Stray capacitance contribution to the electrical measurement of contact angles and areas

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The capacitance of two parallel disks of finite unequal size is calculated by a variational procedure based on the electrostatic energy. It is found that effects due to the edges and the asymmetry can be substantial unless the radii of the disks are very much greater than the thickness of the dielectric interlayer. The trends predicted by the calculations are confirmed by measurements of the capacitance of electrodes deposited on polymer films and of water droplets. The implications for the electrical measurement of the contact angle or contact area of a droplet, and for the dependence of the contact angle on the applied potential in electrowetting, are discussed. © 2003 American Institute of Physics. [DOI: 10.1063/1.1537046]

I. INTRODUCTION

The balance of forces at the three-phase line determines the contact angle and, hence, measurement of the latter gives information about the surface or interfacial energies of the phases via the Young equation. Contact angles may be inferred from tensiometric measurements, or they may be directly measured by optical means. Optical methods can be laborious and have limited accuracy. In principle, they can be automated by digitizing the image and fitting profiles to the interface, but this requires rather sophisticated equipment and specialized software, and it can be sensitive to the lighting used and to optical distortions. For the case of a droplet on a solid substrate, Verheijen and Prins\textsuperscript{1} have proposed measurement of the electrical capacitance, from which the contact area and the contact angle may be deduced. This technique is convenient and easy to automate, and it has been used by a number of authors, particularly in the field of electrowetting.\textsuperscript{2–4}

We have performed such capacitance measurements on droplets and, in some cases, found large discrepancies between the contact angle measured optically and that inferred from the capacitance for infinite plates. By a combination of theoretical calculations and specific experiments, we have traced the origin of the problem to edge effects due to both the finite size of the drop and the asymmetry between the contact area of the drop and the area of the base electrode that acts as a substrate. We find that these effects are important unless the thickness of the dielectric film between the drop and the electrode is very much less than the radius of the contact area. In practice, one cannot always perform experiments in this regime as a thick film may be necessary to prevent dielectric breakdown at high applied voltages, and in other experiments, one may be restricted to small droplets. In these cases, our results may be used to correct the infinite plate result. The results also have implications for the Lipmann equation, which gives the change in contact angle with applied voltage and which is based upon the infinite plate result.

In this article, the electrostatic problem is formulated in terms of energy minimization, which gives the charge distribution on the electrodes. Results are presented for two disks of finite size and the capacitance per unit area is compared to the classic textbook result for infinite plates. We also compare the present calculations with previous estimates of edge effects for droplets.\textsuperscript{1,5} The regime of validity of the textbook formula is delineated, which gives a guide to when the procedure of Verheijen and Prins\textsuperscript{1} may be safely applied to contact area measurements on actual drops.

II. ELECTROSTATIC ENERGY

A. Formalism

1. Variational principle

We consider two electrodes labeled 1 and 2 in an infinite dielectric continuum of relative permittivity $\varepsilon_r$. The electrodes are held at applied voltages $V_1$ and $V_2$, and, at equilibrium, develop nonuniform surface charge densities $\sigma_1(r_1)$ and $\sigma_2(r_2)$, respectively. The constrained electrostatic energy for an arbitrary charge distribution is

$$E(\sigma_1, \sigma_2, V_1, V_2) = \frac{1}{2} \int d \bar{r}_1 \sigma_1(\bar{r}_1) \psi_1(\bar{r}_1) + \frac{1}{2} \int d \bar{r}_2 \sigma_2(\bar{r}_2) \psi_2(\bar{r}_2) - V_1Q_1 - V_2Q_2. \quad (1)$$

Here, electrode 1 has a total charge of

$$Q_1 = \int d \bar{r}_1 \sigma_1(\bar{r}_1), \quad (2)$$

and an electrostatic potential due to the arbitrary charge distribution of

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\[
\psi_1(r_1) = \int_1 d^n r_1 \frac{\sigma_1(r_1)}{e |r_1 - r_1|} + \int_2 d^n r_2 \frac{\sigma_2(r_2)}{e |r_1 - r_2|},
\]

where \(e = 4\pi \varepsilon_0 \varepsilon_r\) is the total permittivity, \(\varepsilon_0 = 8.854 \times 10^{-12} \text{ C}^2/\text{J} \cdot \text{m}\) being the permittivity of free space. Analogous equations hold for the second electrode. Note that here and throughout, the integrals are over the surfaces of the conductors. For a discussion of the utilization and utility of constrained thermodynamic potentials, see Refs. 6 and 7. The first two terms in the constrained electrostatic energy represent the internal energy from the interactions of the charges of the subsystem with themselves, and the final two terms represent the free energy required to move charges from the reservoir or battery to the subsystem.

