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The Impedance of the Planar Diffuse Double Layer: An Exact Low-Frequency Theory

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The classical Gouy–Chapman–Grahame theory for the impedance of the diffuse double layer extending out from a planar electrode is extended to incorporate the effects of ionic diffusion normal to the plane. The resulting theory accounts quantitatively for the divergence of the double-layer resistance at low frequencies (<10 Hz), and provides high-frequency corrections (>10 kHz) to the capacitance due to diffusion effects. The transport equations are solved by a perturbation theory approach, which produces a low-frequency expansion for the diffuse layer small-signal impedance Z_{el} of the form

$$\frac{1}{Z_{el}} = \kappa K(\omega)[\delta^2 A_2 + \delta^3 A_3 + \delta^4 A_4 + \cdots], \qquad [1]$$

where $K(\omega)$ is the complex conductance of the electrolyte solution and δ is a (small) frequency parameter given by

$$\delta^2 = \frac{\omega\bar{\lambda}}{\kappa^2 kT}, \qquad [2]$$

$\bar{\lambda}$ being a typical ion drag coefficient and κ^{-1} the Debye screening length. The resulting series is expected to be valid from DC to at least 10 kHz. Exact analytic expressions for A_2, A_3, and A_4 as functions of the zeta potential ζ of the unperturbed electrode and the electrolyte compositional properties are derived. Thus, the diffuse double-layer contribution to the electrode conductance and capacitance can be explicitly exhibited to leading order in frequency for all values of ζ and electrolyte composition.

1. INTRODUCTION

The traditional view of the small-signal impedance of an inert planar electrode in contact with an arbitrary electrolyte, as developed by Gouy, Chapman, Stern, and Grahame (1–6), has been that the measured impedance may be accounted for by a series combination of the bulk electrolyte resistance, the diffuse outer-layer capacitance, and the Stern (or "inner Helmholtz") layer capacitance. This view is satisfactory, provided the bulk resistance dominates any resistance due to the double-layer region, and provided measurements are made in a regime where ionic diffusion does not substantially affect the standard double-layer capacitance $d\sigma/d\zeta$. It is now experimentally straightforward to take measurements in regimes where one or neither of these two qualifications applies (frequencies below 10 Hz or above 10 kHz, respectively), and as yet no theory has emerged to satisfactorily describe the behavior of the double-layer impedance in these regimes and, in particular, the dependence of this impedance on the physical conditions expected at the surface. It is the authors' view that deviations from the classic Gouy–Chapman–Grahame diffuse layer impedance in such regimes are critically dependent on the surface conditions, and that appropriate impedance measurements may reveal details of the surface physics unobtainable by other means.

We envisage an experimental configuration that maximizes the contribution of the diffuse layer to the overall impedance (low concentrations and a narrow cell), and thus focuses attention on the diffuse double-layer properties rather than those of the inner layer. This is in marked contrast to more typical electrochemistry measurements, where large-amplitude signals and swamping electrolyte are used to minimize the diffuse layer contributions.

The theory of polarization impedance has been treated theoretically by a number of workers (7–11), and with the exception of De Lacey and White (7), all these theoretical treatments have made approximations to a basic set of ion transport equations which have formed the foundation of interfacial and colloidal electrokinetic theory. When "exact" numerical algorithms were developed to treat colloidal transport phenomena (12–14) it became obvious that the classic boundary condition, that of no ion penetration of the "slipping plane" in many important colloidal systems, was distinctly unsound and led to the development of mobile Stern layer theories (15–17) to explain experimental discrepancies with the classic theoretical model predictions. The behavior of ions in the Stern region can be probed by a rigorous examinations of those differences.

It is in this spirit that the De Lacey and White (7) treatment of electrode polarization was developed. By removing the possibility that disagreement between theory and experiment in electrode polarization studies was due to approximation

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in the theory, attention is rightfully focused on the "slipping plane" boundary condition. Disagreement between experiment and classical exact theory will lead to more detailed modeling of the physics of the inner layer.

Furthermore the information thus obtained from electrode studies should be directly transferable to the colloidal state. Historically, electrode studies were vital to the development of modern colloid science (e.g., the dropping mercury electrode experiments, which confirmed the need for an inner layer) and it is to be hoped that they may again play an important role in elucidating the inner double layer.

Two factors have conspired against this happy symbiosis. First, until recently, it has not been experimentally feasible to measure accurately the electrode impedance $Z_{el}(\omega)$ in the Ohm's law regime where Z_{el} is a function of the unperturbed state of the electrode interface (the signal needs to be 25 mV or less). The available applied voltages were of such magnitude that they swamped the ambient ζ potential of the electrode and perturbed even the equilibrium water structure and orientation in the neighborhood of the interface. While such studies are valuable in their own right, they tell us nothing about the state of the inner layer in the absence of large applied fields. Only when we operate in the linear response regime where current and applied voltage are linearly related does the value of $Z_{el}(\omega)$ inform us directly of the unperturbed state of the electrode–electrolyte solution interface.

Second, part of the desired measurements need to be performed at very low frequencies, where $\mathrm{Re}(Z_{el}(\omega))$ is large and competes effectively with the bulk impedance. Unfortunately the "exact" numerical theory of De Lacey and White is difficult to implement at these frequencies, due to numerical difficulties associated with the vastly discrepant length scales κ^{-1} (Debye screening length) and $(kT/\omega\bar{\lambda})^{1/2}$ (typical ion diffusion length) which apply in the problem. Furthermore, the effect of any variation in the "no penetration" ionic boundary condition is not obvious or physically perspicuous in such a numerical theory. It is important to realize that the ratio of these length scales is very small at frequencies of a few hertz. For example,

$$\kappa^{-1}\left(\frac{\omega\bar{\lambda}}{kT}\right)^{1/2} \approx 2 \times 10^{-3} \qquad [3]$$

for a 10^{-3} M KCl solution at 10 Hz and room temperature. It is therefore obvious that a perturbation theory approach that used the smallness of this length scale ratio could provide an accurate low-frequency analytic theory. In such a theory, modifications to the surface boundary conditions would lead directly to modifications of the electrode impedance, and thus greatly facilitate our understanding of the role of the inner double layer and any electrode reactions that may occur at an ordinary reactive electrode.

Some of the early papers by Rangarajan (18) deal with the effects of diffusion at metal–electrolyte interfaces in the presence of fast electrode reactions, but in this paper we are concerned with the simplest conceivable electrode/electrolyte system—the ideally polarizable plane electrode at which no electrolysis reaction is occurring. We do not consider any oscillation in surface charge on the electrode arising from association–dissociation reactions of chemical groups in response to the applied voltage. Such processes are important and have the general effect of modifying $Z_{el}(\omega)$ (via the introduction of complicated boundary conditions into the governing equations), but we are concerned here with developing a general theory of the diffuse double-layer response in which the simplest conceivable surface conditions apply. Nevertheless, one must bear in mind it is just these surface processes that an experimental study of electrode polarization impedance would probe quantitatively. Discrepancy between experimental results and the theory developed below would strongly imply their presence and lead to further inner-layer modeling in the spirit of the philosophy discussed above.

2. THE BASIC EQUATIONS

We consider a plane electrode next to a general electrolyte solution in which the bulk number density, charge, and limiting conductance of the j-type ion ($j = 1, 2, \ldots, N$) are n_j^∞, z_je, and Λ_j^∞, respectively. We imagine the diffuse double layer to occupy the region $x \geqslant 0$, and the exact location of the electrode surface plane is at $x = -b$ and is unspecified further in this model.

The behavior of the diffuse double layer when an oscillating voltage is applied to the electrode is fully described by the electric potential $\Psi(x, t)$, the ion concentrations $n_j(x, t)$ and ion drift velocities $v_j(x, t)\hat{\mathbf{x}}$. All quantities are functions of the normal coordinate x and time t near the plane electrode. For this reason, ion fluxes cause no collective fluid motion since we regard the electrolyte as incompressible. The basic equations in a continuum description of the dynamic response of the diffuse double layer are the Poisson equation

$$\frac{d^2\Psi}{dx^2} = -\frac{4\pi}{\epsilon}\rho(x, t), \qquad [4]$$

where the charge density ρ is given by

$$\rho(x, t) = \sum_{j=1}^{N} z_jen_j(x, t), \qquad [5]$$

and Fick's law for ion transport,

$$-\lambda_jv_j - z_je\frac{\partial\Psi}{\partial x} - kT\frac{\partial \ln n_j}{\partial x} = 0, \qquad [6]$$

together with the continuity equation

$$\frac{\partial(n_j v_j)}{\partial x} = -\frac{\partial n_j}{\partial t}, \qquad j = 1, 2, \ldots, N. \tag{7}$$

The physical significance and limitations of these equations have been discussed at length elsewhere (7, 12). The drag coefficient λ_j for the jth ion is related to its limiting conductance Λ_j^∞ by

$$\lambda_j = \frac{N_A e^2 |z_j|}{\Lambda_j^\infty}, \tag{8}$$

where N_A is Avogadro's number.

