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Nonlinear oscillations in an electrolyte solution under ac voltage

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The response of an electrolyte solution bounded between two blocking electrodes subjected to an ac voltage is considered. We focus on the pertinent thin-double-layer limit, where this response is governed by a reduced dynamic model [L. Højgaard Olesen, M. Z. Bazant, and H. Bruus, Phys. Rev. E **82**, 011501 (2010)]. During a transient stage, the system is nonlinearly entrained towards periodic oscillations of the same frequency as that of the applied voltage. Employing a strained-coordinate perturbation scheme, valid for moderately large values of the applied voltage amplitude V, we obtain a closed-form asymptotic approximation for the periodic orbit which is in remarkable agreement with numerical computations. The analysis elucidates the nonlinear characteristics of the system, including a slow (logarithmic) growth of the zeta-potential amplitude with V and a phase straining scaling as $V^{-1}\ln V$. In addition, an asymptotic current-voltage relation is provided, capturing the numerically observed rapid temporal variations in the electric current.

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The response of an electrolyte solution subjected to a time-dependent voltage is fundamental in numerous practical applications. The simplest electrochemical-cell configuration, where the liquid is bounded by two planar electrodes, is particularly relevant to the study of energy storage [1], microscale cell manipulation [2], and self-assembly of colloidal particles near planar electrodes [3,4]; transient current-voltage measurements may also play an important role in settling the ongoing controversy regarding the characteristics of charge carriers in nonpolar liquids [5–8]. While it is a common engineering practice to represent the electrochemical cell as a linear circuit model, it is well known that such a description is seldom justified beyond low voltages [9,10]. In the general case of nonsmall voltages, transient ionic-species transport is coupled to the electrostatics, as manifested in the nonlinear Poisson-Nernst-Planck (PNP) set of equations.

Recently, Olesen *et al.* [11] considered in detail the case of ideally blocking electrodes. In their paper they provide a reduced model appropriate to the thin-double-layer limit. This model allows for straightforward numerical computations which avoid the scale disparity inherent in the underlying PNP equations [12]. In the low-voltage regime, where the Debye layers adjacent to the electrodes effectively constitute linear capacitors, the (steady-state) response to a time-harmonic voltage is itself harmonic. A prominent feature of the numerical solutions presented in Ref. [11] is that the steady-state response to an ac voltage is periodic even beyond low voltages, having the same period as that of the applied voltage. This periodic response, however, is clearly not time harmonic; rather, it exhibits distinct nonlinear features, such as voltage-dependent amplification and phase shift, as well as rapid temporal variations in the electric current [10,11].

In this paper we exploit the reduced model, first, to rationalize the nonlinear frequency locking, and second, to extract the main features of the limiting oscillations via perturbative methods. Towards this end we employ the thin-double-layer framework to analyze the response of the system beyond low voltages in a regime where the dynamics are inherently nonlinear. Formulating a periodic boundary-value problem governing the steady-state response, we derive a large-voltage asymptotic solution which is in excellent agreement with numerical solutions. Our asymptotic analysis reveals the scaling with voltage of the amplitude and phase shift pertinent to the nonlinear response. The main outcome of this analysis is an asymptotic current-voltage relation.

The problem considered entails a symmetric binary electrolyte solution (permittivity ϵ^*, ionic valencies $\pm\mathcal{Z}$) where the ionic diffusion coefficients $D^*_\pm$ are allowed to differ. (Hereafter, an asterisk denotes a dimensional quantity.) The solution is bounded by two planar electrodes separated a distance L^* apart (see Fig. 1). Initially, the system is in equilibrium so that the anion and cation concentrations are uniform, possessing identical values (say c^*). Our interest lies in the response of the system to an ac voltage of amplitude V^* and frequency $\omega^*/2\pi$, initiated at time $t^*=0$; for definiteness, we take $V^*\cos(\omega^* t^*)$ to be the electric potential of the left electrode relative to the right one. (With no loss of generality we assume $V^*>0$.) The problem may be considered one dimensional.

