Review

Several Derivations for $I = 4Fc^*Da$

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Received February 15, 2017

Three kinds of derivations of the steady-state diffusion-controlled current at an inlaid micro-disk electrode are presented here without using the complex variable theory. The two of them are modifications of equations for capacitors at an ellipsoid, one being a solution of the Laplace equation by use of equi-potential surfaces, the second being a determination of potential in an ellipsoidal shell by the Gauss law. The third is a solution of Laplace equation in the ellipsoidal coordinates.

Introduction

The diffusion-controlled current under the steady state at an inlaid micro-disk electrode radius a has been derived by Saito¹⁾ to be expressed by

$$I = 4Fc^*Da \quad (1-1)$$

where F is the Faraday constant, c^* is the concentration of the diffusing redox species in the bulk with the diffusion coefficient, D . We restrict only the one-electron transfer reaction here because the currents on multiple-charge transfer reactions depend on whether the reactions occurs consecutively or concomitantly. Saito used the angle-symmetrically cylindrical coordinates for the steady-state diffusion equation of the concentration c ,

$$\frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial z^2} = 0 \quad (1-2)$$

where z is the height from the electrode toward the bulk, and r is the radial length from the axis through the center of the disk electrode. He applied the method of separation of variables to

Eq. (1-2) to obtain $\exp(-pz)$ as the height component and the Bessel function of the first order, $J_0(pr)$, as the radial component, where p is a constant. A product of both the functions can express a concentration for satisfying Eq. (1-2). However, neither p nor a coefficient of the product is known simply from the boundary conditions. By representing the coefficient to be $S(p)$ as a function of p , the concentration can be given by

$$c = \int_0^\infty S(p) \exp(-pz) J_0(pr) dp \quad (1-3)$$

S should be determined from the following boundary conditions:

$$\begin{aligned} \left(\frac{\partial c}{\partial z} \right)_{z=0} &= 0 \text{ for } r > a \text{ (wall)} \\ c_{z=0} &= 0 \text{ for } r < a \text{ (electrode)} \\ c &\rightarrow c^* \text{ for } r \rightarrow \infty, z \rightarrow \infty \text{ (bulk)} \end{aligned} \quad (1-4)$$

Saito seemed to find $S(p) = 2\sin(ap)/\pi p$ by screening various formula of infinite integrals in mathematical tables.^{2,3)} A screening is not a derivation motivated by mathematical necessities but is a gift without mathematical logic. The derivation has been abstracted in Appendix of the review on microelectrodes.⁴⁾ Since it is

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based on the theory of complex variables, it is unfamiliar for chemists.

Solutions similar to Eq. (1-1) had been derived in the field of electrostatic capacitances before Saito's publication. Eq. (1-2) is nothing but a Laplace equation for the concentration, whereas capacitance problems lie in a Laplace equation for voltage. Both are mathematically equivalent. There are at least five methods of deriving Eq. (1-1), to my knowledge, which include i) solving the Laplace equation in a conducting charged ellipsoid around which ellipsoidal surfaces with equi-potential surround,⁵⁾ ii) applying the Gauss law to a charged ellipsoidal shell,⁶⁾ iii) solving the Laplace equation in the ellipsoidal coordinates,⁷⁾ iv) solving it in the cylindrical coordinates through the complex variable theory,⁴⁾ and v) solving it in the cylindrical coordinates by use of the Fourier integral.⁸⁾ The derivations of i)–iii) are presented here in the electrochemical form, whereas vi) and v) have already been described in detail.^{4,8)}

Derivations i) and ii) are directed to the capacitance of a conducting ellipsoidal surface. Since the ellipsoid becomes a circular disk by taking limit of the third major axis to zero, the expressions for the capacitance of the ellipsoid can be modified to those of the disk electrode. The mathematical equivalence of the capacitance and the diffusion current is as follows: The capacitive charge of a pair of parallel plates with the area S and the separation d in a dielectric medium ε is given by $V_0 \varepsilon S/d$ at the voltage V_0 , whereas the Faradaic diffusion-controlled current through a pair of parallel plates is represented by $c^*(FD)S/d$. The comparison leads to the correspondence, $V_0 \leftrightarrow c^*$ and $\varepsilon \leftrightarrow FD$.