The application of a voltage $V(t)$ to the slipping plane $x = 0$ gives rise to a field $E(t)\hat{x}$ far from the electrode surface. We must therefore require the electric potential $\Psi(x, t)$ to satisfy

$$\Psi(x, t) \to -E(t)x + \text{decaying terms} \tag{9}$$

as $x \to \infty$. Such a field will cause bulk ion drift motion but no concentration differences. Hence we also require

$$n_j(x, t) \to n_j^\infty \qquad \text{as } x \to \infty. \tag{10}$$

We define a chemical potential function $\Phi_j(x, t)$ by

$$n_j(x, t) = n_j^\infty \exp\left[-\frac{z_j e}{kT}(\Psi(x, t) + \Phi_j(x, t) + xE(t))\right], \tag{11}$$

where we require

$$\lim_{x\to\infty} \Phi_j(x, t) = 0 \tag{12}$$

to satisfy [9] and [10]. In imposing [9] we have set the arbitrary constant in the electric potential to zero with the subsequent result [12] for $\Phi_j(x, t)$. If we had not taken this step so that we allowed a constant term in the limit of $\Psi(x, t)$, then [12] would, of necessity, be adjusted so that Φ_j tended to the negative of this constant. Such a constant can have no bearing on the physics of the double-layer response and can therefore be set to zero with no loss of generality. With this definition, we can write Eq. [6] as

$$v_j(x, t) = \frac{z_j e}{\lambda_j}\left(\frac{\partial \Phi_j}{\partial x} + E(t)\right). \tag{13}$$

In the absence of the applied voltage the basic equations ([4]–[7]) reduce to the Poisson–Boltzmann equation

$$\frac{d^2\Psi^0(x)}{dx^2} = -\frac{4\pi}{\epsilon}\sum_{j=1}^{N} z_j e n_j^0(x, t), \tag{14}$$

where

$$n_j^0(x) = n_j^\infty \exp\left(\frac{-z_j e}{kT}\Psi^0(x)\right). \tag{15}$$

Here the superscript zero denotes the time-invariant equilibrium value of a variable. The equilibrium state is completely specified by the slipping plane boundary conditions

$$\Psi^0(0) = \zeta \tag{16}$$

$$\lim_{x\to\infty} \Psi^0(x) = 0. \tag{17}$$

It is the aim of the theory developed below to express $Z_{el}(\omega)$ as a function of ζ, n_j^∞, z_j, and Λ_j^∞ ($j = 1, 2, \ldots, N$).

We now restrict ourselves to an applied voltage of the form $Ve^{-i\omega t}$. The asymptotic field now has the consequent form $Ee^{-i\omega t}$. We seek a solution of the perturbed problem in the form

$$\Psi(x, t) = \Psi^0(x) + (\psi(x)V - xE)e^{-i\omega t} \tag{18}$$

$$v_j(x, t) = Vv_j(x)e^{-i\omega t} \tag{19}$$

$$\Phi_j(x, t) = V\phi_j(x)e^{-i\omega t} \tag{20}$$

$$n_j(x, t) = n_j^0(x) + V\delta n_j(x)e^{-i\omega t} \tag{21}$$

where

$$\delta n_j(x) = \frac{-z_j e n_j^0(x)}{kT}(\psi(x) + \phi_j(x)) \tag{22}$$

to leading order in the perturbation V.

Substituting these expressions into the basic equations and neglecting products of perturbation quantities where they occur, we derive

$$\frac{d^2\psi}{dx^2} - \frac{4\pi e^2}{\epsilon kT}\sum_{j=1}^{N} n_j^0(x) z_j^2(\psi + \phi_j) = 0 \tag{23}$$

and

$$\frac{d^2\phi_j}{dx^2} + \frac{i\omega\lambda_j}{kT}(\psi + \phi_j) = \frac{z_j e}{kT}\frac{d\Psi^0}{dx}\left(\frac{d\phi_j}{dx} + \frac{E}{V}\right) \qquad j = 1, 2, \ldots, N. \tag{24}$$

We are justified in neglecting higher-order terms in the perturbation voltage since we wish to develop a linear response theory where current and voltage are linearly related in the

Ohm's law regime of applied voltages. The electrode impedance calculated in this first-order perturbation theory will be precisely correct within the limits of this model in this regime.

The boundary conditions on the functions $\psi(x)$ and $\phi_j(x)$ are

$$\left.\begin{matrix}\psi(x)\\ \phi_j(x)\end{matrix}\right\} \to 0 \qquad \text{as } x \to \infty, \qquad [25]$$

$$\psi(0) = 1, \qquad [26]$$

$$\frac{d\phi_j(0)}{dx} = -\frac{E}{V} \qquad (j = 1, 2, \ldots, N). \qquad [27]$$

Equation [27] is the "no penetration" boundary condition of the classic electrokinetic models, since it follows directly from (13) by imposing the constraint

$$v_j(0, t) = 0 \qquad (j = 1, 2, \ldots, N). \qquad [28]$$

Any surface dissociation reaction or ionic electrolysis reaction would negate this boundary condition. We are dealing here with the perfectly polarizable electrode or, at least, the perfectly polarizable "slipping plane." Equation [26] follows directly from the observation that

$$\delta\Psi(0, t) = Ve^{-i\omega t}. \qquad [29]$$

The treatment given here is different from that of DeLacey and White (7), where the far field $Ee^{-i\omega t}$ was used as the perturbation quantity. Since this field vanishes as $\omega \to 0$, the DeLacey and White functions $\psi(x)$ and $\phi_j(x)$ diverge as $\omega \to 0$ for a given applied voltage. It is more convenient to keep the quantities ψ and ϕ_j finite as $\omega \to 0$, so the voltage $Ve^{-i\omega t}$ applied at the slipping plane (which remains finite as $\omega \to 0$) is taken as the fundamental perturbation quantity. We must, however, express the far field E in terms of V since the ratio E/V is obviously required in the differential equations and the boundary conditions.

We denote by $\Delta Ve^{-i\omega t}$ the applied potential difference between the electrolyte at $x = L$ and the slipping plane $x = 0$:

$$\Delta Ve^{-i\omega t} = \delta\Psi(0, t) - \delta\Psi(L, t) = (V + LE)e^{-i\omega t}. \qquad [30]$$

If Z_{tot} is the total impedance per unit area of electrode between $x = 0$ and $x = L$, then

$$\Delta Ve^{-i\omega t} = Z_{\text{tot}} Ie^{-i\omega t}, \qquad [31]$$

where $Ie^{-i\omega t}$ is the current density flowing between $x = 0$ and $x = L$. In the bulk electrolyte where the field is $Ee^{-i\omega t}$, we have

$$Ie^{-i\omega t} = K(\omega)Ee^{-i\omega t}, \qquad [32]$$

where

$$K(\omega) = \sum_{j=1}^{N} \frac{e^2 z_j^2 n_j^\infty}{\lambda_j} - \frac{i\omega\epsilon}{4\pi} \qquad [33]$$

is the complex conductance of the bulk electrolyte. Substituting for $Ie^{-i\omega t}$ using [30] and [31], we obtain

$$V = \left(Z_{\text{tot}} - \frac{L}{K(\omega)}\right) K(\omega)E, \qquad [34]$$

but since the total impedance comprises a bulk electrolyte impedance together with the actual electrode impedance $Z_{\text{el}}(\omega)$;

$$Z_{\text{tot}} = Z_{\text{el}}(\omega) + L/K(\omega), \qquad [35]$$

we must have

$$E/V = \frac{1}{K(\omega)Z_{\text{el}}}. \qquad [36]$$

Equation [24] can now be written as

$$\frac{d^2\phi_j}{dx^2} + \frac{i\omega\lambda_j}{kT}(\psi + \phi_j) = \frac{z_j e}{kT}\frac{d\Psi^0}{dx}\left(\frac{d\phi_j}{dx} + \frac{1}{Z_{\text{el}}K(\omega)}\right) \qquad [37]$$

and the boundary condition [27] becomes

$$\frac{d\phi_j(0)}{dx} = -\frac{1}{Z_{\text{el}}K(\omega)}. \qquad [38]$$

A useful first integral of [23] can be derived with the aid of [37]. Substituting for ϕ_j in (23) we obtain

$$\frac{d^2\psi}{dx^2} - \frac{4\pi e^2}{i\omega\epsilon}\sum_{j=1}^{N}\frac{n_j^0(x)z_j^2}{\lambda_j} \times \left[\frac{z_j e}{kT}\frac{d\Psi^0}{dx}\left(\frac{d\phi_j}{dx} + \frac{1}{Z_{\text{el}}K(\omega)}\right) - \frac{d^2\phi_j}{dx^2}\right] = 0, \qquad [39]$$

which can be integrated to give

$$\frac{d\psi}{dx} + \frac{4\pi e^2}{i\omega\epsilon}\sum_{j=1}^{N}\frac{n_j^0(x)z_j^2}{\lambda_j}\left(\frac{d\phi_j}{dx} + \frac{1}{Z_{\text{el}}K(\omega)}\right) = C, \qquad [40]$$

by using the result (from [15])

$$\frac{dn_j^0(x)}{dx} = -\frac{z_j e}{kT}\frac{d\Psi^0}{dx}n_j^0(x). \qquad [41]$$

The constant of integration C can be found by evaluating [40] at $x = 0$ and using Eq. [38] to obtain

$$\frac{d\psi(0)}{dx} = C. \qquad [42]$$

Evaluating [40] at $x = \infty$ then yields

$$C = \frac{4\pi e^2}{i\omega\epsilon Z_{\mathrm{el}} K(\omega)} \sum_{j=1}^{N} \frac{z_j^2 n_j^\infty}{\lambda_j}, \qquad [43]$$

since both ψ and ϕ_j must vanish along with their derivatives as $x \to \infty$. Thus

$$\frac{d\psi(0)}{dx} = \frac{4\pi e^2}{i\omega\epsilon}\left(\sum_{j=1}^{N} \frac{z_j^2 n_j^\infty}{\lambda_j}\right)\frac{1}{Z_{\mathrm{el}} K(\omega)}. \qquad [44]$$

This extra boundary condition on the problem arises physically from continuity of current in the system and will be useful in what follows.

3. METHOD OF MATCHED ASYMPTOTIC EXPANSIONS

We introduce the scaled distance variable

$$X = \kappa x \qquad [45]$$

where

$$\kappa^2 = \frac{4\pi e^2}{\epsilon kT} \sum_{j=1}^{N} n_j^\infty z_j^2, \qquad [46]$$

so that $X \sim 1$ on the length scale of the double-layer. We introduce the perturbation parameter δ as

$$\delta^2 = \frac{\omega\bar{\lambda}}{\kappa^2 kT} \qquad [47]$$

where $\bar{\lambda}$ is a typical value of λ_j. A convenient definition of $\bar{\lambda}$ for a general salt whose chemical formula is $X_{m_1}^{(1)} X_{m_2}^{(2)} \cdots X_{m_N}^{(N)}$ is

$$\bar{\lambda} = \frac{\sum_{j=1}^{N} m_j \lambda_j}{\sum_{j=1}^{N} m_j}. \qquad [48]$$

This parameter δ, as discussed above, is the ratio of the double-layer thickness to the diffusion length at frequency ω, and is typically very small at the usual frequencies of interest in electrode impedance studies (<100 Hz).