In most cases of practical interest, L^* is much larger than the Debye length,

$$\lambda^* = \sqrt{\frac{\epsilon^* k^* T^*}{2\mathcal{Z}^2 e^{*2} c^*}}, \tag{1}$$

in which k^* is Boltzmann's constant, T^* the absolute temperature, and e^* the elementary charge. In the corresponding asymptotic limit, $\lambda^* \ll L^*$, two $O(\lambda^*)$-wide Debye layers form adjacent to the electrodes, with the bulk liquid outside them being approximately electroneutral; the natural time scale for transport in this system is the "RC time" $\tau^* = L^*\lambda^*/D^*$, D^* being a characteristic diffusivity [10]. When ω^* is not significantly larger than $1/\tau^*$ and the applied voltage is not too high (see Ref. [11] and the discussion at the end of the present paper), this compound structure can be described by a simple macroscale model, wherein the two Debye layers remain in quasisteady equilibrium. Such a model was provided in Ref. [11] (referred to there as "weakly nonlinear") for the case of identical diffusivities. In the Supplemental Material [13] we perform a systematic asymptotic analysis of the underlying transport equations, deriving the comparable model for nonidentical diffusivities [14]. Notably, this description

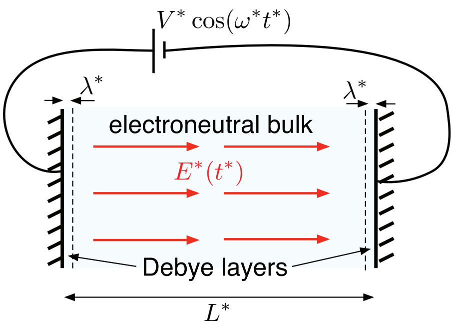

FIG. 1. (Color online) Schematic of the problem.

does not involve the individual diffusivities [15] but only their average $D^* = (D^*_+ + D^*_-)/2$. In this description, the ionic concentrations in the bulk are uniform and constant (namely, c^*). The bulk electric field is also uniform but is of time-dependent magnitude [say $E^*(t^*)$, defined positive to the right].

We denote the zeta potential (i.e., the potential difference between the electrode-electrolyte interface and the outer edge of the adjacent Debye layer) at the left and right electrodes by ζ^*_L and ζ^*_R, respectively. The thin-double-layer model relating these quantities to E^* consists of three equations. The first two represent electrode charging on the RC scale (cf. [4]),

$$\begin{aligned} \sigma^* E^* &= 2\frac{\epsilon^*\varphi^*}{\lambda^*}\frac{d}{dt^*}\left(\sinh\frac{\zeta^*_L}{2\varphi^*}\right), \\ -\sigma^* E^* &= 2\frac{\epsilon^*\varphi^*}{\lambda^*}\frac{d}{dt^*}\left(\sinh\frac{\zeta^*_R}{2\varphi^*}\right), \end{aligned} \tag{2}$$

wherein $\sigma^* = \mathcal{Z}^2 e^{*2} c^* (D^*_+ + D^*_-)/\varphi^*$ is the bulk conductivity, in which $\varphi^* = k^* T^*/\mathcal{Z} e^*$ is the thermal voltage. The right-hand sides in Eqs. (2) are simply the time derivatives of the electrode surface-charge density (or equivalently, the inverse of the total Debye-layer charge per unit area, as given by the Gouy-Chapman relation [16]). The third equation,

$$E^* L^* + \zeta^*_L - \zeta^*_R = V^* \cos(\omega^* t^*), \tag{3}$$

represents the requirement that the total potential drop across the cell equals the applied voltage. These equations are supplemented by the initial conditions

$$\zeta^*_L = \zeta^*_R = 0 \quad \text{for} \quad t^* = 0. \tag{4}$$

Mutual addition of (2) followed by integration with respect to time yields, upon use of conditions (4),

