Strongly nonlinear dynamics of electrolytes in large ac voltages

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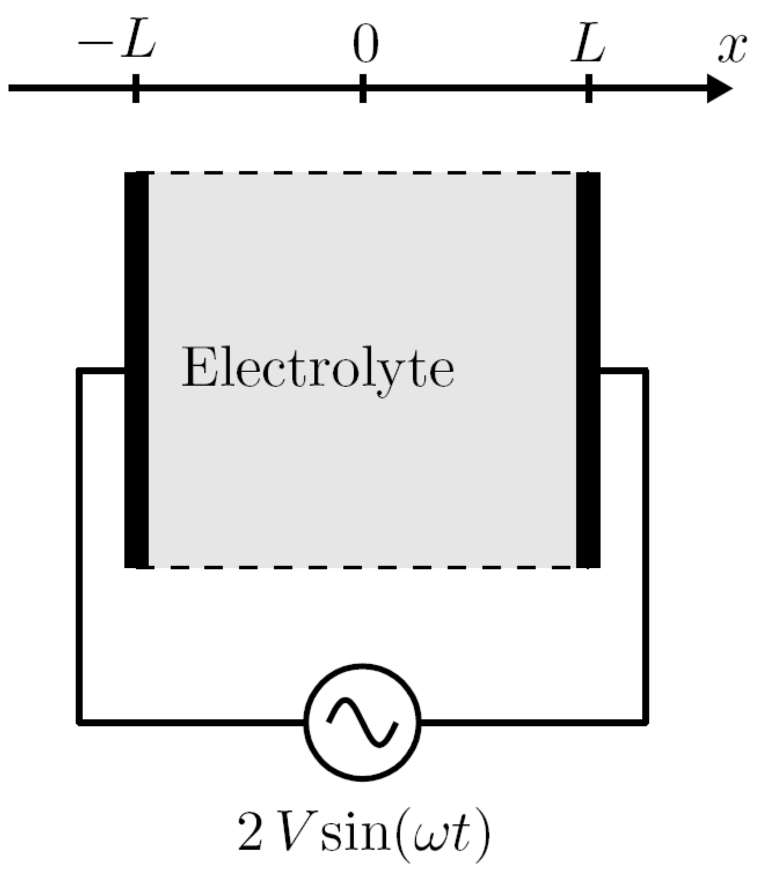
We study the response of a model micro-electrochemical cell to a large ac voltage of frequency comparable to the inverse cell relaxation time. To bring out the basic physics, we consider the simplest possible model of a symmetric binary electrolyte confined between parallel-plate blocking electrodes, ignoring any transverse instability or fluid flow.



We analyze the resulting one-dimensional problem by matched asymptotic expansions in the limit of thin double layers and extend previous work into the strongly nonlinear regime, which is characterized by two novel features:

(1) significant salt depletion in the electrolyte near the electrodes, and

(2) at very large voltage, the breakdown of the quasi-equilibrium structure of the double layers.

Governing equations in dimensionless form

Scales for length L, time $\tau = \lambda_D L/D$, voltage kT/e, and concentration c^*

The Poisson and the Nernst-Planck equation

$$c = \frac{1}{2}(c_+ + c_-) \qquad \partial_t c = -\epsilon \partial_x F$$

$$-\epsilon^2 \partial_x^2 \phi = \rho = \frac{1}{2}(c_+ - c_-) \qquad \partial_t \rho = -\epsilon \partial_x J$$

Ion fluxes and the chemical potential incl. sterics

$$\mu_\pm = \log c_\pm \pm \phi - \log(1 - \nu c)$$

$$F = \tfrac{1}{2}(F_+ + F_-) = -\partial_x c/(1 - \nu c) - \rho \partial_x \phi$$

$$J = \tfrac{1}{2}(F_+ - F_-) = -\partial_x \rho - c \partial_x \phi - \nu \rho \partial_x c/(1 - \nu c)$$

Boundary conditions

$$F = J = 0 \quad \text{and} \quad V_{\text{ext}} - \phi = \mp \epsilon \delta \partial_x \phi \quad \text{at} \quad x = \pm 1$$

