\right\}^2 + \left\{\lambda Y_0(\lambda) - \frac{Y_1(\lambda)}{\beta_\perp}\right\}^2 \tag{42}$$

where $J_n(\lambda)$ and $Y_n(\lambda)$ are, respectively, the n th order Bessel functions of the first and second kinds. In the limit of $t \to \infty$, Equation (41) tends to the transverse steady electrophoretic mobility, viz., [22]

$$\mu_\perp(\infty) = \frac{\varepsilon_r\varepsilon_o\zeta}{2\eta}\left[1 + \frac{1}{\left\{1 + \frac{2.55}{\kappa a(1+e^{-\kappa a})}\right\}^2}\right] \tag{43}$$

which agrees with the following exact expression with negligible errors [22,23].

$$\mu_\perp(\infty) = \frac{\varepsilon_r\varepsilon_o\zeta}{\eta}\left\{1 - \frac{4(\kappa a)^4}{K_0(\kappa a)}\int_{\kappa a}^\infty \frac{K_0(x)}{x^5}dx + \frac{(\kappa a)^2}{K_0(\kappa a)}\int_{\kappa a}^\infty \frac{K_0(x)}{x^3}dx\right\} \tag{44}$$

Equation (41) is the required approximate expression for the transverse transient electrophoretic mobility $\mu_\perp(t)$ with negligible errors. In the limit of large κa ($\kappa a \gg 1$),

$$\mu_\perp(t) = \frac{\varepsilon_r\varepsilon_o\zeta}{\eta}\left[1 - \frac{4}{\pi^2\beta_\perp}\int_0^\infty \frac{\exp\left(-\frac{\nu t}{a^2}\lambda^2\right)}{\lambda\Delta(\lambda)}d\lambda\right] \tag{45}$$

which agrees with the results of Morison [2] and Li and Keh [14]. For small κa ($\kappa a \ll 1$), Equation (41) reduces to

$$\mu_{\perp}(t) = \frac{\varepsilon_r \varepsilon_o \zeta}{2\eta}\left[1 + \frac{4}{\pi^2 \beta_{\perp}^2 \left\{\ln\left(\frac{\kappa a}{2}\right) + \gamma\right\}} \int_0^{\infty} \frac{\exp\left(-\frac{\nu t}{a^2}\lambda^2\right)}{(\kappa^2 a^2 + \lambda^2)\lambda \Delta_{\perp}(\lambda)} d\lambda\right] \tag{46}$$

where γ is Euler's constant ($\gamma = 0.5772$).

2.2. Cylinder in a Tangential Field

We next treat the case where the applied electric field $\boldsymbol{E}(t) = (0, 0, E(t))$ is parallel to the cylinder axis (Figure 1b). The liquid velocity $u(r, t)$ can be expressed as $u = u(0, 0, u_z(r, t))$. The Navier–Stokes equation for $u_z(r, t)$) is given by

$$\rho_o \frac{\partial}{\partial t}\{u_z(r,t) + U(t)\} - \eta \frac{1}{r}\frac{d}{dr}\left\{r\frac{du_z(r,t)}{dr}\right\} - \rho_{el}^{(0)}(r,t)E(t) = 0 \tag{47}$$

By using the Poisson equation $\rho_{el}^{(0)}(r,t) = -\varepsilon_r \varepsilon_o (1/r)(d/dr)\left(r d\psi^{(0)}/dr\right)$ and integrating Equation (47), we finally obtain the following expression for the Laplace transform $\hat{\mu}_{\parallel}(s)$ of the transient tangential electrophoretic mobility $\mu_{\parallel}(t)$:

$$\hat{\mu}_{\parallel}(s) = \frac{\varepsilon_r \varepsilon_o \zeta}{\eta} \frac{K_1\left(\sqrt{\frac{s}{\nu}}a\right) - \frac{1}{\zeta a}\int_a^{\infty} r\psi^{(0)}(r) K_0\left(\sqrt{\frac{s}{\nu}}r\right) dr}{s\left\{K_1\left(\sqrt{\frac{s}{\nu}}a\right) + \beta_{\parallel}\sqrt{\frac{s}{\nu}}a K_0\left(\sqrt{\frac{s}{\nu}}a\right)\right\}} \tag{48}$$