$$\zeta^*_L = -\zeta^*_R \quad \text{for all} \quad t^* \geqslant 0. \tag{5}$$

The antisymmetry (5) allows us to describe the dynamics using a single variable, say $\zeta^* \equiv \zeta^*_L$. It is convenient to write the differential equation governing this variable, obtained by combining (2)–(5), in a dimensionless form. Defining the normalized variables

$$t = t^*/\tau^*, \quad \zeta = \zeta^*/\varphi^*, \quad V = V^*/\varphi^*, \tag{6}$$

we thus obtain (cf. [11])

$$2\frac{d}{dt}\sinh\frac{\zeta}{2} + 2\zeta = V\cos\omega t, \tag{7}$$

where $\omega = \omega^*\tau^*$ is $O(1)$ by assumption. (Dimensionless variables appear without the asterisk decoration.) Equivalently, we may write [17]

$$\frac{dQ}{dt} + 4\sinh^{-1}\frac{Q}{2} = V\cos\omega t, \tag{8}$$

where

$$Q = 2\sinh\frac{\zeta}{2} \tag{9}$$

is the surface-charge density on the left electrode, normalized by $\epsilon^*\varphi^*/\lambda^*$ [cf. (2)]. The corresponding initial condition is $Q(t = 0) = 0$.

Numerical solutions of (8) approach a steady-state periodic solution of angular frequency ω. Its shape is actually independent of the initial condition and is completely determined by the parameters ω and V. While entrainment of the system to the forcing frequency may seem plausible, it is not in any sense evident [18]. In the Supplemental Material [13] we prove that the system indeed approaches a (unique) periodic solution. The steady-state orbit $Q(\theta)$, where $\theta = \omega t$, is governed by the periodic boundary-value problem,

$$\omega\frac{dQ}{d\theta} + 4\sinh^{-1}\frac{Q}{2} = V\cos\theta, \tag{10}$$

$$Q(\theta = 0) = Q(\theta = 2\pi), \tag{11}$$

assured to possess a unique solution for any ω and V. At low voltages $V \ll 1$, one finds the harmonic linear response

$$Q \sim \frac{V}{\sqrt{4+\omega^2}}\cos(\theta - \alpha), \quad \alpha = \arctan\frac{\omega}{2}, \tag{12}$$

with $\zeta \sim Q$. Beyond low voltages, it is in general necessary to solve (10) and (11) numerically. Examples of zeta-potential orbits are shown in Fig. 2 for $V = 30$ and 60, with $\omega = 1$. A comparison of the response at these moderately large voltages with the (low-voltage) linear response (also depicted) clearly demonstrates the voltage dependence of both the amplitude

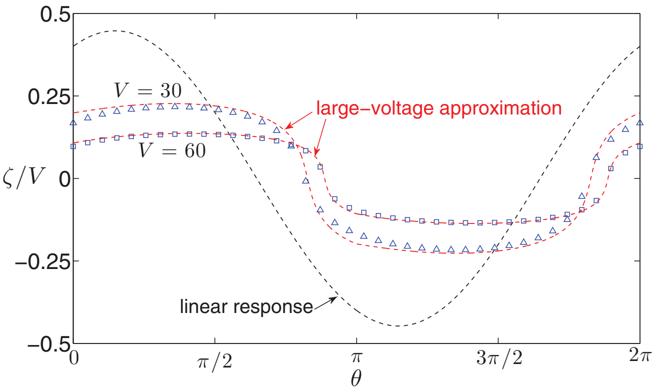

FIG. 2. (Color online) The periodic steady-state zeta potential in response to a time-harmonic ac voltage input of magnitude $V = 30$ and 60, and angular frequency $\omega = 1$; the symbols represent numerical solution of the boundary-value problem (10) and (11), while the lines depict the corresponding large-voltage asymptotic expression (17). The linear (voltage-independent) solution is also shown.

and phase (say at which ζ obtains a maximum) of the nonlinear response.