In terms of these variables the equations become

$$\frac{d^2\psi}{dX^2} - \sum_{j=1}^{N} \beta_j(X)(\psi + \phi_j) = 0 \qquad [49]$$

$$\frac{d^2\phi_j}{dX^2} + i\delta^2\gamma_j(\psi + \phi_j) = z_j \frac{dY^0}{dX}\left(\frac{d\phi_j}{dX} + \frac{1}{\kappa Z_{\mathrm{el}} K(\omega)}\right) \qquad [50]$$

where

$$\beta_j(X) = \frac{n_j^0(X) z_j^2}{\sum_{j=1}^{N} n_j^\infty z_j^2}, \qquad [51]$$

$$Y^0(X) = \frac{e\Psi^0}{kT}, \qquad [52]$$

and

$$\gamma_j = \frac{\lambda_j}{\bar{\lambda}}. \qquad [53]$$

We denote

$$\beta_j^\infty = \beta_j(\infty), \qquad [54]$$

so

$$\beta_j(X) = \beta_j^\infty e^{-z_j Y^0(X)} \qquad [55]$$

and note that

$$\sum_{j=1}^{N} \beta_j^\infty = 1. \qquad [56]$$

The boundary conditions on [49] and [50] are from [25], [26], [27], and [44]:

$$\left.\begin{matrix}\psi(X)\\ \phi_j(X)\end{matrix}\right\} \to 0 \quad \text{as } X \to \infty, \qquad [57]$$

$$\psi(0) = 1, \qquad [58]$$

$$\frac{d\phi_j(0)}{dX} = -\left(\frac{1}{\kappa Z_{\mathrm{el}} K(\omega)}\right), \qquad [59]$$

$$\frac{d\psi(0)}{dX} = \frac{\sum_{j=1}^{N} \beta_j^\infty/\gamma_j}{i\delta^2 \kappa Z_{\mathrm{el}} K(\omega)}. \qquad [60]$$

The δ^2 term in [50] implies that ψ, ϕ_j outside the double-layer change on a length scale of $\delta^{-1} \gg 1$. It is this second length scale that makes a low-frequency perturbation theory complicated and the "exact" numerical solution of DeLacey and White (7) difficult to implement.

We adopt here the method of matched asymptotic expansions (19), wherein we solve Eqs. [49] and [50] in an inner region of length scale X, and match these solutions to the solutions of [49] and [50] in an outer region described by the length scale

$$S = \delta X. \qquad [61]$$

In the double-layer region ($X \sim 1$), S is small and only becomes $O(1)$ far outside the double layer where ionic diffusion is dominant.

3.1. *Formalism for Inner Solutions*

We seek a solution of [49] and [50] in the form

$$\psi(X) = \sum_{n=0}^{\infty} \delta^n \psi_n(X) \qquad [62]$$

$$\phi_j(X) = \sum_{n=0}^{\infty} \delta^n \phi_{jn}(X), \qquad [63]$$

with

$$\frac{1}{\kappa Z_{\mathrm{el}} K(\omega)} = \sum_{n=2}^{\infty} \delta^n A_n. \qquad [64]$$

Such a series solution is asymptotic for fixed X as $\delta \rightarrow 0$, so the relevant equations for the ψ_n and ϕ_{jn} may be obtained simply by equating coefficients of δ^n in the system of equations obtained by substituting [62] and [63] into [49] and [50]. This gives

$$\frac{d^2\psi_n}{dX^2} - \sum_{j=1}^{N} \beta_j(X)(\psi_n + \phi_{jn}) = 0 \qquad n = 0, 1, \ldots, \qquad [65]$$

$$\frac{d^2\phi_{jn}}{dX^2} + i\gamma_j(\psi_{n-2} + \phi_{j,n-2}) = z_j \frac{dY^0}{dX}\left(\frac{d\phi_{jn}}{dX} + A_n\right) \qquad n = 0, 1, \ldots. \qquad [66]$$

The boundary conditions [58]–[60] become

$$\psi_0(0) = 1, \qquad [67]$$

$$\psi_j(0) = 0 \qquad j \geqslant 1, \qquad [68]$$

$$\frac{d\phi_{jn}(0)}{dX} = \begin{cases} -A_n & n \geqslant 2 \\ 0 & n = 0, 1 \end{cases} \qquad [69]$$

$$\frac{d\psi_n(0)}{dX} = -iK_0 A_{n+2}, \qquad [70]$$

where

$$K_0 \equiv \sum_{j=1}^{N} \frac{\beta_j^\infty}{\gamma_j} = \frac{\bar{\lambda}}{e^2 \sum_{k=1}^{N} n_k^\infty z_k^2} K(0). \qquad [71]$$

From Eq. [66] we have, to $O(\delta^0)$ and $O(\delta)$,

$$\frac{d^2\phi_{jn}}{dX^2} = z_j \frac{dY^0}{dX}\frac{d\phi_{jn}}{dX} \qquad n = 0, 1; j = 1, 2, \ldots, N. \qquad [72]$$

Straightforward integration of this equation yields

$$\frac{d\phi_{jn}}{dX} e^{-z_j Y^0(X)} = 0 \qquad n = 0, 1; j = 1, 2, \ldots, N, \qquad [73]$$

and using boundary condition [69] we obtain

$$\phi_{jn} = d_{jn} = \text{const.} \qquad n = 0, 1; j = 1, 2, \ldots, N. \qquad [74]$$

Equation [65] then reads

$$\frac{d^2\psi_n}{dX^2} - \sum_{j=1}^{N} \beta_j(X)\psi_n = \sum_{j=1}^{N} \beta_j(X) d_{jn}, \qquad n = 0, 1, \qquad [75]$$

and the solutions of the corresponding homogeneous equation,

$$\frac{\partial^2\psi_n}{\partial X^2} - \sum_{j=1}^{N} \beta_j(X)\psi_n = 0, \qquad [76]$$

are easily obtained by differentiating [14] and noting that

$$y_1(X) = \frac{dY^0}{dX} \qquad [77]$$

is a decaying solution of Eq. [76]. Factoring off this solution yields a second solution

$$y_2(X) = \frac{dY^0}{dX} \int_0^X dx' \left(\frac{dY^0(x')}{dx'}\right)^{-2} \qquad [78]$$

which grows exponentially with X. A particular solution of [75] is then readily obtained by variation of parameters to be

$$\psi_n^{\mathrm{PS}} = -\frac{dY^0}{dX} \sum_{j=1}^{N} \frac{d_{jn}}{z_j} \int_0^X dx' \left(\frac{dY^0(x')}{dx'}\right)^{-2}, \qquad n = 0, 1, \qquad [79]$$

using integration by parts and Eq. [55], and displays the large X behavior

$$\psi_n^{\mathrm{PS}} \sim \sum_{j=1}^{N} \frac{d_{jn}\beta_j^{\infty}}{z_j}\, y_2(X), \qquad n = 0, 1. \qquad [80]$$

We will see in Section 3.2 that the outer solutions for the ψ_n approach constants for small S (X fixed, $\delta \rightarrow 0$); hence the inner solutions for the ψ_n are not permitted to diverge exponentially with large X. Thus, the only linear combination of the two complementary solutions [77] and [78], and the particular solution [79] which does not diverge exponentially with X is

$$\psi_n(X) = a_n \frac{dY^0}{dX} + \frac{dY^0}{dX} \sum_{j=1}^{N} \frac{d_{jn}}{z_j} \times \int_0^X dx' \,(\beta_j^{\infty} - \beta_j(x'))\left(\frac{dY^0}{dx'}\right)^{-2}, \qquad n = 0, 1, \qquad [81]$$

where we must have

$$a_0 = \left(\frac{dY^0(0)}{dX}\right)^{-1} \qquad [82]$$

and

$$a_1 = 0 \qquad [83]$$

to satisfy [67] and [68].

3.2. *Formalism for Outer Solutions*

Far outside the double-layer region we seek a solution of form

$$\psi(S) = \sum_{n=0}^{\infty} \delta^n \psi_n(S) \qquad [84]$$

$$\phi_j(S) = \sum_{n=0}^{\infty} \delta^n \phi_{jn}(S), \qquad [85]$$

which is asymptotic for fixed S as $\delta \rightarrow 0$. Now $Y^0(X)$ is a solution of the Poisson–Boltzmann equation [14] and decays like $e^{-X} = e^{-S/\delta}$ far outside the double layer, so for fixed S,

$$\lim_{\delta \rightarrow 0} \frac{e^{-S/\delta}}{\delta^p} = 0 \qquad [86]$$

for any finite p. Hence the term proportional to dY^0/dX is dropped from Eq. [50], and $\beta_j(X) \rightarrow \beta_j^{\infty}$, so we obtain the following hierarchy of equations from [49], [50], [84], and [85]:

$$\frac{d^2\psi_{n-2}}{dS^2} - \sum_{j=1}^{N} \beta_j^{\infty}(\psi_n + \phi_{jn}) = 0, \qquad n = 0, 1, \ldots, \qquad [87]$$

$$\frac{d^2\phi_{jn}}{dS^2} + i\gamma_j(\psi_n + \phi_{jn}) = 0, \qquad n = 0, 1, \ldots, \qquad [88]$$

where the boundary condition is

$$\left.\begin{matrix}\psi(S)\\ \phi_j(S)\end{matrix}\right\} \rightarrow 0 \qquad \text{as } S \rightarrow \infty, \qquad [89]$$