Smythe's method

We set an electrically conducting oblate ellipsoid with the first and the second equal semi-axes, a , and the third semi-axis, b , for $b < a$ in a dielectric medium ε ($= \varepsilon_0 \varepsilon_r$, ε_r being the relative permittivity) as shown in Fig. 1.⁵⁾ The surface of the ellipsoid is represented by

Fig. 1 Oblate ellipsoid, in which the limit of the semi-axis length b to zero, provides the circular disk in radius a .

$$(x^2 + y^2)/a^2 + z^2/b^2 = 1 \quad (2-1)$$

on which the electric potential takes a given value, K . Equipotential planes in the medium surround the ellipsoid. They should also be expressed by ellipsoids for positive values of $\theta = \theta(x, y, z)$:

$$(x^2 + y^2)/(a^2 + \theta) + z^2/(b^2 + \theta) = 1 \quad (2-2)$$

A potential on one of the equi-potential surfaces should also be a function of K , and hence we can represent it as $V(x, y, z) = f(K)$, where (x, y, z) is satisfied with Eq. (2-2). Partial differentiations of V with x are

$$\begin{aligned} \partial V / \partial x &= f'(K)(\partial K / \partial x) \\ \partial^2 V / \partial x^2 &= f''(K)(\partial K / \partial x)^2 + f'(K)(\partial^2 K / \partial x^2) \end{aligned}$$

Inserting $\partial^2 V / \partial x^2$, $\partial^2 V / \partial y^2$ and $\partial^2 V / \partial z^2$ into the Laplace equation of V in the Cartesian coordinates yields

$$\begin{aligned} 0 &= \frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} + \frac{\partial^2 V}{\partial z^2} \\ &= f''(K)(\nabla K)^2 + f'(K)(\nabla^2 K) \end{aligned} \quad (2-3)$$

We take the ratio f''/f' , which is defined as $\Phi(K)$

$$-\frac{f''(K)}{f'(K)} = (\nabla^2 K)(\nabla K)^{-2} = \Phi(K) \quad (2-4)$$

By use of $f''/f' = d(\ln f')/dK$, integration of $\Phi(K)$ yields

$$\int \Phi(K) dK = -\ln[f'(K)] + A_1 \quad \text{or} \\ f'(K) = A_2 \exp\left(-\int \Phi(K) dK\right)$$

for constants A_1 and A_2 . Further integration gives $f(K)$ or V , i.e.

$$V = A_2 \int \exp\left(-\int \Phi(K) dK\right) dK + B \quad (2-5)$$

for a constant B .

We proceed to determining f' and f'' as a function of K , to calculating $\Phi(K)$ from Eq. (2-4), and to obtaining a function V through Eq. (2-5). We introduce new functions for integer n :

$$M_n = (x^2 + y^2)(a^2 + \theta)^{-n} + z^2(b^2 + \theta)^{-n} \quad (2-6) \\ N = 2/(a^2 + \theta) + 1/(b^2 + \theta)$$

The partial differentiation of M_1 , which equals 1 by Eq. (2-2), with respect to x becomes $2x/(a^2 + \theta) - M_2(\partial\theta/\partial x) = 0$ or

$$(\partial\theta/\partial x) = 2x/(a^2 + \theta)M_2 \quad (2-7)$$

Then the sum of the squares of $\partial\theta/\partial x$, $\partial\theta/\partial y$ and $\partial\theta/\partial z$ is

$$(\nabla\theta)^2 = \frac{4M_2}{M_2^2} = \frac{4}{M_2} \quad (2-8)$$

Differentiating Eq. (2-7) with respect to x yields

$$\frac{\partial^2\theta}{\partial x^2} = \frac{2}{M_2(a^2 + \theta)} - \frac{2x}{M_2(a^2 + \theta)^2} \frac{\partial\theta}{\partial x} \\ - \frac{2x}{(a^2 + \theta)M_2^2} \left(\frac{2x}{(a^2 + \theta)^2} - 2M_3 \frac{\partial\theta}{\partial x} \right)$$