Our interest is in obtaining a simple asymptotic solution of (10) and (11) in the limit of large voltages. An obvious leading-order approximation $Q \sim (V/\omega)\sin\theta$ is readily obtained by balancing the first and third terms in (10). A comparison of this expression with the numerical solution, however, shows a poor visual agreement. Whereas the amplitude maxima are reasonably close, a small phase shift is evident; apparently, its slow decay with respect to V renders the approximation essentially impractical. It is natural to employ the method of strained coordinates [19] in order to resolve such nonuniformities. Thus we postulate the *ansatz*

$$Q \sim \frac{V}{\omega}\sin[\theta + \epsilon\chi(\theta)], \tag{13}$$

where ϵ is a small parameter which, together with $\chi(\theta)$, remains to be determined. Upon substituting (13) into (10), a dominant-balance analysis implies

$$\epsilon = \frac{\ln(V/\omega)}{V}, \tag{14}$$

whereby to leading order we find that $\chi(\theta)$ [which inherits its 2π periodicity from $Q(\theta)$] satisfies the equation

$$\chi\sin\theta - \frac{d\chi}{d\theta}\cos\theta = 4\,\mathrm{sgn}(\sin\theta). \tag{15}$$

In solving (15), the integration constant is determined so that the solution is continuous, as implied by the principle of minimum singularity [20]. We therefore find

$$\chi = \frac{2\pi - 4\theta + 8(\theta - \pi)\mathcal{H}(\theta - \pi)}{\cos\theta}, \tag{16}$$

where $\mathcal{H}$ is the Heaviside function; note that (16) is 2π periodic.

Substitution of (13) and (14) into (9) provides the asymptotic expression for the zeta potential,

$$\zeta \sim 2\sinh^{-1}\left\{\frac{V}{2\omega}\sin\left[\theta + \frac{\ln(V/\omega)}{V}\chi(\theta)\right]\right\}. \tag{17}$$

A comparison of (17) and the numerical solution is shown in Fig. 2 for $V = 30$ and 60, with $\omega = 1$; the agreement is excellent. (For $V = 80$ the numerical and asymptotic solutions are practically indistinguishable.) Note that at large voltages the maximum amplitude of the zeta-potential asymptotes to

$$\zeta_{\max} \sim 2\ln\frac{V}{\omega}, \tag{18}$$

therefore remaining rather mild even for very large voltages. The collapse on (18) at large voltages of the numerically evaluated zeta-potential amplitudes for several values of ω is shown in Fig. 3. The collapse at low voltages on the linear amplitude [see (12)] is also shown.

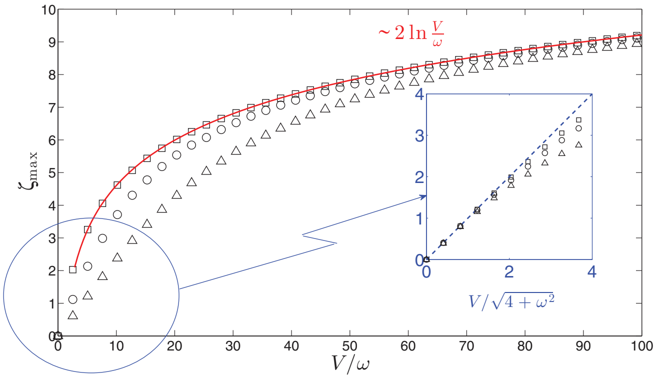

FIG. 3. (Color online) Amplitude of zeta-potential oscillations as a function of V/ω for $\omega = 0.5$ (triangles), 1 (circles), and 7 (squares). At large voltages, all the numerical data collapse on the logarithm (18) (solid line). Upon changing the abscissa to $V/\sqrt{4+\omega^2}$, the low-voltage data collapse on the familiar linear response (12), depicted by the dashed line.

Perhaps of greater practical interest is the electric current density, in principle a directly measurable quantity. (Note that in our approximation level, the measurable current, i.e., the time rate of change of the electrode charge, is equal to the bulk electric current at any moment.) From (2) we find that the current density, normalized by $\mathcal{Z}e^*c^*(D_+^* + D_-^*)/L^*$, is given by

$$I = \omega\frac{dQ}{d\theta}. \tag{19}$$

This quantity can be extracted directly from (10) by substituting either the numerical zeta-potential solution or the large-voltage asymptotic approximation (13). The latter yields

$$I \sim V\cos\theta - 4\sinh^{-1}\left\{\frac{V}{2\omega}\sin\left[\theta + \frac{\ln(V/\omega)}{V}\chi(\theta)\right]\right\}. \tag{20}$$

This asymptotic current-voltage relation is the main outcome of our analysis.