Now if we construct the vector

$$\mathbf{R}^{(n)} = \begin{bmatrix} \phi_{1n} \\ \phi_{2n} \\ \vdots \\ \phi_{Nn} \\ \psi_n \end{bmatrix} \qquad [90]$$

corresponding to the nth-order solution of [87] and [88], it is clear that these equations can be written in terms of $\mathbf{R}^{(n)}$ as

$$\begin{bmatrix} D^2 + i\gamma_1 & 0 & \cdots & 0 & i\gamma_1 \\ 0 & D^2 + i\gamma_2 & \cdots & 0 & i\gamma_2 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & \cdots & D^2 + i\gamma_N & i\gamma_N \\ \beta_1^{\infty} & \beta_2^{\infty} & \cdots & \beta_N^{\infty} & 1 \end{bmatrix} \mathbf{R}^{(n)} = \begin{bmatrix} 0 \\ 0 \\ \vdots \\ 0 \\ D^2\psi_{n-2}(n \geqslant 2) \end{bmatrix} \qquad [91]$$

where $D^2 = d^2/dS^2$. Thus for $n = 0, 1$, this system is homogeneous, and we may use the decaying ansatz $\mathbf{R}^{(n)} = \mathbf{R}_\alpha^{(n)} e^{-\sqrt{\alpha}S}$ to obtain the matrix equation

$$\begin{bmatrix} \alpha + i\gamma_1 & 0 & \cdots & 0 & i\gamma_1 \\ 0 & \alpha + i\gamma_2 & \cdots & 0 & i\gamma_2 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & \cdots & \alpha + i\gamma_N & i\gamma_N \\ \beta_1^{\infty} & \beta_2^{\infty} & \cdots & \beta_N^{\infty} & 1 \end{bmatrix} \mathbf{R}_\alpha^{(n)} = 0 \qquad n = 0, 1. \qquad [92]$$

For a nontrivial solution, the determinant of the coefficient matrix in [92] must vanish, and this leads to the characteristic or eigenvalue equation

$$P_N(\alpha) = \prod_{j=1}^{N} (\alpha + i\gamma_j)\left(1 - \sum_{k=1}^{N} \frac{i\gamma_k\beta_k^{\infty}}{i\gamma_k + \alpha}\right) = 0. \qquad [93]$$

In practice, the γ_j are all different, leading to distinct roots $\alpha \neq -i\gamma_k$, so [93] may be written in the reduced form

$$f(\alpha) = 1 - \sum_{l=1}^{N} \frac{i\gamma_l \beta_l^\infty}{i\gamma_l + \alpha} = 0. \qquad [94]$$

It is then a trivial matter to demonstrate that all the roots of [94] are pure imaginary and have negative imaginary components. For each root α_k of [94], one can construct a solution $\mathbf{R}_k^{(n)}$ of [92] using the sparseness of the coefficient matrix. Such a $\mathbf{R}_k^{(n)}$ has components

$$\mathbf{R}_{jk}^{(n)} = \frac{i\gamma_j}{i\gamma_j + \alpha_k}, \qquad j, k = 1, 2, \ldots, N; n = 0, 1, \qquad [95]$$

$$\mathbf{R}_{N+1,k}^{(n)} = -1, \qquad k = 1, 2, \ldots, N; n = 0, 1. \qquad [96]$$

Hence a complete solution of [92] may be formed by linear superposition, yielding

$$\phi_{jn} = \sum_{k=1}^{N} \frac{i\gamma_j C_k^{(n)}}{i\gamma_j + \alpha_k} e^{-\sqrt{\alpha_k}S}, \qquad n = 0, 1, \qquad [97]$$

$$\psi_n = -\sum_{k=1}^{N} C_k^{(n)} e^{-\sqrt{\alpha_k}S}, \qquad n = 0, 1, \qquad [98]$$

where the $C_k^{(n)}$ are constants yet to be determined. Observe that $\alpha = 0$ is always a solution of [94], since $\sum \beta_k^\infty = 1$; we denote this root by $\alpha_1 = 0$ and conclude that $C_0^{(n)} = 0$, since the ψ_n and ϕ_{jn} must approach zero for large S by boundary condition [89].

3.3. *Matching the Zeroth- and First-Order Solutions*

We now seek to match the asymptotic expansions of [74] (for large X) to the asymptotic forms of [97] for small S (fixed but large X, $\delta \to 0$). In the outer functions, we take $S \to \delta X$ and write the exponentials as power series in δ. To order δ, this yields

$$\phi_j^{(\text{inner})}(X) = \phi_{j0}(X) + \delta\phi_{j1}(X) + \cdots \qquad [99]$$

$$\sim d_{j0} + \delta d_{j1} + \cdots \qquad [100]$$

and

$$\phi_j^{(\text{outer})}(S) = \phi_{j0}(S) + \delta\phi_{j1}(S) + \cdots \qquad [101]$$

$$\sim \sum_{k=1}^{N} \frac{i\gamma_j C_k^{(0)}}{i\gamma_j + \alpha_k}(1 - \sqrt{\alpha_k}\delta X + O(\delta^2))$$

$$+ \delta \sum_{k=1}^{N} \frac{i\gamma_j C_k^{(1)}}{i\gamma_j + \alpha_k}(1 + O(\delta)), \qquad [102]$$

and equating powers of δ we obtain

$$d_{j0} = \sum_{k=1}^{N} \frac{i\gamma_j C_k^{(0)}}{i\gamma_j + \alpha_k} \qquad [103]$$

$$d_{j1} = \sum_{k=1}^{N} \frac{i\gamma_j}{i\gamma_j + \alpha_k}(C_k^{(1)} - \sqrt{\alpha_k} X C_k^{(0)}). \qquad [104]$$

Clearly the only possible match for all X is obtained by setting

$$C_k^{(0)} = 0 \Leftrightarrow d_{j0} = 0, \qquad j, k = 1, 2, \ldots, N, \qquad [105]$$

and

$$d_{j1} = \sum_{k=1}^{N} \frac{i\gamma_j C_k^{(1)}}{i\gamma_j + \alpha_k} \qquad j = 1, 2, \ldots, N, \qquad [106]$$

and thus

$$\phi_{j0}(X) = 0 \qquad \text{(inner)}, \qquad [107]$$

$$\phi_{j0}(S) = 0 \qquad \text{(outer)}, \qquad [108]$$

$$\psi_0(S) = 0 \qquad \text{(outer)}. \qquad [109]$$

Hence we know $\psi_0(X)$ completely; by Eqs. [81] and [105],

$$\psi_0(X) = a_0 \frac{dY^0}{dX}, \qquad [110]$$

and we write

$$a_0(\zeta) = \left(\frac{dY^0(0)}{dX}\right)^{-1} = -\left(\frac{\epsilon k T \kappa}{4\pi e \sigma(\zeta)}\right), \qquad [111]$$

since, from [45] and [52],

$$\frac{\kappa k T}{e}\frac{dY^0(0)}{dX} = \frac{d\Psi^0(0)}{dx} = \frac{-4\pi\sigma(\zeta)}{\epsilon}, \qquad [112]$$

where $\sigma(\zeta)$ is the charge density behind the slipping plane $X = 0$. We obtain the constant a_0 by rewriting the Poisson–Boltzmann equation ([14], [15]) in dimensionless units as

$$\frac{d^2Y^0}{dX^2} = -\sum_{j=1}^{N} \frac{\beta_j^\infty}{z_j} e^{-z_j Y^0(X)} \qquad [113]$$

and obtaining the first integral

$$\left(\frac{dY^0}{dX}\right)^2 = 2\sum_{j=1}^{N} \frac{\beta_j^\infty}{z_j^2}(e^{-z_j Y^0(X)} - 1), \qquad [114]$$

where we have used the electroneutrality condition $\sum \beta_j^\infty / z_j = 0$ and the obvious boundary condition $dY^0/dX \to 0$ as $X \to \infty$. From [111] and [114] we then obtain

$$a_0(\bar{\zeta}) = -\operatorname{sgn}(\zeta)\left[2 \sum_{j=1}^{N} \frac{\beta_j^\infty}{z_j^2} (e^{-z_j\bar{\zeta}} - 1)\right]^{-1/2}, \quad [115]$$

where $Y^0(0) \equiv \bar{\zeta} = e\zeta/kT$ is the scaled potential at the slipping plane.

We then compute A_2 from [70] using the relations [110] and [113];

$$A_2 = \frac{i}{K_0} \frac{d\psi_0(0)}{dX} = \frac{-ia_0(\bar{\zeta})}{K_0} \sum_{n=1}^{N} \frac{\beta_n^\infty}{z_n} e^{-z_n\bar{\zeta}}. \quad [116]$$

The combined expressions [116] and [115] thus constitute an explicit closed formula for the leading order capacitive term A_2. Note that this expression is precisely equivalent to the Gouy–Chapman–Grahame differential capacitance $d\sigma/d\zeta$, since

$$\frac{d\sigma}{d\zeta} = \frac{-iK_0\epsilon\kappa}{4\pi} A_2. \quad [117]$$

We can now extract the large X behavior of $\psi_1(X)$ from Eq. [81], using the fact that for large X,

$$Y^0(X) \sim e^{-X} \quad [118]$$

$$\beta_j^\infty - \beta_j(X) \sim z_j\beta_j^\infty Y^0(X). \quad [119]$$

We thereby obtain

$$\psi_1(X) \sim -\sum_{j=1}^{N} \beta_j^\infty d_{j1}, \quad [120]$$

and if we now match the inner and outer solutions for ψ to $O(\delta)$ using Eqs. [81], [83], and [98], the following equation results:

$$-\sum_{j=1}^{N} \beta_j^\infty d_{j1} = \sum_{k=1}^{N} C_k^{(1)}. \quad [121]$$

Substitution of [106] into [121] and use of the eigenvalue equation [94] shows that the matching is consistent, i.e., matching ψ_1 yields no more information. This phenomenon turns out to be a general property of this problem: the equations obtained from matching the ψ_n are linearly dependent on the equations extracted from matching the ϕ_{jn}.

3.4. Matching the Second-Order Solutions

To find the higher-order A_i, we proceed to examine the higher-order differential equations. Since the outer solution $\psi_0(S) = 0$, Eq. [91] is now homogeneous to second order ($n = 2$), and hence the second-order outer solution may immediately be written down by analogy with Eqs. [97] and [98]:

$$\phi_{j2} = \sum_{k=1}^{N} \frac{i\gamma_j C_k^{(2)}}{i\gamma_j + \alpha_k} e^{-\sqrt{\alpha_k}S} \quad [122]$$

$$\psi_2 = -\sum_{k=1}^{N} C_k^{(2)} e^{-\sqrt{\alpha_k}S}, \quad [123]$$

where the $C_k^{(2)}$ are constants to be determined from the boundary conditions and matching equations.