Replacing $\partial\theta/\partial x$ by $2x/(a^2 + \theta)M_2$ through Eq. (2-7), we have

$$\frac{\partial^2\theta}{\partial x^2} = \frac{2}{M_2(a^2 + \theta)} - \frac{4x^2}{M_2^2(a^2 + \theta)^3} \\ - \frac{4x^2}{M_2^2(a^2 + \theta)^3} + \frac{8x^2M_3}{M_2^3(a^2 + \theta)^2}$$

The sum of $\partial^2\theta/\partial x^2$, $\partial^2\theta/\partial y^2$ and $\partial^2\theta/\partial z^2$ becomes

$$\nabla^2\theta = \frac{2N}{M_2} - \frac{8M_3}{M_2^2} + \frac{8M_2M_3}{M_2^3} = \frac{2N}{M_2} \quad (2-9)$$

Inserting Eqs. (2-8) and (2-9) into the middle term of Eq. (2-4) in which K is replaced by θ yields

$$\Phi(\theta) = (2N/M_2)/(4/M_2) = N/2, \quad \text{or} \\ \Phi(\theta) = \frac{1}{a^2 + \theta} + \frac{1}{2(b^2 + \theta)} \quad (2-10)$$

by referring Eq. (2-6). The integral becomes

$$\int \Phi(\theta) d\theta = -\ln\left[(a^2 + \theta)\sqrt{2(b^2 + \theta)}\right] + C_1 \quad (2-11)$$

The potential can be obtained by substituting Eq. (2-11) into Eq. (2-5). The exponential of Eq. (2-11) becomes

$$\exp\left(\int \Phi(\theta) d\theta\right) = C_2(a^2 + \theta)^{-1}(b^2 + \theta)^{-1/2}$$

The integral domain ranges from θ to ∞ . When we take the potential at infinite (i.e. $\theta \rightarrow \infty$) to be 0, B in Eq. (2-5) should be zero. If b approaches zero so that the ellipsoid tends to a circular disk, we have

$$V = A' \int_{\theta}^{\infty} (a^2 + \theta)^{-1} \theta^{-1/2} d\theta \quad (2-12)$$

The substitution integral, $\theta = a^2 \tan^2 z$, reduces the above integral to be $\pi/a - (2/a)\tan^{-1}(\theta/a)$. We define the potential at the disk as V_0 , which corresponds to Eq. (2-2) at $\theta = 0$. Applying this condition to Eq. (2-12) determines A_2

$$V_0 = A_2(\pi/a) \quad \text{or} \\ V = V_0 \left(1 - (2/\pi)\tan^{-1}(\sqrt{\theta}/a)\right) \quad (2-13)$$

The electric field at r ($= (x^2 + y^2 + z^2)^{1/2}$) is given by $-\partial V/\partial r$ or $-(\partial V/\partial\theta)(\partial\theta/\partial r)$. For extremely large values of r , $r^2 = x^2 + y^2 + z^2$ tends to θ (i.e. $r^2 \approx \theta$) from Eq. (2-2), and thus we have $\partial\theta/\partial r = 2r$. Since $\partial V/\partial\theta \rightarrow -V_0 a/\pi\theta^{3/2}$, the field at extremely large r is expressed by

$$(-\partial V / \partial r)_{\text{large } r} = 2V_0 a / \pi r^2 \quad (2-14)$$

When the ellipsoid has charge q , the Gauss law suggests $-\partial V / \partial r = q / 4\pi r^2 \epsilon$, which equals the right hand side of Eq. (2-14). As a result, we obtain $2V_0 a = q / \pi \epsilon$, which can rewrite

$$q = 8a\epsilon V_0 \quad (2-15)$$

The replacement of $V_0 \leftrightarrow c^*$ and $\epsilon \leftrightarrow FD$ yields the diffusion current at a both sided disk electrode. The current at the inlaid disk is a half the current, providing Eq. (1-1).