Debye length

$$\lambda_D = \sqrt{\frac{\varepsilon k T}{\sum_i c_i^* z_i^2 e^2}}$$

dimensionless parameters

$$\epsilon = \lambda_D / L$$

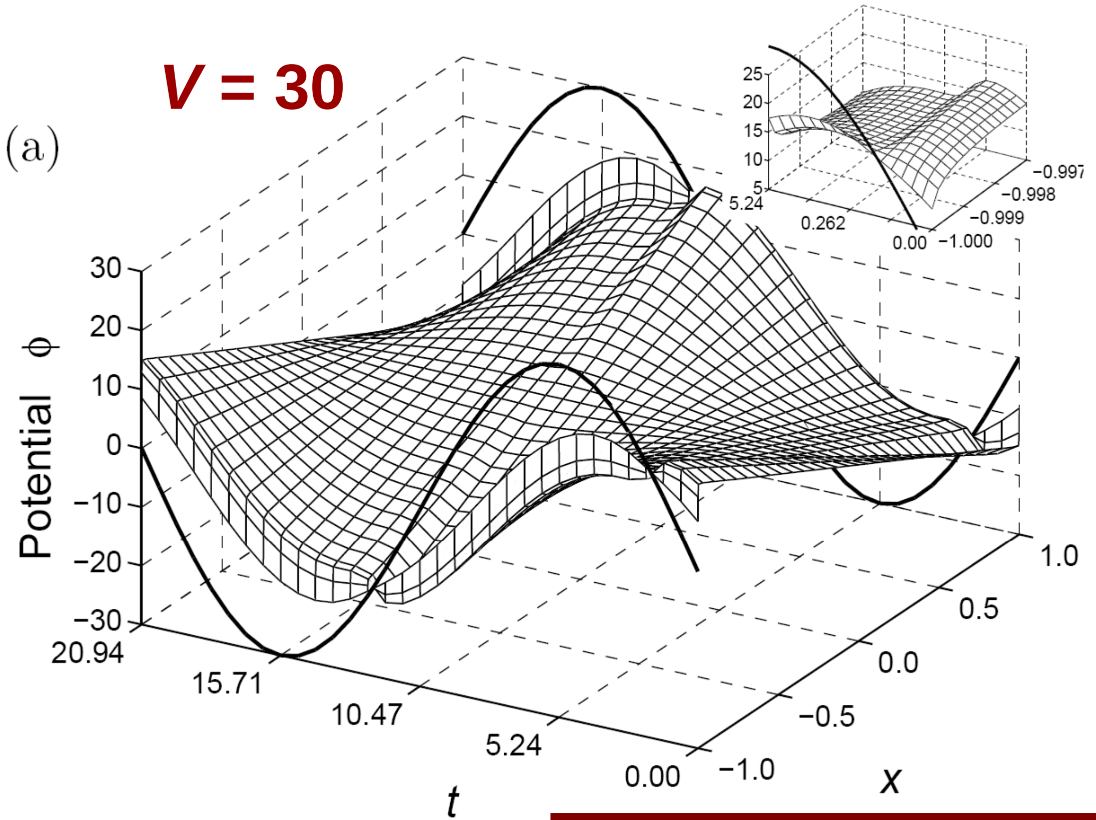
$$\delta = C_D / C_S$$

$$V$$