The inner solution for $\phi_{j2}(X)$ is obtained from the differential equation

$$\frac{d^2\phi_{j2}}{dX^2} - z_j \frac{dY^0}{dX} \frac{d\phi_{j2}}{dX} = (z_jA_2 - ia_0\gamma_j) \frac{dY^0}{dX} \quad [124]$$

which is readily extracted from [66] with use of [110]. This is straightforward to integrate, using the boundary condition [69], yielding

$$\frac{d\phi_{j2}}{dX} = \left(\frac{ia_0\gamma_j}{z_j} - A_2\right) - \frac{ia_0\gamma_j}{z_j} e^{z_j(Y^0(X)-\bar{\zeta})}. \quad [125]$$

A further integration gives

$$\phi_{j2} = \left(\frac{ia_0\gamma_j}{z_j} - A_2\right)X - \frac{ia_0\gamma_j}{z_j} e^{-z_j\bar{\zeta}} \int_0^X e^{z_jY^0(x')}dx' + k_j, \quad [126]$$

where k_j is some constant of integration. In terms of the quantities

$$I_j^{\pm}(\bar{\zeta}) \equiv \int_0^\infty (e^{\pm z_jY^0(x')} - 1)dx', \quad [127]$$

$\phi_{j2}(X)$ has the following large X asymptotic expansion:

$$\phi_{j2}(X) \sim \left(\frac{ia_0\gamma_j}{z_j}(1 - e^{-z_j\bar{\zeta}}) - A_2\right)X - \frac{ia_0\gamma_je^{-z_j\bar{\zeta}}}{z_j} I_j^+ + k_j + O(e^{-X}). \quad [128]$$

Hence, if we collect all $O(\delta^2)$ terms in the inner expansion for $\phi_j = \phi_{j0} + \delta\phi_{j1} + \cdots$, we obtain

$$\phi_j(X) \sim \left(\frac{ia_0\gamma_j}{z_j}(1 - e^{-z_j\bar{\zeta}}) - A_2\right)X - \frac{ia_0\gamma_je^{-z_j\bar{\zeta}}}{z_j} I_j^+ + k_j \quad [129]$$

at $O(\delta^2)$, using [74] and [128]. The outer series obtained from [97] and [122], with $S \to \delta X$, produces the $O(\delta^2)$ terms:

$$\phi_j(S) \sim -\sum_{k=1}^{N} \frac{i\gamma_j\sqrt{\alpha_k}C_k^{(1)}X}{i\gamma_j + \alpha_k} + \sum_{k=1}^{N} \frac{i\gamma_j C_k^{(2)}}{i\gamma_j + \alpha_k}, \quad [130]$$

whence we obtain the following matching equations

$$\sum_{k=1}^{N} \frac{i\gamma_j C_k^{(2)}}{i\gamma_j + \alpha_k} = k_j - \frac{ia_0\gamma_j e^{-z_j\bar{\xi}}}{z_j} I_j^+ \quad [131]$$

and

$$-\sum_{k=1}^{N} \frac{i\gamma_j\sqrt{\alpha_k}C_k^{(1)}}{i\gamma_j + \alpha_k} = \frac{ia_0\gamma_j}{z_j}(1 - e^{-z_j\bar{\xi}}) - A_2,$$

$$j = 1, 2, \ldots, N. \quad [132]$$

The last expression is a set of N simultaneous equations for the $C_k^{(1)}$ which may be solved explicitly using some results derived in the Appendix. Inspired by the relations [189] and [191] in the Appendix, we obtain the $C_k^{(1)}$ by premultiplying both sides of [132] by $\beta_j^\infty/(N_k((i\gamma_j + \alpha_{k'}))$ and summing over j. This gives

$$C_{k'}^{(1)}\sqrt{\alpha_{k'}} = -\sum_{j=1}^{N} \frac{i\beta_j^\infty\gamma_j a_0(1 - e^{-z_j\bar{\xi}})}{N_{k'}z_j(i\gamma_j + \alpha_{k'})}, \qquad k' \neq 0, \quad [133]$$

where N_k is the normalization constant defined by [190], and we know already that $C_0^{(1)} = 0$ since the $\phi_{j1}(S)$ must go to zero as $S \to 0$. Thus, given the roots α_k of [94], we can compute the $C_k^{(1)}$ via [133], and, using [106], we obtain

$$d_{l1} = a_0\gamma_l \sum_{j=1,k=2}^{N} \frac{\alpha_k^{-1/2}\beta_j^\infty\gamma_j(1 - e^{-z_j\bar{\xi}})}{N_k z_j(i\gamma_j + \alpha_k)(i\gamma_l + \alpha_k)}. \quad [134]$$

Now from [70], [81], [83], and using [82], we get

$$A_3 = \frac{i}{K_0}\frac{d\psi_1(0)}{dx} = \frac{ia_0}{K_0}\sum_{l=1}^{N} \frac{d_{l1}\beta_l^\infty}{z_l}(1 - e^{-z_l\bar{\xi}})$$

$$= \frac{ia_0^2}{K_0}\sum_{k=2}^{N} \frac{\alpha_k^{-1/2}}{N_k}\left(\sum_{l=1}^{N} \frac{\gamma_l\beta_l^\infty(1 - e^{-z_l\bar{\xi}})}{z_l(i\gamma_l + \alpha_k)}\right)^2 \quad [135]$$

3.5. Matching the Third-Order Solutions

The third order equation [91] (i.e., $n = 3$) requires the inhomogeneous term

$$\frac{d^2\psi_1(S)}{dS^2} = -\sum_{k=1}^{N} C_k^{(1)}\alpha_k e^{-\sqrt{\alpha_k}S} \quad [136]$$

which we obtain from [98]. This term contains all of the complementary solutions $e^{-\sqrt{\alpha_k}S}$, so a particular solution will be of the form

$$\mathbf{R}_{jk}^{(3)\mathrm{PS}} = \sum_{k=1}^{N} (C_{jk}^{(3,1)}S + C_{jk}^{(3,0)})e^{-\sqrt{\alpha_k}S},$$

$$j = 1, 2, \ldots, N + 1, \quad [137]$$

where $C_{jk}^{(3,1)}$ and $C_{jk}^{(3,0)}$ are constants. It is then straightforward to show that such an ansatz leads to the relations

$$C_{jk}^{(3,1)} = \frac{-i\gamma_j}{\alpha_k + i\gamma_j} C_{N+1,k}^{(3,1)}, \quad [138]$$

$$C_{jk}^{(3,0)} = \frac{-i\gamma_j}{\alpha_k + i\gamma_j}\left(C_{N+1,k}^{(3,0)} + \frac{2\sqrt{\alpha_k}C_{N+1,k}^{(3,1)}}{\alpha_k + i\gamma_j}\right). \quad [139]$$

Once a complementary solution of similar form to Eqs. [122] and [123] is added to the particular solution to form a general solution $\mathbf{R}^{(3)} = (\phi_{13}, \phi_{23}, \ldots, \psi_3)$, it is clear that the small S limit of $\delta^3\phi_{j3}$ (with $S \to \delta X$) contributes no X-dependent terms of order δ^3 to ϕ_j. Hence any $O(\delta^3 X)$ and $O(\delta^3 X^2)$ terms must come from $\phi_{j1}(S)$ and $\phi_{j2}(S)$.

To find the complete inner solution for $\psi_2(X)$, some slightly messy asymptotic expansions are required, so we introduce the notation

$$U_j = \frac{ia_0\gamma_j}{z_j} - A_2 \quad [140]$$

$$V_j = \frac{ia_0\gamma_j}{z_j} e^{-z_j\bar{\xi}} \quad [141]$$

to contain the length of the required expressions. In terms of these constants, the differential equation for the inner solution $\psi_2(X)$ obtained from [65] reads

$$\frac{d^2\psi_2}{dX^2} - \sum_{j=1}^{N} \beta_j(X)\psi_2$$

$$= \sum_{j=1}^{N} \beta_j(X)\left(U_jX - V_j\int_0^X e^{z_jY^0(x')}dx' + k_j\right), \quad [142]$$

using the solution for $\phi_{j2}(X)$ in Eq. [126]. The homogeneous equation has the complementary solutions $y_1(X)$ and $y_2(X)$ given by [77] and [78], so the method of variation of parameters yields the particular solution

$$\begin{aligned}\psi_2^{\mathrm{PS}}&(X)\\ &= -\frac{dY^0}{dX}\int_0^X dx\sum_{j=1}^N \beta_j(x)\left(U_jx - V_j\int_0^x e^{z_jY^0(x')}dx' + k_j\right)\\ &\quad\times\frac{dY^0}{dx}\int_0^x dx''\left(\frac{dY^0}{dx''}\right)^{-2}\\ &\quad+\frac{dY^0}{dX}\int_0^X dx'\left(\frac{dY^0}{dx'}\right)^{-2}\int_0^X dx\sum_{j=1}^N \beta_j(x)\\ &\qquad\times\left(U_jx - V_j\int_0^x e^{z_jY^0(x'')}dx'' + k_j\right)\frac{dY^0}{dx}. \qquad [143]\end{aligned}$$

It is not difficult to show that this particular solution diverges exponentially like $y_2(X)$, and that its large X behavior is

$$\begin{aligned}\psi_2^{\mathrm{PS}}(X) \sim \sum_{j=1}^N\Bigg[&\frac{-k_j\beta_j^\infty}{z_j}(1-e^{-z_j\bar{\zeta}}) + \left(\frac{ia_0\gamma_j}{z_j} - A_2\right)\frac{\beta_j^\infty}{z_j}I^-\\ &+\frac{ia_0\beta_j^\infty\gamma_j}{z_j^2}e^{-z_j\bar{\zeta}}I^+\Bigg]y_2(X). \qquad [144]\end{aligned}$$

Hence the coefficient of $y_2(X)$ in the general solution of [142] must be assigned to cancel this exponential divergence, so if we write

$$\psi_2(X) = a_2y_1(X) + b_2y_2(X) + \psi_2^{\mathrm{PS}}(X), \qquad [145]$$

then

$$\begin{aligned}b_2 = -\sum_{j=1}^N\Bigg[&\frac{-k_j\beta_j^\infty}{z_j}(1-e^{-z_j\bar{\zeta}})\\ &+\frac{ia_0\gamma_j\beta_j^\infty}{z_j^2}(I_j^- + I_j^+e^{-z_j\bar{\zeta}}) - \frac{A_2\beta_j^\infty I_j^-}{z_j}\Bigg]. \qquad [146]\end{aligned}$$

Now, by boundary condition [68], $\psi_2(0) = 0$; therefore

$$a_2 = 0, \qquad [147]$$

since $y_2(0) = \psi_2^{\mathrm{PS}}(0) = 0$.