Gauss method by Thomson

We consider an oblate ellipsoidal shell. The first and the second semi-major axis lengths of the inner shell are commonly a and the third semi-major axis length is b , as illustrated in Fig. 2.⁶⁾ The derivation is composed of loading the charge on the shell of any thickness so that the volume charge density is uniform, making the thickness infinitesimally thin so that the volume charge can be regarded as the surface charge like in an electrically conducting shell, and projecting the charge density on the x - y plane at $z = 0$.

Fig. 2 Cross-section of an oblate ellipsoid on the $y = 0$ plane of Fig. 1.

The shell has a uniform volume charge density ρ . There is no electric field in the interior of the inner ellipsoid, according to the

Gauss law. Let a distance from a point on the inner ellipsoid to the center be r , the perpendicular distance from the tangent plane at the point on the inner ellipsoid to the center be h , and the thickness of the shell at the point be δh , as shown in Fig. 2. Then the surface density is given by

$$\sigma = \rho(\delta h) \quad (3-1)$$

A thinner shell indicates that the charge is condensed and localized on the surface, e.g. the shell may work electrostatically as an electric conducting material. The major axes of the outer ellipsoid can be represented as $a + \delta a$ and $b + \delta b$, where for a very thin shell

$$\delta a / a = \delta b / b = \delta h / h \quad (3-2)$$

Since the volume of an ellipsoid with semi-major axes a and b is $4\pi a^2 b / 3$, the volume of the ellipsoidal shell is $4\pi(a + \delta a)^2(b + \delta b) - 4\pi a^2 b / 3 = 4\pi a^2 b(\delta h / h)$ by Eq. (3-2). The total charge q on the conducting shell is given by the product of ρ by the volume, i.e.

$$q = 4\pi a^2 b(\delta h / h)\rho$$

and hence

$$\sigma = \rho(\delta h) = qh / 4\pi a^2 b \quad (3-3)$$

We try to determine an expression for the distance r to the tangent plane. If we express the inner ellipsoid as

$$f(x, y, z) = (x^2 + y^2)a^{-2} + z^2b^{-2} - 1 = 0$$

then the gradient of f is perpendicular to the tangent plane. Thus, the vector $\mathbf{h}$ from the center of the ellipsoid to the tangent plane is proportional to ∇f . That is,

$$\mathbf{h} \propto \nabla f = 2(xa^{-2}, ya^{-2}, zb^{-2})$$

The unit vector of $\mathbf{h}$ is

$$\hat{\mathbf{h}} = (xa^{-2}, ya^{-2}, zb^{-2}) / \sqrt{(x^2 + y^2)a^{-4} + z^2b^{-4}}$$

The magnitude h of the vector $\mathbf{h}$ is given by the inner product with $\mathbf{r} = (x, y, z)$

$$h = \mathbf{r} \cdot \hat{\mathbf{h}} = \frac{x^2 a^{-2} + y^2 a^{-2} + z^2 b^{-2}}{\sqrt{(x^2 + y^2) a^{-4} + z^2 b^{-4}}} \\ = \frac{1}{\sqrt{(x^2 + y^2) a^{-4} + z^2 b^{-4}}}$$

Then the surface charge density on the conducting ellipsoid is expressed by

$$\sigma = q / 4\pi a^2 b \sqrt{(x^2 + y^2) a^{-4} + z^2 b^{-4}} \quad (3-4)$$

Eliminating z from Eq. (3-4) by use of Eq. (2-1), we obtain

$$\sigma = q / 4\pi a^2 \sqrt{(x^2 + y^2) a^{-4} b^2 + 1 - (x^2 + y^2) a^{-2}} \quad (3-5)$$

The limit of b to zero for $R^2 = x^2 + y^2$ yields the charge density on the disk of one of two sides

$$\sigma' = q / 8\pi a \sqrt{a^2 - R^2} \quad (3-6)$$

When the electric field on the conducting surface, $\varepsilon\sigma$, is integrated with respect to R/a , the voltage of the disk is obtained

$$V_0 = \int_0^a 2\pi(R/a)(\sigma'/\varepsilon) dR \\ = \frac{q}{4\varepsilon a^2} \int_0^a R(a^2 - R^2)^{-1/2} dR = \frac{q}{4\varepsilon a}$$

This is equivalent to $q = 4\varepsilon a V_0$, which is converted to Eq. (1-1).

Diffusion in the ellipsoidal coordinates

This section is devoted to solution of the Laplace equation for the concentration in the ellipsoidal coordinates composed of variables η and ξ , which are related with the angle-independent cylindrical coordinates (r, z) in the following forms

$$z = a\xi\eta \quad (4-1A)$$

$$r = a[(1 + \xi^2)(1 - \eta^2)]^{1/2} \quad (4-1B)$$

The meaning of (η, ξ) is as follows: The electrode surface (at $z = 0$) corresponds to either $\eta = 0$ or $\xi = 0$ from Eq. (4-1A). The former ($r =$

$a(1 + \xi^2)^{1/2}$) represents the insulating wall ($r > a$, $z = 0$), whereas the latter ($r = a(1 - \eta^2)^{1/2}$) does to the electrode surface ($r < a$, $z = 0$). In other words, the boundary conditions for either $r > a$ or $r < a$ can be applied through selection of either η or ξ . Eq. (1-2) is transformed into that in the ellipsoidal coordinates:

$$\frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial z^2} \\ = \left[\frac{\partial}{\partial \xi} \left((1 + \xi^2) \frac{\partial c}{\partial \xi} \right) + \frac{\partial}{\partial \eta} \left((1 - \eta^2) \frac{\partial c}{\partial \eta} \right) \right] \frac{1}{a^2(\xi^2 + \eta^2)} \quad (4-2)$$

Details of the transformation have been given in Appendix 1 and 2. The boundary conditions, Eq. (1-4), can be replaced by $\xi = 0$ or $\eta = 0$ in the ellipsoidal coordinate. If we select $\eta = 0$, the condition $r > a$ is automatically satisfied with $r = a(1 + \xi^2)^{1/2}$ for any value of ξ . Denoting $\xi_z = \partial \xi / \partial z$ and $c_z = \partial c / \partial \xi$, we obtain

$$(c_z)_{z=0} = (\xi_z c_\xi + \eta_z c_\eta)_{\eta=0} = (c_\eta / a\xi)_{\eta=0} \quad (4-3)$$

Then the boundary conditions are replaced by

$$c \rightarrow c^* \text{ for } \xi \rightarrow \infty, (\eta < 1) \quad (4-4A)$$

$$c = 0 \text{ for } \xi = 0, (\eta < 1) \quad (4-4B)$$

$$\partial c / \partial \eta = 0 \text{ for } \eta = 0 \quad (4-4C)$$

The diffusion equation under the steady state in the ellipsoidal coordinates is given by

$$\frac{\partial}{\partial \xi} \left((1 + \xi^2) \frac{\partial c}{\partial \xi} \right) + \frac{\partial}{\partial \eta} \left((1 - \eta^2) \frac{\partial c}{\partial \eta} \right) = 0 \quad (4-5)$$

We express c as the product $H(\eta)X(\xi)$, where $H(\eta)$ and $X(\xi)$ are only the functions of η and ξ , respectively. Inserting $c = HX$ into Eq. (4-5) and dividing the resulting equation by HX yields

$$\frac{1}{X} \frac{\partial}{\partial \xi} \left((1 + \xi^2) \frac{\partial X}{\partial \xi} \right) + \frac{1}{H} \frac{\partial}{\partial \eta} \left((1 - \eta^2) \frac{\partial H}{\partial \eta} \right) = 0$$

The first term is only the function of ξ , whereas the second is only the function of η . Therefore each term should be a constant. Setting the first

term to be a constant k and the second one to be $-k$, we have

$$\begin{aligned} \frac{d}{d\xi} \left((1+\xi^2) \frac{dX}{d\xi} \right) &= kX \\ \frac{d}{d\eta} \left((1-\eta^2) \frac{dH}{d\eta} \right) &= -kH \end{aligned} \quad (4-6)$$

