Theory of Cast Formation in Electrophoretic Deposition

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Electrophoretic deposition (EPD) can be used for precise and easy preparation of any type of particulate layer, ranging from a coating of a few micrometers to a cast of several millimeters thickness. EPD can be used for any geometry, which can be as complex as a complete automobile body. Several materials have been applied successfully by EPD. One of the first applications has been the production of rubber foils from latex.1–3 Currently, most applications are in the area of inorganic materials, as described in a recent and elaborate review by Sarkar and Nicholson.4 As with most suspension-based processes, EPD can result in a highly homogeneous cast with a high mechanical strength and a low surface roughness if a dispersed suspension is used. Homogeneity is further improved in EPD because particle velocity is not highly dependent on particle size or intrinsic density, and, thus, segregation can be avoided during deposition. Because particle velocity depends on the local field strength, which often decreases with an increase in cast thickness, inhomogeneities in cast thickness can be diminished. EPD needs only short processing times; a reduction of a factor of 100 can be accomplished when EPD is compared with other suspension processes, such as slip casting.5

Two equations are used in literature to describe the amount of cast deposited in EPD. The first equation is based on measurements by Hamaker;2 the second is based on a model of Avgustinik.6 The representation of Hamaker’s law has changed over the years, but it principally states that the deposit yield Y (kilograms) corresponds to the product of the electrophoretic mobility μ (m²/V·s), the local field strength E (V/m), the electrode surface S (m²), and the particle mass concentration in suspension c₂ (kg/m³) integrated over time t (s):3,4,7–11

\[ Y = \int_{t_i}^{t_f} \mu E S c \, dt \]  

The efficiency factor \( f_s \), often included to account for the possibility that not all particles that migrate to the electrode form a deposit, has been omitted from Eq. (1).

Equation (1) often is integrated implicitly, assuming that \( \mu, E, c_2, \) and \( S \) remain constant in time to arrive at an explicit expression for cast formation:

\[ Y = \mu E S c_2 t \]  

Avgustinik et al.6 have worked out several elements of Hamaker’s law for deposition on a cylindrical electrode with length \( l \) and radius \( a \) with a coaxially placed counterelectrode of radius \( b (b > a) \) to arrive at an explicit equation for \( Y \). E has been transformed to the electrode distance and the voltage difference \( V \), while \( \mu \) has been represented in terms of the permittivity \( e = \varepsilon_e \varepsilon_0 / (V·m) \), the zeta potential \( \xi \) (volts), and the viscosity \( \eta \) (Pars):

\[ \frac{IV\xi E S c}{6 \ln (a/b) \eta} \]  

Avgustinik et al.6 implicitly assume that the parameters \( \xi, e, c_2, \) and \( E \) at the cast–suspension boundary remain constant in time. Avgustinik et al. furthermore use Eq. (12) for \( \mu \), as explained later. Because \( V \) is defined as a positive number in their paper, \( \xi \) must have been negative to obtain a positive \( Y \).

It is the objective of the present paper to summarize the basic elements necessary to describe the rate of cast formation in EPD and the assumptions that have to be made to arrive at the equations of Hamaker and Avgustinik. The same set of elements can be used to construct models of increasing complexity that describe, for instance, the change of the formation rate in time, while the assumptions made in the present paper must be eliminated one-by-one.

Three elements must be combined to describe cast formation in EPD, namely Kynch theory12 for the movement of the cast–suspension boundary, the equation of continuity for the suspension phase, and expressions for the particle velocity in suspension. First, these elements are combined to give an expression for cast formation on a flat surface with a parallel counterelectrode (see Fig. 1). The relation obtained for this planar geometry is compared with Hamaker’s law. Second, a similar combination of these elements is made to describe deposition on a cylindrical electrode with a coaxially placed counterelectrode (see Fig. 1). The result for this cylindrical geometry is compared with Avgustinik’s law.

II. Theoretical Background

(1) Introduction

If a batch of suspension is allowed to sediment without being stirred, particles move through the liquid, which results in the formation of a supernatant phase devoid of particles and a cast layer (see Fig. 2).13–16 Both phases increase in size at the expense of the shrinking suspension phase, and, when they meet, cast formation ends. The force causing sedimentation can either be a gravitational, a centrifugal, or an electrostatic force as in EPD.

In the present paper, EPD is described as such a batchwise
primary discontinuities (kinematic shocks) or secondary discontinuities (kinematic waves) develop at the suspension–cast boundary.\textsuperscript{13,14} In the first case, a single, sharp discontinuity develops between suspension and cast, at which the particle concentration rapidly increases from $\phi_s$ to $\phi_c$ (see Fig. 2). In the second case, $\phi_s$ increases gradually to $\phi_c$. In the present paper, it is assumed that a kinematic shock develops at the suspension–cast boundary, because shocks are more straightforward to describe, and this choice leads toward the laws of Hamaker and Avgustinik. The velocity of the shockwise movement of the cast into the suspension $u_c$ now can be derived from a simple balance over the moving suspension–cast boundary,\textsuperscript{12} including the particle velocity in suspension at the suspension–cast boundary, $v_s$, which results in

$$ u_c = \frac{d\delta}{dt} = -\frac{\phi_s}{\phi_c - \phi_s} \frac{d\phi_c}{dt} $$

(6)

where it is assumed that the cast does not densify in time, which is a reasonable assumption if a dispersed suspension is used.\textsuperscript{22} The increase of cast thickness $\delta$ with $t$ is given by solutions to Eq. (6), which require knowledge of the particle velocity and concentration in the suspension at the suspension–cast boundary. The latter follows from the equation of continuity for the suspension phase. Equation (6) shows that, when $\phi_s$ approaches $\phi_c$, $u_c$ becomes infinite. This is possible because cast growth is actually the sum of particle deposition due to sedimentation and of cast expansion due to particle absorption.\textsuperscript{16} For larger values of $\phi_s$, this latter effect becomes more and more important.

(3) Equation of Continuity

Assuming that the mass density of the liquid and the particles is constant, the following expression for the mass balance for the solids in suspension is obtained:

$$ \frac{\partial \phi_c}{\partial t} = -\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 J) $$

(7)

For a planar geometry, $\sigma = 0$, whereas, for a cylindrical geometry, $\sigma = 1$ (see Fig. 1). The flux $J$ (m/s) is given by the product of $\phi_s$ and $v$:

$$ J = \phi_s v $$

(8)

(4) Particle Velocity

The velocity $v$ of a suspended particle in an electric field $E$ is given by\textsuperscript{23}

$$ v = \mu E $$

(9)

The sign convention used in the present paper results in negative values for $V$ in the suspension and, thus, a negative value for either $\mu$ or $E$; both are evaluated in the next sections. Ordinary diffusion as a means of particle transport in the suspension phase has been omitted from Eq. (9), because gradients $\partial \phi_c/\partial r$ do not develop in the suspension phase, as explained later.

(A) Mobility: $\mu$ of a colloidal particle can be derived from the Navier–Stokes equations, in which an electrical body force caused by the charges in the liquid appears as an extra term. For a sufficiently small $\xi$, the result is the Henry equation,\textsuperscript{13,14,23,24}

$$ \mu = \frac{2\varepsilon f_1(\kappa r_p)}{3\eta} $$

(10)

where $\kappa$ is the inverse of the Debye screening length ($\text{m}^{-1}$) and $r_p$ the particle radius. The function $f_1$ increases from 1.0 at $\kappa r_p = 0$ (Debye–Hückel equation) to 1.50 at $\kappa r_p = \infty$ (Helmholtz–Smoluchowski equation). The expression used by Ishihara \textit{et al.}\textsuperscript{21} and Hirata \textit{et al.}\textsuperscript{25} is valid for a low value of $\kappa r_p$:...
Other expressions include the factor $4\pi$, because they are based on Gaussian units:

$$\mu = \frac{2\varepsilon \zeta}{3\eta} \quad (11)$$

where $\varepsilon$ is the local ionic strength and acidity (pH) of the suspension. For an electrolytic solution, a net positive or negative charge develops at the electrodes that is directly related to an ionic strength and pH different from the values in the bulk of the suspension, resulting in changing particle velocities. These effects are not described in the present paper.

**B) Field Strength:** The electrical field is described by the Poisson equation

$$\nabla^2 V = -\frac{\rho}{\varepsilon} \quad (14)$$

where $V$ is the electrical potential and $\rho$ the charge density (C/m$^3$). If the field depends only on the coordinate $r$, then the Laplacian $\nabla^2$ is given by

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right)$$

To solve the Poisson equation, $\rho$ and permittivity must be known at every location between the electrodes. $\rho$ follows from the simultaneous solution of the equation of continuity for all charged particle species and ion types; the permittivity of a particle–liquid (two-phase) medium depends on the volume fraction of particles and, thus, differs between the cast and the suspension. In an electrolyte, net positive and negative charges build up at the electrodes after the start of the process, resulting in an increase of $V$ over these regions and a decrease of $E$ in the bulk of the solution. This decrease can be augmented if the permittivity of the cast layer is lower than that of the suspension, which is true if the permittivity of the cast layer is lower than that of the liquid (e.g., water, $\varepsilon = 80$). Combination of the Poisson equation with mass balances for particles and ions has not been done yet for EPD.