Proceeding to third order, the differential equation for $\phi_{j3}(X)$ obtained from [66] is

$$\frac{d^2\phi_{j3}}{dX^2} - z_j\frac{dY^0}{dX}\frac{d\phi_{j3}}{dX} = z_jA_3\frac{dY^0}{dX} - i\gamma_j(\psi_1 + \phi_{j1}), \qquad [148]$$

and using the boundary condition

$$\frac{d\phi_{j3}}{dX} = -A_3 \qquad [149]$$

obtained from [69], it is straightforward to integrate [148] and obtain

$$\begin{aligned}\frac{d\phi_{j3}}{dX} = -A_3 - i\gamma_je^{z_jY^0(X)}\Bigg(&\int_0^X \psi_1(x)e^{-z_jY^0(x)}dx\\ &+ d_{j1}\int_0^X e^{-z_jY^0(x)}dx\Bigg), \qquad [150]\end{aligned}$$

using [74]. Now both of these integrals are linearly divergent, so to find an asymptotic form for $\phi_{j3}(X)$ for large X, we first compute

$$\begin{aligned}\int_0^X e^{-z_jY^0(x)}dx &= X + \int_0^X (e^{-z_jY^0(x)} - 1)dx\\ &= X + I_j^- + O(e^{-X}), \qquad [151]\end{aligned}$$

and using [120] we obtain

$$\begin{aligned}\int_0^X \psi_1(x)e^{-z_jY^0(x)}dx &= \int_0^X (\psi_1(x)e^{-z_jY^0(x)}\\ &\quad+\sum_{j=1}^N \beta_j^\infty d_{j1})dx - X\sum_{j=1}^N \beta_j^\infty d_{j1}\\ &\sim \int_0^\infty (\psi_1(x)e^{-z_jY^0(x)} + \sum_{j=1}^N \beta_j^\infty d_{j1})dx\\ &\qquad - X\sum_{j=1}^N \beta_j^\infty d_{j1} + O(e^{-X}). \qquad [152]\end{aligned}$$

Use of Eq. [81] and integration by parts reveals that the definite integral

$$\begin{aligned}\int_0^\infty (\psi_1(x)e^{-z_jY^0(x)} &+ \sum_{j=1}^N \beta_j^\infty d_{j1})dx\\ &= \sum_{j=1}^N \beta_j^\infty d_{j1}(1 - L_j), \qquad [153]\end{aligned}$$

where

$$L_j(\bar{\zeta}) \equiv \int_0^\infty\left[\left(\frac{1 - e^{-z_jY^0(X)}}{z_j}\right)^2\left(\frac{dY^0}{dX}\right)^{-2} - 1\right]dX \qquad [154]$$

is implicitly a function of the zeta potential via $Y^0(X)$. [Note that explicit expressions for the $L_j(\bar{\zeta})$ and $I_j^\pm(\bar{\zeta})$ (Eq. [127]) can usually be found by changing the variable of integration from X to $\exp(-Y^0(X))$ via the first integral [114], and performing the resulting integral. A full solution $Y^0(X)$ of the nonlinear Poisson–Boltzmann equation is thus not required.]

Hence $d\phi_{j3}/dX$ has the large X behavior

$$\frac{d\phi_{j3}}{dX} = -A_3 - i\gamma_j(\sum_{k=1}^{N} \beta_k^\infty d_{k1}(1 - L_k - X) + d_{j1}(I_j^- + X)) + O(e^{-X}), \quad [155]$$

which may be integrated to give

$$\phi_{j3}(X) \sim \frac{i\gamma_j}{2}(\sum_{k=1}^{N} \beta_k^\infty d_{k1} - d_{j1})X^2 - (A_3 + i\gamma_j(\sum_{k=1}^{N} \beta_k^\infty d_{k1}(1 - L_k) + d_{j1}I_j^-))X + \mathrm{O}(1, e^{-X}). \quad [156]$$

We now match the inner and outer solutions for ϕ_j to $O(\delta^3)$. Equations [97], [122], and [123] contribute the following $O(\delta^3)$ expression to the outer expansion:

$$\phi_j(S) \sim \sum_{k=1}^{N} \frac{i\gamma_j}{i\gamma_j + \alpha_k}\left(\frac{\alpha_k X^2 C_k^{(1)}}{2} - \sqrt{\alpha_k} X C_k^{(2)} + O(X^0)\right) \quad (\text{at } O(\delta^3)). \quad [157]$$

Matching the powers of X to the inner expansion of $O(\delta^3)$, Eq. [156], yields the equations

$$\sum_{k=1}^{N} \frac{i\gamma_j \alpha_k C_k^{(1)}}{i\gamma_j + \alpha_k} = i\gamma_j(\sum_{k=1}^{N} \beta_k^\infty d_{k1} - d_{j1}), \quad [158]$$

and

$$\sum_{k=1}^{N} \frac{i\gamma_j \sqrt{\alpha_k} C_k^{(2)}}{i\gamma_j + \alpha_k} = A_3 + i\gamma_j(\sum_{k=1}^{N} \beta_k^\infty d_{k1}(1 - L_k) + d_{j1}I_j^-)). \quad [159]$$

It is trivial to show that the former of these two equations is identically satisfied by Eq. [106], using the eigenvalue equation [94], and thus provides no more information. The second equation [159] can be manipulated to give explicit solutions for the $C_k^{(2)}$ using the same technique applied to Eq. [132]. If we multiply by $\beta_j^\infty/(N_{k'}(i\gamma_j + \alpha_{k'}))$ and sum over j, we obtain

$$\begin{aligned}\sqrt{\alpha_k} C_k^{(2)} &= \sum_{j=1}^{N} \frac{i\beta_j^\infty \gamma_j}{N_k(i\gamma_j + \alpha_k)} \times (\sum_{l=1}^{N} \beta_l^\infty d_{l1}(1 - L_l) + d_{j1}I_j^-), \qquad k \neq 0,\\ &= \frac{1}{N_k}(\sum_{j=1}^{N} \beta_j^\infty d_{j1}(1 - L_j) + \sum_{j=1}^{N} \frac{i\beta_j^\infty \gamma_j d_{j1} I_j^-}{(i\gamma_j + \alpha_k)}\right), \qquad k \neq 0, \quad [160]\end{aligned}$$

using [94]. Naturally $C_0^{(2)} = 0$ by the same arguments advanced previously. We now use [131] to obtain the k_j,

$$k_j = \frac{ia_0\gamma_j e^{-z_j\bar{\zeta}} I_j^+}{z_j} + \sum_{k=2}^{N} \frac{i\gamma_j \alpha_k^{-1/2}}{N_k(i\gamma_j + \alpha_k)} \times \sum_{l=1}^{N}\left(\beta_l^\infty d_{l1}(1 - L_l) + \frac{i\beta_l^\infty \gamma_l d_{l1} I_l^-}{(i\gamma_l + \alpha_k)}\right), \quad [161]$$

and then find b_2 from [146],

$$b_2 = \sum_{j=1}^{N}\left\{\frac{A_2\beta_j^\infty I_j^-}{z_j} - \frac{ia_0\gamma_j\beta_j^\infty}{z_j^2}(I_j^- + I_j^+ e^{-z_j\bar{\zeta}}) + \frac{\beta_j^\infty}{z_j}(1 - e^{-z_j\bar{\zeta}}) \times \left(\frac{ia_0\gamma_j e^{-z_j\bar{\zeta}} I_j^+}{z_j} + \sum_{k=2}^{N} \frac{i\gamma_j \alpha_k^{-1/2}}{N_k(i\gamma_j + \alpha_k)} \sum_{l=1}^{N}\left(\beta_l^\infty d_{l1}(1 - L_l) + \frac{i\beta_l^\infty \gamma_l d_{l1} I_l^-}{(i\gamma_l + \alpha_k)}\right)\right)\right\}, \quad [162]$$

where d_{l1} is given by Eq. [134].

Thus, using Eqs. [70], [145], [146], [147], and [143], we obtain

$$A_4 = \frac{i}{K_0}\frac{d\psi_2(0)}{dX} = \frac{ia_0 b_2}{K_0}, \quad [163]$$

which is readily computable from formulas [162], [134], [127], and [154], given the roots α_k of [94].

4. SOME PROPERTIES OF THE COEFFICIENTS A_2, A_3, AND A_4

4.1. General Comments

It is important to note that the A_i are independent of concentration: the dependence of $Z_{el}\kappa K(\omega)$ on concentration is confined entirely to the κ dependence of the various powers of δ. Thus, while in an experimental situation a change in concentration might result in a shift in the zeta potential, nevertheless the measured values of A_i must still lie on the same universal curve $A_i(\bar{\zeta})$.

Furthermore, the real and imaginary parts of the A_i follow the following general scheme. From [116] and [115] it is clear that $A_2(\bar{\zeta})$ is always pure imaginary, and since the α_k are always pure imaginary, it is easy to show from [135] and [190] that $A_3(\bar{\zeta})$ has equal real and imaginary parts. Similarly, it is not too difficult to show from [163], [162], and [134] that $A_4(\bar{\zeta})$ is always pure real.

As one might expect, the A_i generally increase in magnitude for fixed $\bar{\zeta}$ as one goes to higher order (see, for example, Figs. 2 and 4). Such a phenomenon is typical of asymptotic series. Note also that the growth of the A_i curves is regulated by the counterion charge, so highly charged counterions lead to extremely rapid growth in the higher-order A_i.