In order to evaluate k , we consider the similarity of concentration profiles at the disk electrode for large values of r or z to those at a spherical electrode for large values of r . The asymptotic form is $c \approx c^*(1 - a/r)$ or $c \approx c^*(1 - a/z)$. Eq. (4-1B) indicates that $\eta = 1$ is equivalent to $z = a\xi$. We consider the behaviors of X at ξ with large values of z or ξ . The first of Eq. (4-6) is approximated as $d(\xi^2 dX/d\xi)/d\xi = kX$, which is close to $d(z^2 dc/dz)/dz \approx kc$ after the replacement of $\xi = z/a$ and multiplication of the both sides by H . Substituting $c^*(1 - a/z)$ for c yields $d(z^2(c^*a/z^2))/dz \approx kc^*$. Consequently, we have $k = 0$. Then the terms in the parentheses in Eq. (4-6) are constants, k_2 and k_3 .

$$\begin{aligned} (1+\xi^2) \left(dX/d\xi \right) &= k_2, \\ (1-\eta^2) \left(dH/d\eta \right) &= k_3 \end{aligned} \quad (4-7)$$

The integration yields

$$\begin{aligned} X &= k_2 \int_0^\xi (1+\xi^2)^{-1} d\xi + k_5 \\ H &= k_3 \int_0^\eta (1-\eta^2)^{-1} d\eta + k_6 \end{aligned} \quad (4-8)$$

The substitution, $\xi = \tan\theta$, makes X be

$$X = k_2 \arctan \xi + k_5 \quad (4-9)$$

Applying the equality $(1-\eta^2)^{-1} = [(1-\eta)^{-1} + (1+\eta)^{-1}]/2$ to the integral for H yields

$$H = (k_3/2) \ln[(1+\eta)/(1-\eta)] + k_6 \quad (4-10)$$

When η approaches 1 corresponding to $r \rightarrow 0$, $\ln(1+\eta)/(1-\eta)$ tends infinity. Consequently, we have $k_3 = 0$. Application of condition (4-4B) ($c = 0$ or $X = 0$ at $\xi = 0$) to Eq. (4-9) yields $k_5 = 0$. Condition (4-4A) ($c \rightarrow c^*$ for $\xi \rightarrow \infty$) makes $c^* = k_2(\pi/2)/k_6$ in Eq. (4-9) or $k_2 k_6 = (2/\pi)c^*$. Finally

we have

$$c = XH = (2/\pi)c^* \arctan \xi \quad (4-11)$$

The flux at the electrode is given by diffusion, $j/F = D(\partial c/\partial z)_{z=0}$, where j is the current density varying with r . We express $\partial c/\partial z$ as function of η and ξ through the relation, $c_z = \xi_z c_\xi + \eta_z c_\eta$. The explicit forms of ξ_z and η_z can be obtained by the inverse matrix as shown in Appendix 2, and are

$$\xi_z = \frac{\eta(1+\xi^2)}{a(\xi^2+\eta^2)}, \eta_z = \frac{\xi(1-\eta^2)}{a(\xi^2+\eta^2)} \quad (4-12)$$

Then the flux at the electrode or ($\xi = 0$ and $0 < \eta < 1$) is given by

$$j/F = (D/a\eta)(c_z)_{z=0} \quad (4-13)$$

The differentiation, $d(\arctan\xi)/d\xi = 1/(1+\xi^2)$, reduces Eq. (4-14) to

$$\frac{j}{F} = \frac{2c^*D}{\pi a\eta} = \frac{2c^*D}{\pi a\sqrt{1-r^2/a^2}}$$

where we have used $r_{z=0} = a(1-\eta^2)^{1/2}$ in Eq. (4-1B). The current density at the edge ($r = a$) becomes infinity. The total current is given by