The equilibrium charge distribution is the one that minimizes the constrained energy. The functional derivative of the latter with respect to the charge density of the first electrode is

\[
\frac{\delta E}{\delta \sigma_1(r_1)} = \psi_1(r_1) - V_1,
\]

and similarly for the second electrode. One sees that the equilibrium charge distribution is the one that leads to a constant potential on the electrode that is equal to the applied voltage,

\[
\bar{\psi}_1(r_1) = V_1.
\]

This is, of course, the expected result. Substitution of this into the constrained energy expression yields the equilibrium or minimum energy,

\[
\bar{E}(V_1, V_2) = E(\bar{\sigma}_1, \bar{\sigma}_2|V_1, V_2) = -\frac{1}{2} [\bar{Q}_1 V_1 + \bar{Q}_2 V_2],
\]

which again is the known result.

The capacitance is taken to be half of the ratio of the equilibrium charge difference to the voltage difference,

\[
C = \frac{1}{2} \frac{\bar{Q}_1 - \bar{Q}_2}{V_1 - V_2}.
\]

2. Ideal capacitor

For the case of two disks of area \(A = \pi R^2\) separated by \(t \ll R\) with a charge density constrained to be uniform, \(\sigma_1(r) = Q/A, \quad \sigma_2(r) = -Q/A\), the electrostatic potential at the center of disk 1 is readily shown to be

\[
\psi_1(0) = \frac{2\pi Q R}{eA} + \frac{2\pi Q}{eA} [R - t] = \frac{2\pi Q t}{eA}.
\]

With \(\psi_1(r)\) constant over the disk, this gives the constrained electrostatic energy as

\[
E(Q|V) = \frac{2\pi t}{eA} Q^2 - 2VQ,
\]

which achieves its minimum value when \(\bar{Q} = V\epsilon A/2\pi t\). Accordingly, the capacitance is

\[
C \approx \frac{\pi \epsilon \epsilon_0 R^2}{t}, \quad t \ll R.
\]

This formula is strictly valid in the limit of large plates where edge effects such as fringing electric fields are negligible. This result will be called the ideal capacitance next.

3. Scaling laws and boundary conditions

For both the exact capacitance of a finite system and the ideal capacitance of an infinite system, the following scaling laws hold. If all lengths are scaled by \(\lambda\), then the capacitance itself is also scaled by \(\lambda\). Similarly, if both charge densities are scaled by \(\mu\), then both charges and both voltages are also scaled by \(\mu\), with the result that the capacitance is unchanged. For given charge densities, the voltages are inversely proportional to the relative permittivity and the capacitance is linearly proportional to the permittivity.

Usually in electrostatic problems only voltage differences are of significance. However, in Eq. (1), we have invoked Coulomb’s law, which sets the electrostatic potential to be zero at infinity. Accordingly, in the present formulation, the absolute value of the applied voltage is important, which is to say that the charge depends upon \(V_1\) and \(V_2\) individually, not on their difference alone. One, therefore, has some choice in specifying these, the two extremes of which are equal and opposite voltage on each electrode, or equal and opposite charge. For a symmetric system, these two are equivalent, but not more generally. Many would argue that the subsystem should be electroneutral and, hence, that equal and opposite charge is the appropriate condition. This is the case that we pay most attention to next. However, one can imagine physical situations where equal and opposite voltage might be appropriate (e.g., if the external voltage source were due to a very large, symmetric capacitor). Next, in one figure, we compare the capacitance for both conditions, and conclude that the experimental data appear to be measured under equal and opposite voltage conditions.