Figure 4 shows an excellent agreement between (20) and the numerical data already at $V = 40$. The rapid temporal variations in the electric current (a feature also mentioned in Ref. [11]) are well captured by our asymptotic approximation. Indeed, note that

$$\sinh^{-1}\left\{\frac{V}{2\omega}\sin\phi\right\} \sim \mathrm{sgn}(\sin\phi)\ln\left\{\frac{V|\sin\phi|}{\omega}\right\}. \tag{21}$$

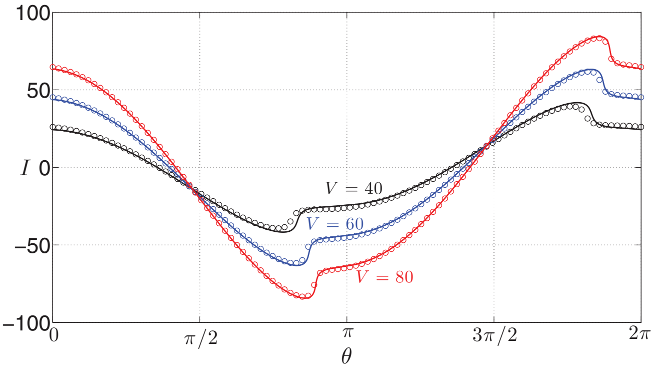

FIG. 4. (Color online) The periodic steady-state current in response to a harmonic ac voltage input of magnitude $V = 40$, 60, and 80, with $\omega = 0.5$. The symbols represent the numerical solution; the solid lines depict the corresponding large-voltage asymptotic approximation (20).

This "outer" approximation is valid outside two $O(1/V)$-wide regions about $\phi = \pi$ and $\phi = 2\pi$ across, which the left-hand side of (21) changes by $O(\ln V)$. Thus, in the uniform approximation (20), these near discontinuities appear at θ values shifted by $O(V^{-1}\ln V)$ phases relative to π and 2π; this is observed in Fig. 4. It is remarkable that the delicate resolution of the transition regions is also in good agreement with the numerical data.

We conclude with remarks concerning the range of validity of the above results. As described by Olesen *et al.* [11], when the nonlinear capacitance of the double layer comes into play [cf. (9)], net salt (in addition to charge) is transported in and out of the Debye layer. As the associated flux is incompatible with the homogenous bulk, a diffusive boundary layer of $O(\delta^{1/2})$ width is formed outside the double layer. For $V = O(1)$ the concentration deviation in this layer is asymptotically small and thereby has, to leading order, no effect on our present analysis. For $V = O(\delta^{-1/2})$, however, this deviation becomes appreciable and the asymptotics reshuffle. While the voltage on the thin diffusive layer remains small, the concentration deviation intermittently drives the diffuse layer out of equilibrium. As the thin-double-layer model employed herein breaks down at these moderately large voltages, this restricts the range of validity of our analysis. Olesen *et al*. [11] provide a (more involved) "strongly nonlinear" model [21] which is solved numerically and is seen to agree well with the numerical solution of the full PNP model for all voltages. Whether it is possible to apply the methods employed in the present contribution to the strongly nonlinear regime is left as an open question.