4.2. *Limiting Values for $\zeta = 0$*

Some care needs to be taken when computing $A_2(\zeta)$, $A_3(\zeta)$, and $A_4(\zeta)$ from Eqs. [116], [135], and [163] for small ζ, since $a_0(\zeta) \rightarrow \infty$ as $\zeta \rightarrow 0$. The limiting forms of these equations are

$$\lim_{\zeta\to 0} A_2(\zeta) = \frac{-i}{K_0}, \qquad [164]$$

$$\lim_{\zeta\to 0} A_3(\zeta) = \frac{-i}{K_0} \sum_{k=2}^{N} \frac{\alpha_k^{-1/2}}{\left(\sum_{j=1}^{N} \frac{i\beta_j^{\infty}\gamma_j}{(i\gamma_j + \alpha_k)^2}\right)}, \qquad [165]$$

$$\lim_{\zeta\to 0} A_4(\zeta) = \frac{-i}{K_0}\left[\frac{i}{K_0} - \frac{3i}{2}\sum_{j=1}^{N} \beta_j^{\infty}\gamma_j + \left(\sum_{k=2}^{N} \frac{\alpha_k^{-1/2}}{\left(\sum_{j=1}^{N} \frac{i\beta_j^{\infty}\gamma_i}{(i\gamma_j + \alpha_k)^2}\right)}\right)^2\right]. \qquad [166]$$

4.3. *Simplified Results for Two Ion Systems*

These results simplify considerably if $N = 2$. The eigenvalue α_2 is the only nonzero root of the quadratic characteristic equation of the system [94]:

$$\alpha_2 = -i(\gamma_1\beta_2^{\infty} + \gamma_2\beta_1^{\infty}). \qquad [167]$$

Hence we have, from Eqs. [116] and [135],

$$A_2 = \frac{-ia_0}{K_0} \sum_{j=1}^{2} \frac{\beta_j^{\infty}}{z_j} e^{-z_j\bar{\zeta}}, \qquad [168]$$

and

$$A_3 = \frac{a_0^2}{K_0} \frac{(1+i)\sqrt{1/(2(\gamma_1\beta_2^{\infty} + \gamma_2\beta_1^{\infty}))}}{\left(\sum_{j=1}^{2} \frac{\beta_j^{\infty}\gamma_j}{(\gamma_j - (\gamma_1\beta_2^{\infty} + \gamma_2\beta_1^{\infty}))^2}\right)} \times \left(\sum_{j=1}^{2} \frac{\beta_j^{\infty}\gamma_j(1 - e^{-z_j\bar{\zeta}})}{z_j(\gamma_j - (\gamma_1\beta_2^{\infty} + \gamma_2\beta_1^{\infty}))}\right)^2, \qquad [169]$$

where

$$a_0 = -\mathrm{sgn}(\zeta)\left[2\sum_{j=1}^{2} \frac{\beta_j^{\infty}}{z_j^2}(e^{-z_j\bar{\zeta}} - 1)\right]^{-1/2} \qquad [170]$$

is readily obtained from [115].

One interesting characteristic of two ion systems is that there is always some value of ζ for which A_3 vanishes. To see this, Eq. [169] can be manipulated to reveal the factor

$$(f_1(\bar{\zeta}) - f_2(\bar{\zeta}))^2, \qquad [171]$$

where

$$f_i(\bar{\zeta}) = \gamma_i(1 - e^{-z_i\bar{\zeta}})/z_i. \qquad [172]$$

Now without loss of generality we may set $z_1 > 0 > z_2$, so $f_1(\bar{\zeta}) \rightarrow \gamma_1/z_1$ as $\bar{\zeta} \rightarrow \infty$, and $f_2(\bar{\zeta}) \rightarrow \gamma_2/z_2$ as $\bar{\zeta} \rightarrow -\infty$. But clearly $f_i(0) = 0$, so the two curves $f_1(\bar{\zeta})$ and $f_2(\bar{\zeta})$ must intersect twice (at $\bar{\zeta} = 0$ and some other value) if their slopes do not match at $\bar{\zeta} = 0$, i.e., $\gamma_1 \neq \gamma_2$. If the salt is symmetric with $|z_1| = |z_2| = z$, it is straightforward to show that $A_3(\bar{\zeta})$ vanishes at

$$\bar{\zeta} = \frac{1}{z}\log(\gamma_1/\gamma_2) = \frac{1}{z}\log(\Lambda_2^{\infty}/\Lambda_1^{\infty}). \qquad [173]$$

and that the curve $A_3(\bar{\zeta})$ is symmetric about this root.

5. DISCUSSION

There are essentially two experimental regimes that reveal the effect of ionic diffusion on the impedance of planar electrodes. First, since the resistance of the diffuse double layer is controlled entirely by ionic diffusion and diverges at low frequencies, it is straightforward to show from the above theory that the diffuse layer resistance effectively competes with the bulk resistance at frequencies of order 10 Hz or less. The signal-to-noise ratio of such measurements clearly improves with decreasing cell dimensions, so we propose a electrode cell spacing of 1 mm or less to maximize the relative contribution of the double-layer resistance.

Second, ionic diffusion effects begin to modify the standard Gouy–Chapman–Grahame differential capacitance when the period of excitation compares to characteristic diffusion time constants or, equivalently, when the Debye screening length κ^{-1} is of the same order as a characteristic diffusion length $(kT/\omega\lambda)^{1/2}$. This is typically in the 100-kHz regime, but for the above theory to be valid, we require typically $\delta < 0.3$ for the asymptotic series (or a suitable accelerated transformation of it) to converge. This amounts to limiting the upper frequency to 10–100 kHz or so, depending on the concentration of the electrolyte.

Any experimental attempt to measure the electrode impedance Z_{el} will have to incorporate a series Stern layer capacitive impedance $Z_{st} = i/\omega C_s$, where C_s is the Stern layer capacitance. This will be a function of the electrode type, the salt concentration, and the zeta potential in general (6). Typically the Stern layer capacitance dominates the diffuse layer capacitance unless the concentration is low, so practical measurements should work with dilute electrolytes (0.001 *M* or less) to maximize the signal-to-noise ratio. Figure 1 is a typical plot of the resistance and capacitance of the

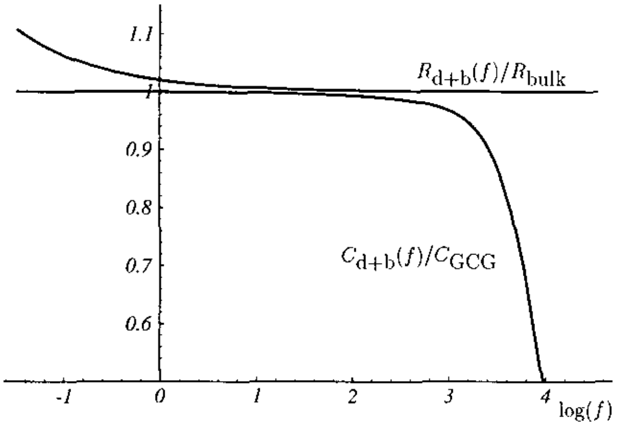

FIG. 1. Typical bulk plus diffuse layer resistance, $R_{d+b}(f)$, and capacitance, $C_{d+b}(f)$, plotted against log(frequency). Calculations are for a 0.001 M KCl electrolyte in a 1-mm cell, with dimensionless zeta potential $\bar{\zeta} = 3$. The resistance is normalized by the bulk resistance R_{bulk}, and the capacitance by the standard Gouy–Chapman–Grahame (GCG) diffuse layer capacitance C_{GCG}. Note that the capacitance of the inner (Stern) layer is omitted.

diffuse layer plus bulk versus log(frequency), taking into account that there are two electrodes. This was computed for 0.001 M KCl in a cell of width 1 mm, where the dimensionless zeta potential was taken arbitrarily to be 3 (i.e., $\zeta = 75$ mV). Note that the values have been normalized by the bulk resistance (for the total resistance) and the Gouy–Chapman–Grahame (GCG) diffuse layer capacitance (for the total capacitance).

Probably the most serious experimental difficulty will be that of impedance dispersion due to surface roughness of the electrodes: this is evident if the capacitance of the cell decreases with increasing frequency in the low-frequency regime. As yet, no completely satisfactory account of this effect has been forthcoming [see, e.g., (20–22)]. One possible experimental solution in this context is to use dropping mercury electrodes (which unfortunately implies large cell dimensions) or electrodes formed from the melt or from single crystals. These restrictions are fairly severe, however, and greatly restrict the applicability of the technique to colloidal systems. More realistically, standard well-polished electrodes could be used, and measurements in strong electrolyte made to determine the dependence of the inner layer capacitance on frequency. In systems where the inner layer capacity is only weakly dependent on electrolyte concentration, this would enable the frequency dependence of the diffuse layer capacitance to be isolated from that of the Stern layer at low concentrations. Notwithstanding the effects of surface roughness, the onset of ionic diffusion effects in the regime 10–100 kHz certainly provides a plausible explanation of the drop in the polarization capacitance observed at these frequencies in the literature; see, e.g., [21, Fig. 7] in Peterson *et al.* (23).

For an ideally smooth electrode exhibiting a constant inner layer capacitance, we may write $Z_{el+st}(\omega)$ to represent the series Stern and double-layer impedance, and from [64], [33], and [47] we construct the series

$$\hat{Z}(\delta) \equiv \left[\frac{\kappa^3 \epsilon k T \delta^2}{4\pi\bar{\lambda}} Z_{el+st}\right]^{-1}$$
$$= B_2 + B_3\delta + B_4\delta^2 + \cdots, \qquad [174]$$

where

$$B_2 = \left(\frac{1}{K_0 A_2} + \frac{i\epsilon\kappa}{4\pi C_s}\right)^{-1} \qquad [175]$$

$$B_3 = \frac{A_3 B_2^2}{K_0 A_2^2} \qquad [176]$$

$$B_4 = \frac{B_2^2(-iA_2^3 + K_0 A_2(A_2 A_4 - A_3^2) + B_2 A_3^2)}{K_0^2 A_2^4}. \qquad [177]$$

Clearly B_2 is pure imaginary, B_3 has equal real and imaginary parts, and B_4 is pure real, by the properties of the A_i discussed previously. Thus, a plot of $\text{Im}\{\hat{Z}(\delta)\}$ vs δ (for $\delta < 1$) should yield a straight line with limiting slope $\text{Im}\{B_3\}$ and $\text{Im}\{Z\}$-intercept B_2. Note that this graph will depict the higher-frequency modifications of the capacitance due to ionic diffusion, so most of the points should be taken "above" $\delta = 0.01$, which is in the kilohertz regime. Similarly, a plot of $\text{Re}\{\hat{Z}(\delta)/\delta\}$ vs δ should give a straight line of limiting slope B_4 and intercept $\text{Re}\{B_3\}$. Sensible measurements of $\text{Re}\{Z_{el+st}(\omega)\}$ can be obtained only below 10 Hz or so (since the bulk impedance has to be subtracted off), hence this second graph will contain points chiefly in the regime $\delta < 0.005$.