B. Numerical formulation

1. Iteration procedure

Variational procedures such as the aforementioned electrostatic energy minimization are popular numerically because they tend to be quite robust, lend themselves to monotonically convergent iteration procedures, and because errors in the constrained quantity have only a second-order effect on the quantity being minimized. In the present case, the new iterate of the charge density, denoted by a prime, can be obtained from the old charge density by using the functional derivative as a force,

\[
\sigma'_1(r_1) = \sigma_1(r_1) - \alpha_1 \frac{\delta E}{\delta \sigma_1(r_1)}
\]

\[
= \sigma_1(r_1) - \alpha_1 [\psi_1(r_1) - V_1],
\]

and analogously for \(\sigma'_2(r_2)\). Here, the positive “masses” \(\alpha_1\) and \(\alpha_2\) control the convergence of the iteration procedure.
Provided that they are small enough so that second-order terms can be neglected, a functional Taylor expansion yields for the new constrained electrostatic energy as

$$E' = E + \int_{1} d\mathbf{r}_1 \left[ \sigma'_1(r_1) - \sigma_1(r_1) \right] \frac{\partial E}{\partial \sigma_1(\mathbf{r}_1)}$$

$$+ \int_{2} d\mathbf{r}_2 \left[ \sigma'_2(r_2) - \sigma_2(r_2) \right] \frac{\partial E}{\partial \sigma_2(\mathbf{r}_2)}$$

$$= E - \alpha_1 \int_{1} d\mathbf{r}_1 \left[ \psi_1(\mathbf{r}_1) - V_1 \right]^2$$

$$- \alpha_2 \int_{2} d\mathbf{r}_2 \left[ \psi_2(\mathbf{r}_2) - V_2 \right]^2. \quad (12)$$

Since the integrand is positive, this shows that the constrained electrostatic energy decreases during the iteration procedure.

A convenient starting guess for the charge densities is to take them to be uniform and equal to their values for an ideal infinite capacitor. Similarly, the mass can be taken to be proportional to the ideal capacitance per unit area, and it can be increased or decreased during the course of the iteration to control the convergence properties.

The aforementioned procedure is suitable for fixed, known applied voltages $V_1$ and $V_2$. For the case of equal and opposite charge, the appropriate values of $V_1$ and $V_2$ are not known a priori. In this case, one adjusts the applied voltage during the course of the simulation in such a way that the electrode charges remains equal and opposite. This is accomplished by replacing $V_1$ by the average internal potential

$$\langle \psi_1 \rangle = \frac{\int_{1} d\mathbf{r}_1 \psi_1(\mathbf{r})}{\int_{1} d\mathbf{r}_1}. \quad (13)$$

Hence, the new iterate is now taken to be

$$\sigma'_1(\mathbf{r}_1) = \sigma_1(\mathbf{r}_1) - \alpha_1 \left[ \psi_1(\mathbf{r}_1) - \langle \psi_1 \rangle \right]. \quad (14)$$

With this prescription, the total charge on each electrode remains fixed during the iteration procedure. After convergence, one simply multiplies the charge densities by $(V_1 - V_2)/[(\langle \psi_1 \rangle - \langle \psi_2 \rangle)]$ to achieve the desired voltage difference between the electrodes.

2. Axisymmetric systems

The aforementioned formalism is quite general, but we now wish to particularize to systems with cylindrical symmetry so that the charge density is only a function of the distance form the central axis, $\sigma(r)$. The following analysis can be applied to general axisymmetric systems, (e.g., a drop on a planar substrate), but for simplicity, we only give explicit results for two disks.

The most time consuming part of the computations is the evaluation of the two-dimensional integral for the electrostatic potential at each iteration step. For an axisymmetric system, the angular integral may be performed analytically by defining

$$I(r_1, r_2, z) = \int_{0}^{2\pi} \frac{d\theta}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2 \cos \theta}}. \quad (15)$$

For the case of two planar electrodes separated by $z_{12}$, in terms of this function, the electrostatic potential on the first electrode becomes

$$\psi_1(r_1) = \frac{1}{\epsilon} \int_{0}^{r_1} dr_1' \sigma_1(r_1') I(r_1, r_1', 0)$$

$$+ \frac{1}{\epsilon} \int_{0}^{r_2} dr_2 \sigma_2(r_2) I(r_1, r_2, z_{12}), \quad (16)$$

and analogously for the second electrode.

