Comment on "electrophoretic deposition-mechanisms, myths and materials" by Y. Fukuda, N. Nagarajan, W. Mekky, Y. Bao, H.-S. Kim and P. S. Nicholson (*J. Mater. Sci.* 39 (2004) 787)

P. M. BIESHEUVEL
Laboratory of Physical Chemistry and Colloid Science, Wageningen University, Dreijenplein 6,
6703 HB Wageningen, The Netherlands
E-mail: maarten.biesheuvel@wur.nl

H. VERWEIJ*
Department of Materials Science and Engineering, College of Engineering, The Ohio State University,
2041 N College Road, 291A Watts Hall, Columbus, OH 43210-1178, USA
E-mail: Verweij.1@osu.edu

Recently, Fukuda *et al.* [1] reviewed explanations of the deposition process during electrophoretic deposition (EPD) and critically discussed our theory [2] to derive the assumptions underlying the well-known laws by Hamaker and Avgustinik. Their [1] three main points of criticism are:

1. "Their analysis involves [the] assumption [that] particle charge can be ignored whilst calculating the electric field strength from the Poisson equation [. . . which] infers the particles have no surface charge or double layer i.e., they have no ζ-potential (or $\zeta = 0$). This implies their electrophoretic mobility μ is zero. If $\zeta = 0$ the particle velocity will be zero (if $\mu = 0$). Thus the particles (uncharged) will not move under an impressed electrical field so no electrophoretic deposition will occur"
2. "[They assume that] the diffusion flux of particles is negligible. [...] The authors ignored the diffusion flux in the continuity equation [because] "gradients [in the particle concentration in suspension] do not develop." [...] However, their explanation is based on the assumption that the diffusion flux is equal to zero in the continuity equation. [...] This argument is circular and therefore fallacious."
3. "The cast-formation-rate equation deviates from experiment at high suspension concentrations. The authors explain that the (cast) structure becomes more porous as the suspension concentrates. This 'crowding effect' leads to particle interference, which prevents particulate settling into a dense network. [...] However, if the crowding of particles leads to particle interference, their analysis is bound to give erroneous results because all particles are assumed to have a constant velocity with time and position i.e., they are assumed to move independently"

However, these reservations are unnecessary. We will discuss the three points of criticism one after the other:

1. Let us consider a suspension at thermodynamic equilibrium. Particles have a certain ζ-potential and a double layer extending from the particle surface into the solution. Now, the net overall charge (fixed charge at the particle surface plus charge in the surrounding diffuse layer) is zero. If an electric field is applied across the suspension, it is well possible that the net overall charge ρ (at the scale of particle plus diffuse layer) remains close enough to zero for the assumption of $\rho_{\text{overall}} = 0$ to hold. This assumption is valid at the initial stage of the process (when charge separation has not yet occurred) and might well remain valid throughout the EPD process when the suspension is mixed, as well as for non-aqueous media in which the few counterions remain close to the particle surface and charge separation is energetically unfavorable. The assumption $\rho_{\text{overall}} = 0$ is used in our theory to describe the macroscopic electric field between the two electrodes [2, 3] and is (implicitly) used in the theory by Hamaker and Avgustinik. It may be suggested that this assumption is certainly useful as a first approximation to describe the EPD process. However, using the assumption of $\rho_{\text{overall}} = 0$ in no way implies that we believe in (or that our theory critically depends on) a zero ζ-potential of the particles.

2. For concentration diffusion we need concentration gradients, and as we start off with a mixed suspension (homogeneous suspension concentration), we need some means to generate such a concentration gradient in the first place. If that means, in this case forced diffusion due to the electric field, does not result in concentration gradients, then concentration diffusion can be safely neglected, because what will create the concentration gradient in the first place?

It is one of the key results of [2] that forced diffusion does not result in concentration gradients in EPD, both for planar and cylindrical geometries (as long as the Laplace equation can be used, and kinematic waves are not formed). The absence of concentration gradients underlies the equations of Hamaker and Avgustinik.

---

*Author to whom all correspondence should be addressed.

Interestingly, the phenomenon of zero concentration gradients is observed more generally, e.g., also in gravitational and centrifugal sedimentation processes [4, 5].

3. Crowding at the cast-suspension interface (due to kinematic waves) may possibly lead to a more porous cast, for which literature references were given. However, this does not influence the movement of particles in suspension (which determines the flux of particles to the surface) as long as the kinematic waves arising at the surface do not penetrate far enough into the solution (e.g., due to limited time, or due to mixing). In a sense, the particles in solution are oblivious to the upcoming events—i.e., that they are going to meet the dense cast layer.

We believe that, given the assumptions that we have detailed in [2] (constant voltage, Laplace equation, no kinematic waves, voltage decrease over cast negligible) the derived expressions are valid. The assumption of a negligible voltage decrease over the growing cast is removed in reference [3], but the other assumptions are still used. In [3] the dielectric constants of suspension and cast are coupled to the particle fraction in each phase via a Claussius-Mossotti approach to describe data on cast growth in EPD by Zhang *et al.* [6], and obtain a simple explanation for the cause of anomalous cast growth in certain combinations of particle/solvent in terms of the values of the respective dielectric constants. The usefulness of the extended theory in [3] in describing these experimental observations underpins the theoretical approach of [2].

References

1. Y. FUKUDA, N. NAGARAJAN, W. MEKKY, Y. BAO, H.-S. KIM and P. S. NICHOLSON, *J. Mater. Sci.* **39** (2004) 787.
2. P. M. BIESHEUVEL and H. VERWEIJ, *J. Amer. Ceram. Soc.* **82** (1999) 1451.
3. M. GONZALEZ-CUENCA, P. M. BIESHEUVEL and H. VERWEIJ, *AIChE J.* **46** (2000) 626.
4. P. M. BIESHEUVEL, A. NIJMEIJER and H. VERWEIJ, *ibid.* **44** (1998) 1914.
5. M. SAMBUICHI, H. NAKAKURA, K. OSASA and F. M. TILLER, *ibid.* **33** (1987) 109.
6. Z. ZHANG, Y. HUANG and Z. JIANG, *J. Amer. Ceram. Soc.* **77** (1994) 1946.

Reply to: Comment to "electrophoretic deposition-mechanisms, myths and materials" by P. M. Biesheuvel and H. Verweij

Use of the Poisson equation. The Laplace equation has been used to determine the electric field strength in the suspension. In the comment, the authors have argued that the use of Poisson's equation together with the electro-neutrality condition is justified, because $\rho_{\text{overall}} = 0$ at least during the initial stages of deposition. However, according to Newman [1], "the use of both Poisson's equation and electroneutrality would be inconsistent," and that, "electroneutrality does not imply Laplace's equation for the potential: $\nabla^2 \varphi = 0$". The inconsistency arises from several issues as follows [2]:

(a) For an electrolytic cell, the assumption that $\nabla^2 \varphi = 0$ is not valid, where ∇^2 is the Laplacian. This is because the assumption, $\nabla^2 \varphi = 0$, implies the current in the cell follows the path of minimum energy dissipation, i.e., the equation for potential distribution in a conducting medium implies current follows lines of minimum ohmic resistance. According to Levich [2], "It should be stressed that this principle is not valid in the electrolytic cell." Even if this assumption is made as a first approximation, as stated in the comment, the assumption does not hold if there is a 'concentration over-potential' in the EPD cell.

(b) Van der Biest and Vandeperre [3] noted the existence of the concentration overpotential in the EPD cell. They indicate the transient nature of the voltage increase in an EPD cell under constant current conditions, "....is more easily understood if the increase in potential drop is caused by concentration overvoltage." Furthermore, Levich [2] points out, the minimization of dissipated energy in an electrolytic cell leads to the current following lines of lower chemical potential, which is also a function of the applied current density. These considerations are not applicable when the concentration overpotential is not negligible.

The inconsistency referred to, manifests itself in derivation of $v = \mu \cdot E$, (Equation 9 in the authors' original paper [4]). The Equation is derived from the Poisson equation, accounting for the charge on the particle and the double layer. Therefore, if the Poisson's equation is used assuming particle charge, and then, in a different context, no particle charge, the latter implies zero mobility μ.

Hence, we believe that the use of the Laplace equation is not rigorous for analysis of an EPD cell.

On the concentration gradients in the EPD cell. The assumption [4] that diffusion can be neglected as a mechanism of transport infers there are no concentration gradients any time during deposition. While this is observed, as rightly pointed out in the authors' comment, in sedimentation and centrifugal casting/separation, it is not strictly true in electrophoretic motion. When electrophoretic deposition occurs from a suspension containing charged particles in an electrolyte (that takes part in electrode reactions, e.g., evolution of H_2), there is always a concentration gradient of electrolyte near the electrode. This electrolyte concentration gradient must give rise to diffusion, and hence, gradient, of charged particles, i.e., diffusiophoresis. This has been observed [5]. Hence, we are critical of the earlier statement [4] that the gradient of φ is zero at all times when the initial gradient of the volume fraction Φ is zero. The criticism is not of the assumption per se, but the reasoning thereof. Of course, whether diffusion occurs during the later stages of deposition or not, depends on many factors, so it is possible the assumption is valid under specific conditions, in which case, our criticism is invalid.

EPD of concentrated suspensions. Particle-particle interactions become important in electrophoresis in concentrated suspensions. Numerous studies have shown that electrophoretic velocity depends on the concentration of solids in suspension. For example, in a paper by Johnson and Davis [6], the electrophoretic velocity drops considerably (about 25% for a zeta potential of -100 mV, and about 40% for zeta potential of -50 mV), for a 10% solid suspension. This reduction in velocity must be due to particle-particle and double layer-double layer interactions, which resist motion.

Similarly, Tiller and Khatib [7] write of sedimentation, "The velocity of fall of particles depends on their concentration. Particles in dilute slurries settle independently. As the concentration increases, particle interaction results in zone settling in which all particles sediment with same velocity." At very high particle concentrations, a network structure may form in the suspension. For the above reasons, the particle velocity 'v' (or mobility μ) cannot be assumed independent of solids concentration. Hence, in our opinion, for higher solids concentration, one cannot simultaneously assume, particle interactions at the electrode are significant, and particles move at a constant electrophoretic velocity. The effect of solids loading on the electrophoretic velocity must be considered. This was not done in the authors' original paper [4].

The change in mobility with solids loading is accounted for in their later paper [8] through the use of the effective permittivity of the suspension. Their results indicate that the cast formation rate is increased with increased solids loading (by comparing the initial part of the weight-time curve for $\Phi = 0.00276$ and $\Phi = 0.276$), which trend is predicted in Fig. 4 in [4]. However, since no comparison was made between Fig. 4 in ref. [4] and their refined model in ref. [8], we cannot ascertain how well the model predictions match the experimental data of Fig. 4 in ref. [4].

References

1. J. S. NEWMAN, "Electrochemical Systems" (Prentice-Hall, N.J., 1972, c1973).
2. V. G. LEVICH, "Physicochemical Hydrodynamics" (Prentice Hall Inc. 1962).
3. O. O. VAN DER BIEST and L. J. VANDEPERRE, *Ann. Rev. Mater. Sci.* **29** (1999) 327.
4. P. MAARTEN BIESHEUVEL and HENK VERWEIJ, *J. Amer. Ceram. Soc.* **82**(6) (1999) 1451.
5. (a) A. A. KOROTKOVA and N. V. CHURAEV, *Coll. J. the USSR (English Translation of Kolloidnyi Zhurnal)* **49**(5) (1987) 881; (b) J. P. EBEL, J. L. ANDERSON and D. C. PRIEVE, *Langmuir* **4**(2) (1987) 396.
6. TIMOTHY J. JOHNSON and E. JAMES DAVIS, *J. Coll. Interf. Sci.* **215**(2) (1999) 397.
7. FRANK M. TILLER and Z. KHATIB, *J. Coll. Interf. Sci.* **100**(1) (1984) 55.
8. MERCEDES GONZALEZ-CUENCA, P. MAARTEN BIESHEUVEL and HENK VERWEIJ, *AIChE Journal* **46**(3) (2000) 626.

Y. FUKUDA, N. NAGARAJAN, W. MEKKY, Y. BAO, H.-S. KIM and P. S. NICHOLSON, Co-authors of Electrophoretic Deposition—Mechanisms, Myths and Materials **39** (2004) 787.

*Received 23 March
and accepted 20 May 2004*