A first experimental check of this theory would then be a comparison of the measured real and imaginary parts of B_3. Second, by Eq. [176], the quantity

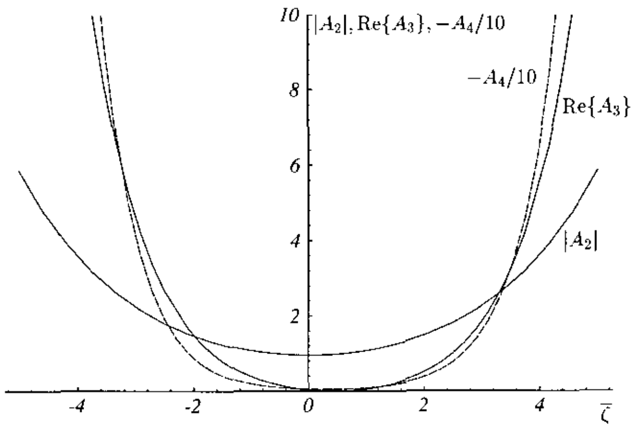

FIG. 2. $|A_2|$, $\text{Re}\{A_3\}$, $A_4/10$ versus $\bar{\zeta} = e\zeta/kT$ for NaCl.

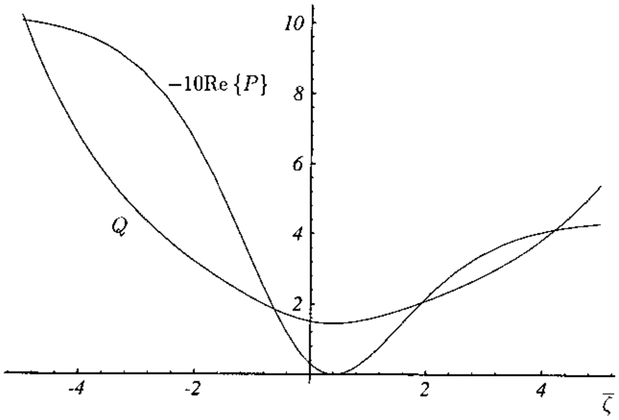

FIG. 3. −10 Re{P} and −Q versus $\bar{\zeta} = e\zeta/kT$ for NaCl.

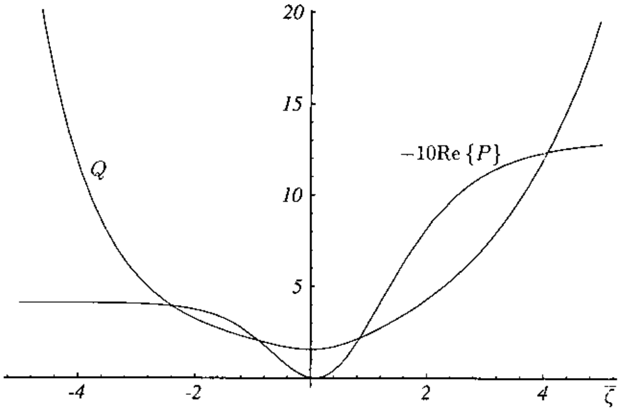

FIG. 5. −100 Re{P} and −Q versus $\bar{\zeta} = e\zeta/kT$ for Ba(NO$_3$)$_2$.

$$P \equiv B_3/B_2^2 = A_3/K_0A_2^2, \qquad [178]$$

and thus the dimensionless zeta potential $\bar{\zeta}$ can be determined from a graph of Re{P} vs $\bar{\zeta}$ and the experimentally determined B_2 and B_3. The Stern layer capacitance may then be determined from [175] to be

$$C_s = \frac{-i\epsilon\kappa K_0 B_2 A_2(\bar{\zeta})}{4\pi(B_2 - K_0 A_2(\bar{\zeta})}, \qquad [179]$$

and, if desired, a further self-consistency check can be obtained by computing B_4 from [177] and comparing this with the experimental result. Note that Eq. [177] can be written as

$$B_4 = B_2^3 Q + B_2^3 P^2, \qquad [180]$$

where

$$Q \equiv \frac{-iA_2^2 + K_0(A_2A_4 - A_3^2)}{K_0^2 A_2^3}, \qquad [181]$$

so clearly graphs of Q and Re{P} vs $\bar{\zeta}$ (which are universal for a particular electrolyte) are useful to exhibit.

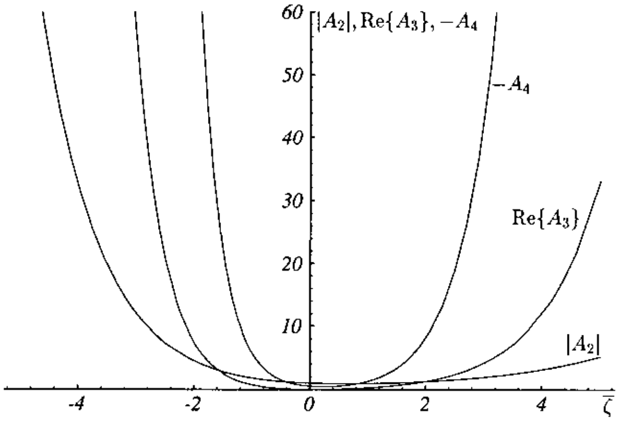

FIG. 4. |A_2|, Re{A_3}, A_4 versus $\bar{\zeta} = e\zeta/kT$ for Ba(NO$_3$)$_2$.

Figure 2 is a plot of the functions |$A_2(\bar{\zeta})$|, Re{$A_3(\bar{\zeta})$}, and $A_4(\bar{\zeta})$ for common salt (NaCl). To aid the determination of $\bar{\zeta}$ from [178] and the subsequent computation of A_4, Fig. 3 plots Q and Re{P} versus $\bar{\zeta}$. Figures 4 and 5 are the same plots for the 2:1 salt Ba(NO$_3$)$_2$. These graphs were computed using the value of $\bar{\lambda}$ obtained from Eq. [48].

It is clear that there will be considerable noise in the experimental value of A_4, principally from the subtraction of the bulk electrolyte impedance and the curve-fitting routines. It is possible that the A_4 term will be meaningful only for lightly charged electrodes ($|\zeta| < 50$ mV) at very low frequencies in the presence of large valency counterions.

Inability to fit experimental data to theoretical forms for A_2, A_3, and A_4 will then necessitate higher-order modeling of the inner region as discussed in the Introduction.

APPENDIX: SOME USEFUL ORTHOGONALITY RELATIONS

Observe that Eq. [92], for $l = 1$, may be written in matrix form as

$$(M + \alpha_k I_D) \cdot \mathbf{R}_k^{(1)} = 0, \qquad [182]$$

with the components of $\mathbf{R}_k^{(1)}$ as per Eqs. [95] and [96], M as the coefficient matrix in [92] with $\alpha \rightarrow 0$, and I_D as the defective identity matrix

$$I_D = \mathrm{diag}(1, 1, \ldots, 1, 0). \qquad [183]$$

Now it is straightforward to construct left "eigenvectors" $\mathbf{L}_k^{(1)}$ of the matrix M, satisfying

$$\mathbf{L}_k^{(1)}\cdot(M+\alpha_k I_{\mathrm{D}})=0, \qquad [184]$$

and a left eigenvector corresponding to the eigenvalue $\alpha_{k'}$ will have components

$$\mathbf{L}_{k'j}^{(1)}=\frac{\beta_j^{\infty}}{i\gamma_j+\alpha_{k'}}, \qquad j, k'=1, 2, \ldots, N, \qquad [185]$$

$$\mathbf{L}_{k',N+1}^{(1)}=-1, \qquad k'=1, 2, \ldots, N. \qquad [186]$$

Now if we premultiply [182] by $\mathbf{L}_{k'}^{(1)}$, postmultiply [184] by $\mathbf{R}_k^{(1)}$, and subtract the resulting equations, we obtain

$$(\alpha_k-\alpha_{k'})(\mathbf{L}_{k'}^{(1)} I_{\mathrm{D}} \mathbf{R}_k^{(1)})=0, \qquad [187]$$

which implies that if the eigenvalues are distinct, we have the following "orthogonality" relation:

$$\mathbf{L}_{k'}^{(1)} I_{\mathrm{D}} \mathbf{R}_k^{(1)}=\sum_{j=1}^{N}\frac{i\beta_j^{\infty}\gamma_j}{(i\gamma_j+\alpha_k)(i\gamma_j+\alpha_{k'})}=0,$$
$$k'\neq k. \qquad [188]$$

Note that if we choose $k'=1$, i.e., $\alpha_{k'}=0$, this orthogonality relation takes the special form

$$\sum_{j=1}^{N}\frac{\beta_j^{\infty}}{i\gamma_j+\alpha_k}=0, \qquad \alpha_k\neq 0, \qquad [189]$$

and if we define the normalization factor N_k by

$$N_k=\sum_{j=1}^{N}\frac{i\beta_j^{\infty}\gamma_j}{(i\gamma_j+\alpha_k)^2}, \qquad k=1, 2, \ldots, N, \qquad [190]$$

then we have

$$\sum_{j=1}^{N}\frac{i\beta_j^{\infty}\gamma_j}{N_k(i\gamma_j+\alpha_k)(i\gamma_j+\alpha_{k'})}=\delta_{kk'}. \qquad [191]$$

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