Now, for the integrations on the same plane, $z=0$, the angular integral may be expressed in terms of the complete elliptic integral of the first kind of parameter $m, K(m)$,

$$I(r, s, 0) = \begin{cases} \frac{(4/\epsilon) K(s^2/r^2)}{4}, & s < r \\ \frac{(4/\epsilon) K(r^2/s^2)}{4}, & r < s. \end{cases} \quad (17)$$

This elliptic integral can be efficiently evaluated using a fast nome expansion. The contribution to the discretized kernel from the logarithmic singularity at $s = r$ may be evaluated by analytic integration over the grid cell.

For the contribution from different planes, $z \neq 0$, one can proceed by defining a parameter $\beta > 0$ that scales the radial coordinates,

$$\rho_1 = \beta r_1, \quad \rho_2 = r_2/\beta, \quad (18)$$

in such a way that

$$z^2 + r_1^2 + r_2^2 - 2r_1r_2 \cos \theta = \rho_1^2 + \rho_2^2 - 2\rho_1\rho_2 \cos \theta. \quad (19)$$

This is satisfied if one takes

$$\beta^2 = \frac{(z^2 + r_1^2 + r_2^2) \pm \sqrt{(z^2 + r_1^2 + r_2^2)^2 - 4r_1^2r_2^2}}{2r_1^2}. \quad (20)$$

with either root being acceptable. With these definitions, one can convert an angular integral between points on different planes to an angular integral between points on the same plane,

$$I(r_1, r_2, z) = I(\rho_1, \rho_2, 0). \quad (21)$$

The right-hand side is efficiently evaluated as just described. These angular integrals are evaluated and stored at the beginning of the computations, and one is only left with one dimensional integrals (i.e., a sum over grid points) during the iteration procedure.

III. RESULTS

A. Theoretical

Figure 1 shows the results for the equilibrium potential and charge density on two unequally sized planar electrodes. It can be seen that the potential is constant, as it should be, with the small departure at the edge in each case indicative of the quality of the numerical results. The surface charge density has an integrable divergence at the edge that goes like $(R-r)^{-1/2}$. This increase in charge at the edge compensates for the lack of charge beyond the edge and is nec-
necessary to keep the potential constant. The odd spike in the charge density on the larger electrode opposite the edge of the smaller electrode does not appear to be a numerical artifact and probably reflects the singularity at the edge of the small electrode. The edge singularity is one consequence of finite size and it also occurs for the symmetric system. On the large electrode, the charge spills out beyond the opposite small electrode and is nonzero everywhere on it, which is a necessary consequence of the constant potential condition. This is a second consequence of finite size and obviously can only occur for the asymmetric system. As the size asymmetry is increased, the charge density and the voltage on the larger electrode approach zero.

Figure 2 shows the actual capacitance relative to the ideal capacitance (infinite size model) of disks of radius \( R_1 \). In general, the specific capacitance for the finite-sized system is larger than that of the infinite system due to the two edge effects discussed in the context of Fig. 1 (the increase in charge density approaching an edge, and the spill out of charge on the larger electrode beyond the edge of the smaller electrode). When the radius of the smaller electrode is comparable to the separation, the capacitance can be many times greater than the ideal value. Conversely, when the radius of the smaller electrode is much larger than the separation, the capacitance approaches the ideal value, being within 10% of it for radii more than five times the separation. The discrepancy between the actual and the ideal capacitance increases with increasing asymmetry of the system. The straight line fits indicate that the discrepancy is inversely proportional to the radius, which is what one would expect for an edge effect.