A decreasing $E$ at the cast–suspension boundary $r_0$, results in a decreasing $V_s$ and a decreasing $u_s$ as noted by several authors.5,6,25 These explanations for a decreasing $u_s$ are additional to the depletion effect, as discussed by Zhang et al.17,18 and Sarkar and Nicholson.5,19

Simplifications can be made if the (net) charge density is zero in the entire system. This is true at the start of the process, when suspended particles and all ions are homogeneously distributed over the entire suspension, and also is valid for a pure nonelectrolyte. Possibly, as a first approximation, oxide particles in an organic solvent can be modeled as a pure nonelectrolyte. The charges at the particle surface and in the surrounding cloud are then neglected in the calculation of $E$. In this case, the Poisson equation simplifies to the Laplace equation

$$\nabla^2 V = 0 \quad (16)$$

Solutions for $E = -V = -\nabla V = -\partial V/\partial r$ now result in

$$\begin{align*}
\sigma = 0 & \quad E = \frac{-V}{b - a} \\
\sigma = 1 & \quad E = \frac{-V}{r \ln b/a}
\end{align*} \quad (17)$$

where $V = V_b - V_a$ over the electrode distance $b - a$. In Eq. (17), the influence of the growing cast on the field $E$ is neglected.

### III. Results

**Case I: Hamaker’s Equation Derived for a Planar Geometry**

Hamaker’s law (Eq. (2)) can be easily checked for a planar geometry (see Fig. 1) when the correct expression for $Y$ is given as a function of $\delta$:

$$Y = \delta \delta \rho_p \rho_s \quad (18)$$

First, the equation of continuity (Eq. (7)) must be solved using Eqs. (8) and (9) and $\sigma = 0$. Because $E$ is independent of place and time if the Laplace equation is used, it follows that, for a nonstirred suspension, $\rho_s$ remains independent of place and time as well, which simplifies the following calculations. If the suspension is stirred, these calculations also can be used when the amount of solids present in the suspension largely exceeds the amount of solids deposited (e.g., at short processing times), because, in that case, $\rho_s$ remains almost constant.

Combining Eqs. (6) and (9) at the initial condition $\delta|_{t=0} = 0$ results in

$$\delta = -\mu E \frac{\partial \rho_s}{\partial \rho_s} t \quad (19)$$

Substituting Eqs. (19) and (4) into Eq. (18) results in

$$Y = -\mu E \delta \frac{\rho_s}{\rho_s - \rho_e} t \quad (20)$$

Hamaker’s law (Eq. (2)) is obtained if $\rho_e$ is appreciably lower than $\rho_s$ and, thus, neglected in the denominator in Eq. (20), Eq. (4) is implemented, and an extra minus sign is added.

Figure 3 shows the effect of $\rho_s$ on $Y$ for $\delta = 0.6$, using Eqs. (2) and (20). Any value for the group $\mu$, $E$, $\rho_p$, $S$, and $t$ can be used to compare Eqs. (2) and (20), which always gives the same result: no $y$-axis values are therefore shown in Fig. 3. Equation (20) shows that $Y$ increases more than linearly, with an asymptote at $\rho_s = \rho_e$. The necessary correction factor $X$ to Eq. (2) is obtained by division of Eq. (20) by Eq. (2):

$$X = \frac{\rho_e}{\rho_s - \rho_e} \quad (21)$$

$X$ is always $>1$ and approaches $1$ as $\rho_e$ approaches zero, $X$ is not related to $f^*$, which accounts for the possibility that not all particles that migrate to the electrode form a deposit: $f$ is, by definition, $<1$.
Suspension concentration follows from the equation of continuity (Eq. (7)) after substitution of Eqs. (8), (9), and (17) and \( \sigma = 1 \):

\[
\frac{\partial \phi_s}{\partial t} = \frac{1}{r \partial r} \left( \frac{\phi_s \mu V}{\ln b/a} \right)
\]

Because, initially, \( \partial \phi_s / \partial t = 0 \), no changes of \( \phi_s \) in time or with place occurs. This situation is similar to case I and again simplifies calculations considerably. An analogous simplification can be made in the description of cast formation by a centrifugal force.\(^{13,15,16} \)

After substitution of Eqs. (9), (17), and (22) into Eq. (6) and integration with initial condition \( \delta_{t=0} = 0 \), the following expression for \( \delta \) is obtained.

\[
\delta = a \left( 1 + \frac{2 \mu V \phi_s t}{a \left( \phi_s - \phi_c \right) \ln b/a} \right)^{1/2} - 1
\]

where \( Y \) is given by

\[
Y = b \phi_c \rho_p \pi \left( a^2 - a^2 \right)
\]

Substitution of Eq. (24) into Eq. (25) results in

\[
Y = \frac{2 \pi \mu V \phi_s}{\ln b/a} \frac{\phi_s}{\phi_s - \phi_c} t
\]

For dilute suspensions, \( \phi_s \ll \phi_c \), and, after substitution of Eqs. (4) and (12) and an extra minus sign (for reasons explained in the Introduction), the equation of Avgustinik (Eq. (3)) is obtained. Obviously, the increase in the cast–suspension surface area \((2 \pi r \rho_p)\) is exactly matched by a decrease in \( E \) at the suspension–cast boundary \( r_c \), which results in Eq. (26). For higher suspension concentrations, Eq. (26) should be used instead of Eq. (3). When Eq. (26) is compared with Eq. (3)—using Eq. (12)—the \( X \) again evolves as for planar geometry (see Eq. (21)).

Attention is focused below on Eqs. (2) and (20). A similar result would be obtained from an evaluation of Eqs. (3) and (26).

IV. Discussion

Measurements of the influence of \( \phi_c \) on the cast formation rate \((dY/dt = Yt)\) show a more-than-linear increase of rate with concentration (see Fig. 4).\(^{7,8,20} \)

According to Krishna Rao and co-workers,\(^{7,8} \) this rate deviation from Hamaker’s law (Eq. (2)) may be due to an increase with suspension concentration of \( f_c \), which is the fraction of particles arriving at the cast that deposits, or the higher drag exerted by faster particles on slower ones.

It is possible to describe the measurements better using Eq. (20) instead of Eq. (2). However, the formation rate remains higher than expected at higher concentrations (\( \phi_c > 0.17 \)).

Of all possible causes for the remaining discrepancy, we focus on the influence of \( \phi_c \) on \( dY/dt \), because it is this parameter that does not appear in Hamaker’s law or Avgustinik’s law but is important in the equations derived in the present paper.

With reference to Tiller and Shirato,\(^{29} \) Tiller and Khatib\(^{30} \) state that, “as the suspension concentrates, the (cast) structure becomes more porous. The ‘crowding effect’ leads to particle interference, which prevents particulates from settling out in a dense network.” This phenomenon explains the higher cast formation rate, because a more porous cast is associated with a lower \( \phi_c \) (see Eq. (5)) that results in a higher cast formation rate. This can be calculated directly from Eqs. (4) and (20). It is not particle concentration as such that results in the crowding effect, but particle flux (see Eq. (8)).Particle flux also changes in a simulation study by Hong,\(^{31} \) who has used a discrete-element method to study cast defect formation in colloidal filtration. At a higher filtration rate, thus a higher particle flux, more structural cast defects are formed, which results in a less-dense cast and, according to Eq. (20), in a higher cast formation rate.

V. Summary

The Hamaker and Avgustinik laws for the cast formation rate in electrophoretic deposition can be derived from a combination of Kynch theory, the equation of continuity for the suspension phase, and the appropriate expression for particle velocity. To arrive at the integral form of Hamaker’s law (Eq. (1)), it is necessary to assume that, at the suspension–cast interface, a kinematic shock develops instead of a kinematic wave, the cast concentration remains constant in time, and the suspension concentration is sufficiently low. The explicit form of Hamaker’s law (Eq. (2)) also requires a constant particle flux, which requires a constant velocity in suspension and a constant concentration. A constant velocity implies a constant field strength and a constant mobility. This is possible only if charge buildup at the electrodes is negligible and the cast remains sufficiently thin. A constant concentration requires a stagnant (nonstirred) suspension or a low amount of deposited particles compared to the amount present in suspension.

Experiments to determine the influence of suspension concentration on cast formation rate are better described by a new equation than by Hamaker’s law. The agreement remains unsatisfactorily, which can be explained by a decreasing cast concentration at a higher suspension concentration. The set of equations presented poses a useful starting point for the refinement of the description of cast formation rates in EPD.

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References