$$I = \int_0^a 2\pi j dr = 4Fc^*Da \quad (4-14)$$

Appendix 1

We describe some relations of partial derivatives of a function f with respect to (r, z) and (ξ, η) . We represent the partial derivative $\partial f/\partial z$ as f_z . The relations, $f_\xi = f_z z_\xi + f_r r_\xi$ and $f_\eta = f_z z_\eta + f_r r_\eta$ can be expressed by the matrix

$$\begin{pmatrix} f_\xi \\ f_\eta \end{pmatrix} = \begin{pmatrix} z_\xi & r_\xi \\ z_\eta & r_\eta \end{pmatrix} \begin{pmatrix} f_z \\ f_r \end{pmatrix} = \begin{pmatrix} a\eta & a\xi\sqrt{(1-\eta^2)/(1+\xi^2)} \\ a\xi & -a\eta\sqrt{(1+\xi^2)/(1-\eta^2)} \end{pmatrix} \begin{pmatrix} f_z \\ f_r \end{pmatrix} \quad (A1)$$

where we have used the following direct

derivatives: $z_{\xi} = a\eta$, $r_{\xi} = a\xi [(1 - \eta^2)/(1 + \xi^2)]^{1/2}$, $z_{\eta} = a\xi$, and $r_{\eta} = -a\eta[(1 + \xi^2)/(1 - \eta^2)]^{1/2}$. In contrast, the derivatives of f_r and f_z are represented by

$$\begin{pmatrix} f_z \\ f_r \end{pmatrix} = \begin{pmatrix} \xi_z & \eta_z \\ \xi_r & \eta_r \end{pmatrix} \begin{pmatrix} f_{\xi} \\ f_{\eta} \end{pmatrix} \quad (\text{A2})$$

The matrix in Eq. (A1) alters the vector (f_{ξ}, f_{η}) to (f_z, f_r) whereas the matrix in Eq. (A2) functions inversely. Therefore the former matrix is the inverse of the latter, i.e.

$$\begin{pmatrix} \xi_z & \eta_z \\ \xi_r & \eta_r \end{pmatrix} = \begin{pmatrix} a\eta & a\xi\sqrt{(1-\eta^2)/(1+\xi^2)} \\ a\xi & -a\eta\sqrt{(1+\xi^2)/(1-\eta^2)} \end{pmatrix}^{-1} \quad (\text{A3})$$

Carrying out the inverse matrix, we have

$$\begin{pmatrix} \xi_z & \eta_z \\ \xi_r & \eta_r \end{pmatrix} a(\xi^2 + \eta^2) = \begin{pmatrix} \eta(1+\xi^2) & \xi(1-\eta^2) \\ \xi\sqrt{(1+\xi^2)(1-\eta^2)} & -\eta\sqrt{(1+\xi^2)(1-\eta^2)} \end{pmatrix} \quad (\text{A4})$$

Appendix 2

The Laplacian in the ellipsoidal coordinate (Eq. (4-2)) is derived from that in the cylindrical coordinates in this appendix. The second derivatives in Eq. (4-2) can be obtained by further differentiating $c_z = c_{\xi}\xi_z + c_{\eta}\eta_z$ and $c_r = c_{\xi}\xi_r + c_{\eta}\eta_r$. The derivative of c_z with respect to z is given by

$$c_{zz} = (c_{\xi}\xi_z + c_{\eta}\eta_z)_z = (c_{\xi}\xi_z + c_{\eta}\eta_z)_{\xi}\xi_z + (c_{\xi}\xi_z + c_{\eta}\eta_z)_{\eta}\eta_z \quad (\text{A5})$$

Derivatives of the four terms with respect to ξ and η yields eight terms:

$$c_{zz} = \xi_z(c_{\xi}\xi_{\xi\xi} + c_{\xi\xi}\xi_z + c_{\eta}\eta_{\xi\xi} + c_{\eta\xi}\eta_z) + \eta_z(c_{\xi}\xi_{\xi\eta} + c_{\xi\eta}\xi_z + c_{\eta}\eta_{\xi\eta} + c_{\eta\eta}\eta_z) \quad (\text{A6})$$