An additional large-voltage limitation may appear to arise from the condition of total ion conservation in the cell, which follows from the assumption of ideally blocking electrodes. According to the thin-double-layer model, the bulk ionic concentrations are uniform and constant, equal to the equilibrium concentration. This assumption is easily justified when the zeta potential is moderate, as the amount of ions absorbed in the Debye layers is then only an $O(\delta)$ fraction of their amount in the bulk, and net ion conservation is satisfied at the order of approximation of our analysis (see Supplemental Material [13]). If the zeta potential becomes mildly large, however, this fraction is modified to $O(\delta e^{|\zeta|/2})$ (essentially the Dukhin number [16]), which in principle may become $O(1)$. Employing our large-voltage result (18) for the zeta-potential amplitude, we find that this fraction is actually $O(\delta V)$, implying a breakdown of the underlying asymptotic model at $V = O(\delta^{-1})$. This places a less stringent limitation on the model than that related to salt absorption in the diffusive layer.

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[1] G. Girishkumar, B. McCloskey, A. C. Luntz, S. Swanson, and W. Wilcke, J. Phys. Chem. Lett. **1**, 2193 (2010).
[2] J. Voldman, Annu. Rev. Biomed. Eng. **8**, 425 (2006).
[3] W. D. Ristenpart, I. A. Aksay, and D. A. Saville, Phys. Rev. Lett. **90**, 128303 (2003).
[4] D. C. Prieve, P. J. Sides, and C. L. Wirth, Curr. Opin. Colloid Interface Sci. **15**, 160 (2010).
[5] D. C. Prieve, J. D. Hoggard, R. Fu, P. J. Sides, and R. Bethea, Langmuir **24**, 1120 (2008).
[6] F. Beunis, F. Strubbe, M. Karvar, O. Drobchak, T. Brans, and K. Neyts, Curr. Opin. Colloid Interface Sci. **18**, 129 (2013).
[7] A. Dukhin and S. Parlia, Curr. Opin. Colloid Interface Sci. **18**, 93 (2013).
[8] T. Lin, T. E. Kodgerb, and D. A. Weitz, Soft Matter **9**, 5173 (2013).
[9] J. S. Newman, *Electrochemical Systems* (Prentice-Hall, Englewood Cliffs, NJ, 1973).
[10] M. Z. Bazant, K. Thornton, and A. Ajdari, Phys. Rev. E **70**, 021506 (2004).
[11] L. Højgaard Olesen, M. Z. Bazant, and H. Bruus, Phys. Rev. E **82**, 011501 (2010).
[12] In their paper, Olesen *et al.* [11] have actually shown that the predictions of such numerical computations agree with comparable simulations of the underlying PNP equations.
[13] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevE.89.032302 for a derivation of the thin-double-layer model and the subsequent proof of frequency locking.
[14] On the other hand, we incorporate neither steric effects nor a Stern-layer capacitance. The nonlinearity ingrained in the present model limits the electrode ζ potentials to rather mild values, even at large voltages [see (18)], thereby hindering nondilute effects.
[15] The asymptotic analysis fails when there is a significant difference between the two diffusivities, as may be the case with the charge carriers in nonpolar liquids [7].
[16] J. Lyklema, *Fundamentals of Interface and Colloid Science* (Academic, New York, 1995), Vol. II.
[17] Since the dependence of the thin-double-layer model upon the ionic diffusivities appears only through their sum, the governing differential equation [either Eq. (7) or (8)] is equivalent to that appearing in Ref. [10], where it was given in several forms.
[18] G. Russo, M. Di Bernardo, and E. D. Sontag, PLoS Comput. Biol. **6**, e1000739 (2010).
[19] E. J. Hinch, *Perturbation Methods* (Cambridge University Press, Cambridge, UK, 1991).
[20] M. Van Dyke, *Perturbation Methods in Fluid Mechanics* (Academic Press, New York, 1964).
[21] In Ref. [11] the model corresponding to $V \ll \delta^{-1/2}$ is termed "weakly nonlinear," in distinction from their "strongly nonlinear" model. Note, however, that the term "weakly nonlinear" is commonly understood to represent a small deviation from linearity [22]; the transport occurring at voltages satisfying $V \ll \delta^{-1/2}$, and in particular, $V = O(1)$, is inherently nonlinear.
[22] S. Strogatz, *Nonlinear Dynamics and Chaos: With Applications to Physics, Biology, Chemistry, and Engineering* (Perseus Books, New York, 2001).