There have been some previous attempts to estimate edge effects for droplets. Verheijen and Prins\(^1\) estimated the stray capacitance from the field around an equipotential hemispherical shell, open at the base, and sitting above a zero-potential infinite plane. The data in Fig. 8 of Ref. 1, after including a factor of \( \varepsilon_r \), is fitted by

\[
\frac{C}{C_\infty(R_1')} = 1 + \frac{t}{\pi a} \left[ 3 - 4.3 \ln \left( \frac{t}{a} \right) \right],
\]

where \( t/a = (t/R_1)/\sqrt{1 + t^2/R_1^2} \). It can be seen in Fig. 2 that this does not agree with the present calculations. Note that the calculations in Ref. 1 were only intended for the regime \( t \ll R_1 \), and it is probably not valid to apply them over the whole regime in Fig. 2. A possible reason for the remaining discrepancy at small \( t \) could be the different models used, since in the model analyzed by Verheijen and Prins\(^1\) the potential on the flat base of the open hemisphere, which is just above the planar electrode, is close to zero, whereas for real drops, it is equal to the potential on the hemisphere. It is arguable that a closed equipotential hemispherical shell would be a better model of the physical situation, and it would be expected to give results closer to the two flat disks model that are analyzed here.

Vallet et al.\(^5\) estimated the edge effects of a real three-dimensional drop by application of the solution of a two-dimensional problem with a sharp edge. For the case of the zero-contact angle, which is appropriate for comparison with the present disk model, their three-dimensional result is

\[
\frac{C}{C_\infty(R_1')} = 1 + \frac{t}{\pi R_1} \ln \frac{\pi R_1^2}{t^2}.
\]

Again, Fig. 2 shows little agreement between this and the present results, possibly reflecting the limitations of the two-dimensional analog.

### B. Experiment

Measurements were made of the capacitance of two metal disks (Au on Cr) evaporated onto plastic film to form a parallel-plate capacitor. The films used were poly(ethylene terephthalate) (PET) 104 \( \mu \)m thick with relative permittivity \( \varepsilon_r = 3.65 \) and poly(tetrafluoroethylene) (PTFE) 267 \( \mu \)m thick with relative permittivity \( \varepsilon_r = 2.1 \). The capacitor was held in space by two rigid wires, 0.8 mm in radius, in contact with the far sides of the disks and normal to them, and these were connected to an impedance analyzer, (HP4192A, Agilent Technologies, USA).

It can be seen in Fig. 3 that the measured capacitance approaches the ideal value when the radii of the disks is much larger than the thickness of the intervening film. As the ratio of the radius to the thickness decreases, the capacitance gets larger than the ideal infinite plate result, in agreement...
with the results in Fig. 2. To leading order, the departure from ideality appears to be given by the present calculations. (For this case of $R_1 = R_2$, there is no difference between the condition $Q_1 = -Q_2$ and $V_1 = -V_2$.) In view of the scaling discussed in Sec. II A 3, the PTFE and PET results are predicted to lie on the same curve when plotted as in Fig. 3, and within experimental error this does indeed appear to be the case, which again confirms the applicability of the model. At the smallest size ratio measured, when the disk radius is about ten times larger than the film thickness, the measured capacitance is between 40% and 60% larger than the ideal value. In this case, there is some departure from the present calculations, which predict an increase of about 25%. There is evidently some scatter in the experimental data in this regime and it is possible that the discrepancy might be attributed to slight misalignment of the disks or else to contributions from the contact wire, which had radius 0.8 mm, compared with a radius of 1 mm for the PET and 2.5 mm for the PTFE.

Figure 4 presents the measured and the calculated capacitance for asymmetric systems. For a fixed radius of the small disk and fixed thickness, the capacitance measurably increases with increasing size of the lower electrode. In the present case, there is up to a factor of 2 difference between the measured and the ideal capacitance. The ratio $R_1 / l$ was 9.4 for PTFE and 9.6 for PET and, hence, according to the scaling analysis of Sec. II A 3, they should lie on the same curve, as they apparently do.

For this asymmetric case, $R_1 < R_2$, there is a difference between the condition $Q_1 = -Q_2$ and $V_1 = -V_2$. It can be seen in Fig. 4 that the calculated capacitance continues to increase with increasing size disparity for $V_1 = -V_2$, whereas it saturates for $Q_1 = -Q_2$. It is evident that since the voltage is measured with respect to zero at infinity, for equal and opposite voltage, one can continue to pack charge on the large electrode as its size is increased. One expects the amount of charge on the large electrode to be ultimately given by $Q = 2\pi \varepsilon_0 \varepsilon R_2 V_2$. If this is the case, then it is arguable that for equal and opposite voltage, it would be appropriate to normalize the capacitance $C_2$ rather than by $C_0(R_1)$.