Similarly, we have

$$\begin{aligned} c_{rr} &= \xi_r(c_{\xi}\xi_r + c_{\eta}\eta_r)_{\xi} + \eta_r(c_{\xi}\xi_r + c_{\eta}\eta_r)_{\eta} \\ &= \xi_r(c_{\xi}\xi_{r\xi} + c_{\xi\xi}\xi_r + c_{\eta}\eta_{r\xi} + c_{\eta\xi}\eta_r) + \\ &\quad \eta_r(c_{\xi}\xi_{r\eta} + c_{\xi\eta}\xi_r + c_{\eta}\eta_{r\eta} + c_{\eta\eta}\eta_r) \end{aligned} \quad (\text{A7})$$

Explicit forms of ξ_z , η_z , ξ_r and η_r have already been given in Eq. (A3). The second derivatives of $\xi_{z\xi}$, $\eta_{z\xi}$, $\xi_{z\eta}$, $\eta_{z\eta}$, $\xi_{r\xi}$, $\eta_{r\xi}$, $\xi_{r\eta}$ and $\eta_{r\eta}$ can be obtained by simply differentiating ξ_z , η_z , ξ_r and η_r . An example is shown below:

$$\begin{aligned} \xi_{r\xi} &= \frac{\partial}{\partial \xi} \frac{\xi\sqrt{(1+\xi^2)(1-\eta^2)}}{a(\xi^2 + \eta^2)} \\ &= \frac{\sqrt{1-\eta^2}(-\xi^2 + \eta^2 + 2\xi^2\eta^2)}{a(\xi^2 + \eta^2)^2\sqrt{1+\xi^2}} \end{aligned} \quad (\text{A8})$$

It is convenient to use some simple relations:

$$\begin{aligned} \xi_r^2 + \xi_z^2 &= \frac{1+\xi^2}{a^2(\xi^2 + \eta^2)} \\ \eta_r^2 + \eta_z^2 &= \frac{1-\eta^2}{a^2(\xi^2 + \eta^2)} \\ \xi_r\eta_r + \xi_z\eta_z &= 0 \end{aligned} \quad (\text{A9})$$

A key of successful derivation is to arrange $c_{rr} + c_r/r + c_{zz}$ to the form of $Ac_{\eta} + Bc_{\xi} + c_{\xi\xi}(\xi_r^2 + \xi_z^2) + c_{\eta\eta}(\eta_r^2 + \eta_z^2)$, where

$$\begin{aligned} A &\equiv \xi_r\eta_{r\xi} + \eta_r\eta_{r\eta} + \eta_r/r + \xi_z\eta_{z\xi} + \eta_z\eta_{z\eta} \\ &= -\frac{2\eta}{a^2(\xi^2 + \eta^2)} \end{aligned} \quad (\text{A10})$$

$$\begin{aligned} B &\equiv \xi_r\xi_{r\xi} + \eta_r\xi_{r\eta} + \xi_r/r + \xi_z\xi_{z\xi} + \eta_z\xi_{z\eta} \\ &= \frac{2\xi}{a^2(\xi^2 + \eta^2)} \end{aligned} \quad (\text{A11})$$

Then Eq. (4-2) can be obtained.

References

- 1) Y. Saito, *Rev. Polarogr.* **15**, 177 (1968).
- 2) S. Moriguchi, S. Hitotsumatsu, H. Utagawa, "Mathematical Formulae III", Iwanami (in Japanese), 1987, p. 203.
- 3) M. Abramowitz and I. A. Stegun, "Handbook of Mathematical Functions", Dover, New York,

- 1972, p. 487.
- 4) K. J. Aoki, *J. Electroanal. Chem.*, **779**, 7 (2016).
5) W. R. Smythe, "Static and Dynamic Electricity",
3rd Ed. McGraw-Hill, New York, Chap. 5, 1950.
6) K. T. McDonald,
<http://www.physics.princeton.edu/~mcdonald/examples/ellipsoid.pdf>, 2002.
- 7) E. I. Burstein, *Celestial Mechanics* **11**, 79 (1975).
8) K. Aoki, J. Osteryoung, *J. Electroanal. Chem.*,
122, 19 (1981).