with

$$\beta_{\parallel} = \frac{\rho_p}{2\rho_o} \tag{49}$$

For the low ζ-potential case, Equation (48) becomes

$$\hat{\mu}_{\parallel}(s) = \frac{\varepsilon_r \varepsilon_o \zeta}{\eta} \frac{K_0(\kappa a) K_1\left(\sqrt{\frac{s}{\nu}}a\right) - \frac{1}{\kappa}\sqrt{\frac{s}{\nu}} K_1(\kappa a) K_0\left(\sqrt{\frac{s}{\nu}}a\right)}{s\left(1 - \frac{s}{\kappa^2 \nu}\right) K_0(\kappa a)\left\{K_1\left(\sqrt{\frac{s}{\nu}}a\right) + \beta_{\parallel}\sqrt{\frac{s}{\nu}}a K_0\left(\sqrt{\frac{s}{\nu}}a\right)\right\}} \tag{50}$$

with

$$\beta_{\parallel} = \frac{\rho_p}{2\rho_o} \tag{51}$$

As in the case of $\mu_{\perp}(t)$, by using the inverse Laplace transform $\hat{\mu}_{\perp}(s)$, i.e.,

$$\mu_{\parallel}(t) = \frac{1}{2\pi i}\int_{\gamma - i\infty}^{\gamma + i\infty} \hat{\mu}_{\parallel}(s) e^{st} ds \tag{52}$$

We obtain the following expression for $\mu_{\parallel}(t)$:

$$\mu_{\parallel}(t) = \frac{\varepsilon_r \varepsilon_o \zeta}{\eta}\left[1 - \frac{4}{\pi^2 \beta_{\parallel}}\left\{1 + \frac{K_1(\kappa a)}{\kappa a K_0(\kappa a)\beta_{\parallel}}\right\} \int_0^{\infty} \frac{\exp\left(-\frac{\nu t}{a^2}\lambda^2\right)}{\left(1 + \frac{\lambda^2}{\kappa^2 a^2}\right)\lambda \Delta_{\parallel}(\lambda)} d\lambda\right] \tag{53}$$

with

$$\Delta_{\parallel}(\lambda) = \left\{\lambda J_0(\lambda) - \frac{J_1(\lambda)}{\beta_{\parallel}}\right\}^2 + \left\{\lambda Y_0(\lambda) - \frac{Y_1(\lambda)}{\beta_{\parallel}}\right\}^2 \tag{54}$$

In the limit of $t \to \infty$, Equation (53) tends to the tangential steady electrophoretic mobility [22,23], viz.,

$$\mu_{\parallel}(\kappa a, \infty) = \frac{\varepsilon_r \varepsilon_o \zeta}{\eta} \tag{55}$$

In the limit of large κa, Equation (53) tends to

$$\mu_{\parallel}(t) = \frac{\varepsilon_r \varepsilon_o \zeta}{\eta}\left[1 - \frac{4}{\pi^2 \beta_{\parallel}}\int_0^{\infty} \frac{\exp\left(-\frac{\nu t}{a^2}\lambda^2\right)}{\lambda \Delta(\lambda)} d\lambda\right] \tag{56}$$

while for small κa, Equation (53) tends to

$$\mu_{\parallel}(t) = \frac{\varepsilon_r \varepsilon_o \zeta}{\eta}\left[1 + \frac{4}{\pi^2 \beta_{\parallel}^2\left\{\ln\left(\frac{\kappa a}{2}\right) + \gamma\right\}}\int_0^{\infty} \frac{\exp\left(-\frac{\nu t}{a^2}\lambda^2\right)}{(\kappa^2 a^2 + \lambda^2)\lambda \Delta_{\parallel}(\lambda)} d\lambda\right] \tag{57}$$

It should be noticed that as in the case of a sphere [18], there is a simple correspondence between the Laplace transform of the transient mobility of a cylinder and its dynamic mobility. That is, $\hat{\mu}_{\perp}(s)$ and $\hat{\mu}_{\parallel}(s)$ of the transient electrophoretic mobilities $\mu_{\perp}(t)$ and $\mu_{\parallel}(t)$, respectively, can be obtained from the dynamic electrophoretic mobility $\mu_{\perp}(\omega)$ and $\mu_{\parallel(}\omega)$ of a cylinder under an oscillating electric field of frequency ω by replacing -$i\omega$ with s and $G(r)$ by $G(r)/s$.