It is interesting to note that for large radius ratios, there is quantitative agreement between the measured capacitance and the calculated capacitance for the equal and opposite voltage condition, whereas the behavior of the capacitance for equal and opposite charge is qualitatively different. This suggests that the impedance analyzer is most appropriately treated as imposing $V_1 = -V_2$, and that the condition $Q_1 = -Q_2$ does not hold.

In addition to these metal disk capacitors, we also performed measurements on water droplets. For a droplet of size $R_1 = 1.83$ mm and a base electrode of size $R_2 = 8.5$ mm, we measured a capacitance of 8.89 pF. For an almost identical droplet of size $R_1 = 1.78$ mm on an electrode of size $R_2 = 4.75$ mm, we found that the capacitance had decreased to 6.36 pF. The thickness of the dielectric film in these measurements was 104 $\mu$m. This confirms that for typical droplets the size of the capacitance does increase with the size of the base electrode, and supports the application of the present disk model to the droplet system.

IV. DISCUSSION

The present calculations of the equilibrium distribution of charge on a parallel-plate capacitor comprising two finite-sized disks of unequal radius show that the capacitance per unit area of the small electrode is larger than that for infinite disks. It is interesting to discuss the origin of the edge effects that lead to this result namely the buildup of charge near the edge of the disks due to the lack of charge beyond the disk, and the spilling over of charge on the larger electrode beyond the opposite smaller electrode due to the need to maintain uniform potential on the electrode. The correction to the infinite capacitance result varies inversely with the radius of the smaller electrode, with a proportionality factor that increases with increasing asymmetry, and that appears to saturate at large size ratios, at least for the case of equal and opposite charge on each plate. The correction can be quite significant for realistic parameter values. It is about 130% when the disk radius ratio is $3:1$ and the radius of the small disk is twice the separation, (Fig. 2), and it is on the order of 13% for large asymmetry when the small electrode is ten times larger than the separation.
The theoretical calculations may be discussed in the context of actual measurements of capacitance that we performed on metal disks that were sandwiched between thin plastic films. These confirmed that the edge effects were significant and were broadly in accord with the calculated values. Unexpectedly, we found that the measured capacitance depended upon the size of the base electrode. We concluded from this that the measurements indicate that equal and opposite voltage on the plates of the capacitor is the appropriate condition to impose on the calculations.

These results have implications for the inductive measurement of contact areas and contact angles. Typically in this method, an electrolyte drop is placed on a film covering a planar electrode and the capacitance is measured. The contact area is deduced from the known thickness and dielectric constant of the film using the ideal formula. The contact angle can be deduced from this if the droplet volume is known, (gravity must be taken into account unless the droplet is small). As mentioned in Sec. I, this method is very convenient, particularly for real-time dynamic measurements. It does not appear that previously published results that use the technique were in the regime where the edge effects identified here would significantly alter the results. However, some of the unpublished results obtained by Quinn et al. definitely showed a discrepancy in the contact angle determined by optical and capacitance methods. According to the present results, caution should be exercised in using the capacitance method if small droplets are being used, particularly for thick dielectric films and large base electrodes.

The results also have implications for electrowetting. The decrease in contact angle with applied voltage is generally taken to be given by

\[ \cos \theta(V) = \cos \theta_0 + \frac{\varepsilon_0 \varepsilon_r V^2}{2 \gamma_{lv}}. \]  

This result is derived by energy minimization and is based upon the ideal capacitance formula. It is possible that edge effects could make significant contributions to the droplet shape. The present results suggest that further investigation is warranted.

The present approach could form the basis for correcting contact areas inferred from measured capacitances, depending upon the size ratio of the system. To leading order, one expects the present two-disk model to be an acceptable approximation for the droplet system. The generalization to a closed hemisphere on a plane certainly poses no conceptual difficulties, although the computer program is more complicated than the present two-disk problem. The present results for two disks likely give the dominant estimate of the finite-size effects and they can be used either to estimate the accuracy of the results for a given experiment, or even correct those results quantitatively.

\[ \cos \theta(V) = \cos \theta_0 + \frac{\varepsilon_0 \varepsilon_r V^2}{2 \gamma_{lv}}. \]

References: