Reply to Comment on Electroding Force Acting on Solid Particles at a Fluid Interface

In the beginning, let us specify the subject of the present discussion. In the first step, in our previous paper, we reported direct experimental evidence for the existence of normal electric force (electroding force), $F^{(el)}$, acting on solid particles at the oil–water or air–water interface. We found that this force is independent of the electrolyte concentration in the aqueous phase, and we concluded that it is probably due to charges at the particle–oil (rather than at the particle–water) interface. Indications about the existence of electric charges at the particle–oil interface have been found by other authors in different experiments. In ref 1, our second step was to develop a detailed quantitative theory of the electroding force. With the help of this theory, using the experimental value of the electroding force, we determined the surface electric charge density, $\sigma_m$, at the boundary of the particle–nonpolar fluid (oil, water). Next, knowing the value of $\sigma_m$, we numerically solved the electrostatic problem, and computed the electric field in the particle and the nonpolar fluid (oil or air). From the computed electric field, we obtained numerical data for the electric pressure, $p_e(r)$, acting on the oil–water interface ($r$ is the radial coordinate). In the third step, we determined the shape of the oil–water interface around the charged particle, numerically solving the Laplace equation of capillarity, which was linearized for the case of a small meniscus.

Here, $\zeta(r)$ describes the meniscus profile, which decays at infinity, $\zeta(\infty) = 0$; $\gamma$ is the interfacial tension, and $q = (\Delta \rho g \gamma)^{1/2}$ is the inverse capillary length. Finally, in the fourth step, in addition to the numerical solution for $\zeta(r)$, we derived some approximate analytical expressions allowing easier calculations of $\zeta(r)$. In fact, only this last, fourth step is affected by the critical comments by Oettel et al., and it is the main subject of the present discussion.

Oettel et al. are right that the detailed analysis of eq 1 leads to the conclusion that $\zeta(r)$ has the following asymptotic behavior:

$$\zeta(r) \approx \frac{F^{(g)}}{2\pi \gamma} \ln \left( \frac{r}{r_c} \right) \text{ for } r_c \ll r \ll q^{-1}$$

$r_c$ is the radius of the contact line on the particle surface, and $\ln(n_0)$ is an additive constant. Note that the logarithmic prefactor in eq 2 contains only the gravitational force, $F^{(g)}$, instead of $F^{(el)} + (1 - \lambda)F^{(el)}$, as incorrectly assumed in our paper. Equation 2 implies a faster decay of the meniscus deformation at $r \gg r_c$ insofar as $F^{(el)} \ll F^{(el)}$ for the investigated particles. As a consequence, our matched asymptotic expansions for the meniscus profile $\zeta(r)$ and the interaction energy $U(r)$, eqs 3.25 and 3.26 in ref 1, turn out to be incorrect for $r r_c \geq 4$. We have also noticed this mistake, and we will soon publish a detailed paper focused on the problem concerning the shape of the capillary meniscus around a charged particle.

The procedure for the numerical integration of eq 1 using the data for $p_e(r)$ is nontrivial because of the infinite integration domain ($r_c < r < \infty$) and because of an integrable divergence of $p_e(r)$ at $r \to r_c$. In Figure 1, we present the computed $\zeta(r)$ for a particle of contact-line radius $r_c = 226 \mu$m; this is the particle shown in Figure 2 of ref 1. The experimental points for $\zeta(r)$ for the same particle are also plotted in Figure 1 here. One sees that the numerical solution agrees very well with the experimental points. The coordinate origin on the $z$ axis is fixed by setting $\zeta(r_c) = 0$. The dashed–dotted line in Figure 1 presents the meniscus profile in the case where electric effects are missing ($F^{(el)} = 0; p_e = 0$) and the interfacial deformation is determined solely by the gravity force, $F^{(g)}$.

The most important conclusions from Figure 1 are (i) that the electric forces create a concavity (dimple) of significant depth in the fluid interface around the particle and (ii) that the effect of the electric forces on $\zeta(r)$ disappears for $r > 4r_c$. At greater distances, the meniscus shape is governed solely by the gravitational deformation, $\zeta(r)$. In other words, the electric field produces a deformation of medium range: it is neither long-ranged (significant for $r \gg r_c$, as the gravity-induced capillary force) nor short-ranged (significant only for $r - r_c \ll r_c$, as the van der Waals attraction).

The lateral capillary force between two attached particles is due to the overlap of the dimples formed around the particles. Therefore, the range of this capillary force is determined by the range of these interfacial deformations. Hence, we could expect that the capillary interaction engendered by the electroding force, $F^{(el)}$, is of medium range. The profile in Figure 1 indicates that the capillary interaction between two floating particles (the
electric-field-induced capillary attraction\(^5\)) could be very strong for \(r < 4r_c\).

What concerns the numerical solution of eq 1 is that to calculate the meniscus profile \(\zeta(r)\) one needs to know the dependence \(p_d(r)\). As mentioned above, we obtain \(p_d(r)\) by using the numerical procedure from section 5.2 in ref 1, along with eq 6.1 therein. There, we have given sufficient information about the principles of the numerical procedure, which would allow the reproduction of our results. If numerical data for \(p_d(r)\) are used to calculate \(\zeta(r)\), then computational problems such as those reported in ref 4 (in relation to Figure 1 therein) do not appear. In addition, we succeeded in obtaining an analytical solution of the electrostatic boundary problem.\(^6\) The results from this analytical solution agree very well with the numerical solution based on the procedure described in section 5.2 of ref 1.

In relation to the comment by Oettel et al.\(^4\) about “inconsistency in the data presentation in ref 1”, we note that the experimental points for \(\zeta(r)\), like those presented in Figure 1, are obtained by averaging the left- and right-hand-side meniscus profiles in the respective photograph. Thus, we remove an undesired influence of an occasional small tilt of the \(x\) axis on the photograph with respect to the actual horizontal direction. In Figure 2 of ref 1, for illustrative purposes, we have presented primary raw data for the right-hand-side meniscus, which is seen in the respective photograph. It is not surprising that from these incomplete data the authors of ref 4 have obtained a meniscus slope different from the correct one.

There is a misprint, noticed by the authors of ref 4, in the form of eq 6.2 in ref 1, which is the Laplace equation in toroidal coordinates. The correct form of the latter equation is

\[
\frac{x_1^3}{r_c^2} \frac{d}{dx_1} \left( \frac{x_1}{r_c^2} \frac{d\zeta}{dx_1} \right) - q^2 \zeta = \frac{1}{\gamma} p_d
\]

Equation 3 can be obtained by substituting \(r = r_c/x_1\) in eq 1. Equation 6.2 in ref 1 was given only for completeness; it was not used in our calculations, and it had not affected the results reported therein.

Oettel et al.\(^4\) write “The error in the analysis of ref 1 resides in the evaluation of \(F^{(\text{men})}\) (eq 4), with the interfacial stress \(p_d(r)\) replaced by its asymptotic behavior that is valid for \(r \gg r_c\) (eq 3.9).” This is definitely not the case. In our paper,\(^1\) a detailed procedure for calculating the electrodipping force, \(F^{(el)}\) (eq 2), is developed: see eq 3.4 and Table 4 in ref 1. The approximate expressions, eqs 3.25 and 3.26 in ref 1, have been obtained by matching eq 3.15, which is valid near the contact line (Figure 1) with the outer asymptotics, \(AK_0(\nu)\), and the constant \(A\) has been determined by using the conventional Prandtl procedure for matching the outer and inner asymptotic expansions.\(^7\) However, as mentioned above, it turns out that this procedure is inapplicable to our case because of the presence of two (rather than one) characteristic scaling parameters, related to the gravitational and electric forces, scaled by the capillary force.

The application of a correct numerical procedure gives the meniscus shape, \(\zeta(r)\), accurately as a solution of the Laplace equation (eq 1). The computed \(\zeta(r)\) agrees very well with the experimental data; see Figure 1. Such agreement of theory and experiment is observed for all sets of experimental data processed by us. Thus, our experimental results do not support the hypothesis by Oettel et al.\(^4,8\) concerning the “mechanical nonisolation of the experimental system” (i.e., in reference to the existence of an external force that pushes the particles into water but is different from the gravitational and electrodipping forces considered in ref 1). Indeed, if such an external force were present, then it would be detected as a difference between theory and experiment.

In summary, Oettel et al.\(^4\) are right that the analysis of eq 1 leads to the conclusion that the logarithmic prefactor in the long-range asymptotic solution of the Laplace equation contains only the gravitational force, \(F^{(g)}\), and does not contain the electric force, \(F^{(el)}\) (eq 2). Nevertheless, the electric force creates a significant interfacial deformation of medium range (up to four-particle radii, see Figure 1), which is expected to give rise to a strong lateral capillary attraction of the same range. What concerns the validity of our paper\(^1\) is the matched asymptotic expansions, eqs 3.25 and 3.26, and that the conclusions drawn from them are incorrect; the validity of eqs 3.15 and 3.16 is restricted to \(1 < r/r_c < 2\). The rest of our paper\(^1\) (see steps 1–3 described in the beginning of this reply), which is the main part of our study, including the experiment, the theoretical expressions for the electrodipping force (\(F^{(w)}\) and \(F^{(n)}\)), and the numerical solutions, is correct. In particular, the calculated and experimental meniscus profiles are in very good agreement (Figure 1), which confirms the adequacy of the developed theoretical model and shows that it is not necessary to introduce any external forces, different from the gravitational and electrodipping force, to interpret our experimental data.

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