3. Results and Discussion

The principal results of the present paper are Equations (41) and (53) for the transverse and tangential transient electrophoretic mobilities, respectively. We define the time-dependent transient Henry function as

$$\mu_{\perp}(t) = \frac{\varepsilon_r \varepsilon_o \zeta}{\eta} f_{\perp}(\kappa a, t) \tag{58}$$

$$\mu_{\parallel}(t) = \frac{\varepsilon_r \varepsilon_o \zeta}{\eta} f_{\parallel}(\kappa a, t) \tag{59}$$

We thus obtain

$$f_{\perp}(\kappa a, t) = \frac{1}{2}\left[1 + \frac{1}{\left\{1 + \frac{2.55}{\kappa a(1+e^{-\kappa a})}\right\}^2}\right]\left[1 - \frac{4}{\pi^2 \beta_{\perp}}\left\{1 + \frac{K_1(\kappa a)}{\kappa a K_0(\kappa a)\beta_{\perp}}\right\}\int_0^{\infty} \frac{\exp\left(-\frac{\nu t}{a^2}\lambda^2\right)}{\left(1 + \frac{\lambda^2}{\kappa^2 a^2}\right)\lambda \Delta(\lambda)} d\lambda\right] \tag{60}$$

and

$$f_{\parallel}(\kappa a, t) = 1 - \frac{4}{\pi^2 \beta_{\parallel}}\left\{1 + \frac{K_1(\kappa a)}{\kappa a K_0(\kappa a)\beta_{\perp}}\right\}\int_0^{\infty} \frac{\exp\left(-\frac{\nu t}{a^2}\lambda^2\right)}{\left(1 + \frac{\lambda^2}{\kappa^2 a^2}\right)\Delta(\lambda)} d\lambda \tag{61}$$

As $t \to \infty$, the transverse transient Henry functions $f_{\perp}(\kappa a, t)$ and $f_{\parallel}(\kappa a, t)$ given by Equations (60) and (61), respectively, tend to the following steady Henry functions [22]:

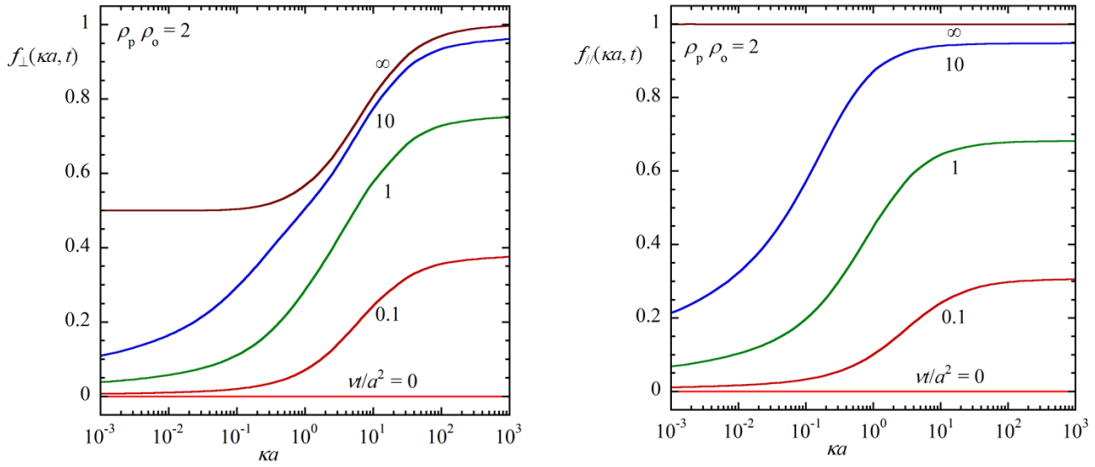
$$f_{\perp}(\kappa a, \infty) = \frac{1}{2}\left[1 + \frac{1}{\left\{1 + \frac{2.55}{\kappa a(1+e^{-\kappa a})}\right\}^2}\right] \tag{62}$$

$$f_{\parallel}(\kappa a, \infty) = 1 \tag{63}$$

Note that Equations (41) and (60) are approximate expressions (with negligible errors) that have been derived from the approximation given by Equation (36), while Equations (53) and (61) are exact results.

It is of interest to note that the ratio of the transient Henry function to the steady Henry function takes the same form for the transverse and tangential transient Henry functions, that is, $f_{\perp}(\kappa a, t)/f_{\perp}(\kappa a, \infty)$ and $f_{\parallel}(\kappa a, t)/f_{\parallel}(\kappa a, \infty)$ are the same except for the difference between $\beta_{\perp}$ and $\beta_{\parallel}$.

Figure 3 shows some examples of the calculation of $f_{\perp}(\kappa a, t)$ (Figure 3a) and $f_{\parallel}(\kappa a, t)$ (Figure 3b) plotted as a function of κa at several values of scaled time $\nu t/a^2$ at $\rho_p/\rho_o = 2$. Figure 3 shows how $f_{\perp}(\kappa a, \infty)$ and $f_{\parallel}(\kappa a, \infty)$ approach their steady values $f_{\perp}(\kappa a, \infty)$ and $f_{\parallel}(\kappa a, \infty)$ with time.



(**a**) (**b**)

Figure 3. Time-dependent transient Henry functions $f_{\perp}(\kappa a, t)$ (**a**) and $f_{\parallel}(\kappa a, t)$ (**b**) of a cylindrical colloidal particle of radius a and mass density ρ_p in an electrolyte solution of mass density ρ_o, kinematic viscosity ν, and Debye–Hückel parameter κ plotted as a function of κa for various values of scaled time $\nu t/a^2$ at $\rho_p/\rho_o = 2$. The values of $f_{\perp}(\kappa a, t)$ and $f_{\parallel}(\kappa a, t)$ at $t \to \infty$, i.e., $f_{\perp}(\kappa a, \infty)$ and $f_{\parallel}(\kappa a, \infty)$ are the steady Henry functions.

In the present paper, we treat an infinitely long cylinder, neglecting the end effects. Sherwood [25] demonstrated that the end effects can be neglected under the condition that the cylinder length is much longer than the double-layer thickness $1/\kappa$, Under this condition, it can also be assumed that there is no interaction between cylinders when we consider a dilute suspension of infinitely long cylinders.

Finally, let us consider a cylindrical particle oriented at an arbitrary angle between its axis and the applied electric field. In the present paper we have treated the two types of fields, that is, transverse and tangential electric fields. When an electric field is applied at an arbitrary angle relative to the cylinder axis, the electrophoretic mobility is given by the weighted average of $f_{\perp}(\kappa a, t)$ and $f_{\parallel}(\kappa a, t)$. Thus -the transient electrophoretic mobility $f_{av}(\kappa a, t)$ averaged over a random distribution of orientation is given by [26]:

$$f_{av}(\kappa a, t) = \frac{2}{3} f_{\perp}(\kappa a, t) + \frac{1}{3} f_{\parallel}(\kappa a, t) \tag{64}$$

Figure 4 shows some examples of the calculation of $f_{av}(\kappa a, t)$ of an arbitrarily oriented cylinder (solid curves) as a function of κa for several values of scaled time $\nu t/a^2$ at $\rho_p/\rho_o = 2$ in comparison with the transient mobility $f_{sp}(\kappa a, t)$ of a sphere [18] (dotted curves) with the same radius a and mass density ρ_p as the cylinder.

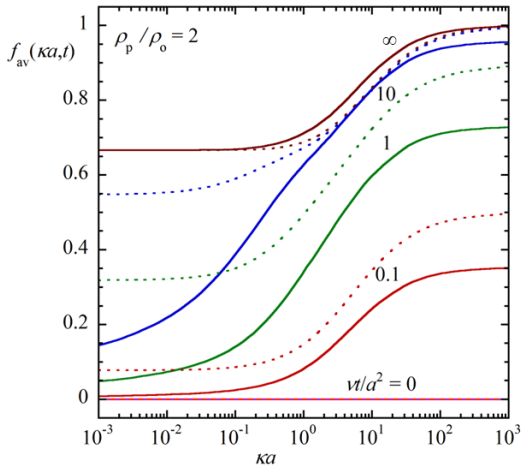


Figure 4. Time-dependent transient Henry function $f_{av}(\kappa a, t)$ of an arbitrarily oriented cylinder with radius a and mass density ρ_p in an electrolyte solution of mass density ρ_o, kinematic viscosity ν, and Debye–Hückel parameter κ plotted as a function of κa for various values of scaled time $\nu t/a^2$ at $\rho_p/\rho_o = 2$ (solid curves). The transient Henry function $f_{sp}(\kappa a, t)$ for a sphere [18] is also shown for comparison (dotted curves).

It is seen from Figure 4 that the average transient Henry function $f_{av}(\kappa a, t)$ of a cylinder at a finite time is considerably lower than the transient Henry function $f_{sp}(\kappa a, t)$ of a sphere with the same radius a and mass density ρ_p so that a cylinder requires a much longer time to reach its steady mobility than the corresponding sphere, in contrast to the case of steady electrophoresis, where $f_{av}(\kappa a, t)$ is quite similar to $f_{sp}(\kappa a, t)$.

The shape and size dependence of the steady Henry function decreases as its size relative to the Debye length $(1/\kappa)$ increases and vanishes in the thin double-layer limit (i.e., in the limit of $\kappa a \to \infty$ for a sphere and a cylinder, each with radius a) so that a sphere and a cylinder exhibit the same mobility value as that of a particle with a planar surface. On the other hand, even in this limit, the transient Henry function always depends on the particle shape and size.

The present theory can be extended to other types of applied electric fields. It can be shown that in the case where the applied field is an oscillating electric field with frequency ω (i.e., the applied electric field is proportional to $e^{-i\omega t}$), the inverse Laplace transforms $\hat{\mu}_\perp(s)$ and $\hat{\mu}_\parallel(s)$ of the transient electrophoretic mobilities $\mu_\perp(t)$ and $\mu_\parallel(t)$, respectively, can be obtained by replacing s with s-$i\omega$ in Equations (37) and (50).

4. Conclusions

We developed the theory of transient electrophoresis of a weakly charged, infinitely long cylindrical colloidal particle under an application of a transverse or tangential step electric field. We derived closed-form expressions for the transient electrophoretic mobilities $\mu_\perp(\kappa a, t)$ and $\mu_\parallel(\kappa a, t)$ of a cylinder (Equations (41) and (53)) without involving numerical inverse Laplace transformations and the corresponding time-dependent transient Henry functions $f_\perp(\kappa a, t)$ and $f_\parallel(\kappa a, t)$ (Equations (60) and (61)). The transient Henry function $f_{av}(\kappa a, t)$ of an arbitrarily oriented cylinder is also derived (Equation (64)). It is shown that in contrast to the case of steady electrophoresis, the transient Henry function $f_{av}(\kappa a, t)$ of an arbitrarily oriented cylinder at a finite time is significantly smaller than the transient Henry function $f_{sp}(\kappa a, t)$ of a sphere with the same radius a and mass density ρ_p as the cylinder so that a cylinder requires a much longer time to reach its steady mobility than the corresponding sphere. It is also shown that, unlike the steady Henry function, the transient Henry function for a cylinder differs from that of a sphere even in the limit of large κa.

Funding: This research reserved no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The author declares no conflict of interest.

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