Numerical results for ϕ and $c_{\pm}$ at V = 30 and V = 120

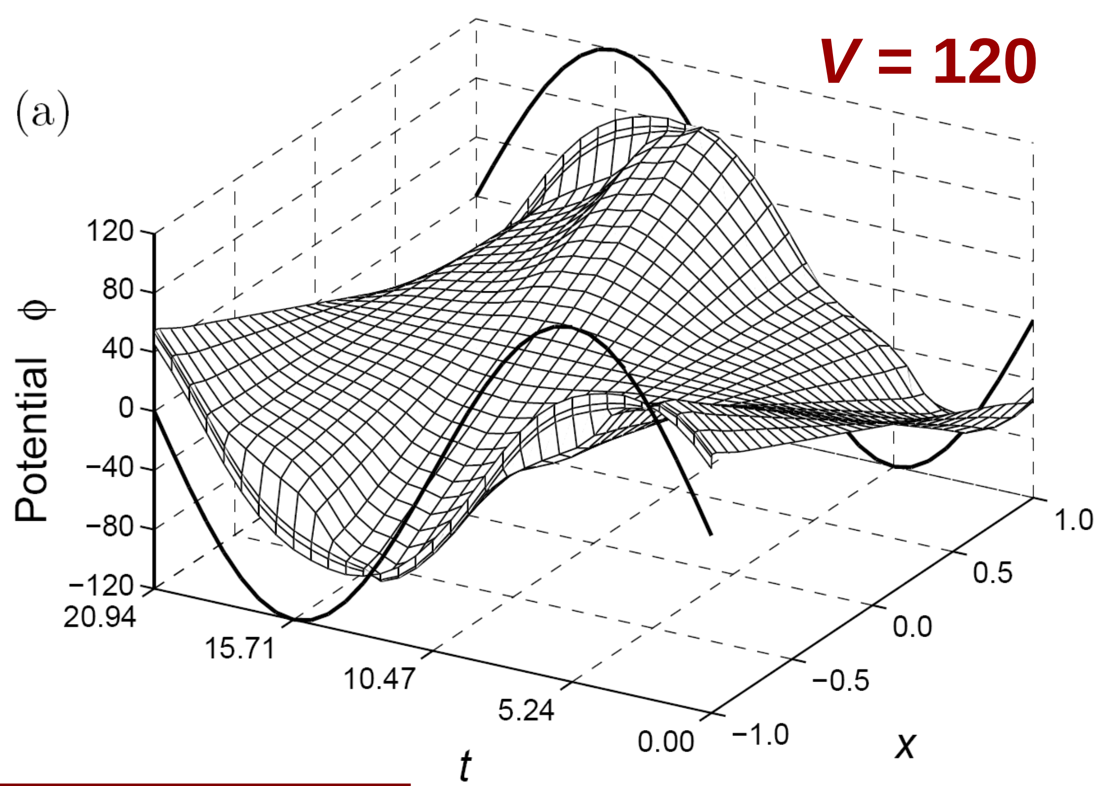
V = 30

(a)



V = 120

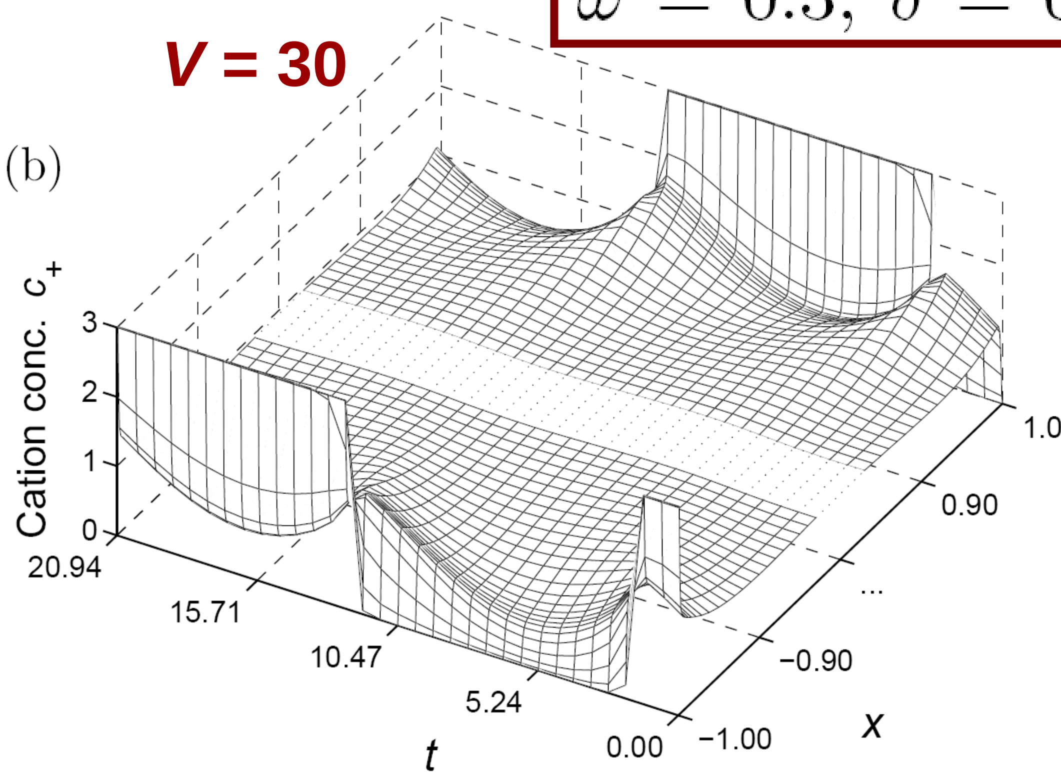
(a)



$\omega = 0.3,\ \delta = 0.3,\ \text{and}\ \epsilon = 0.001$

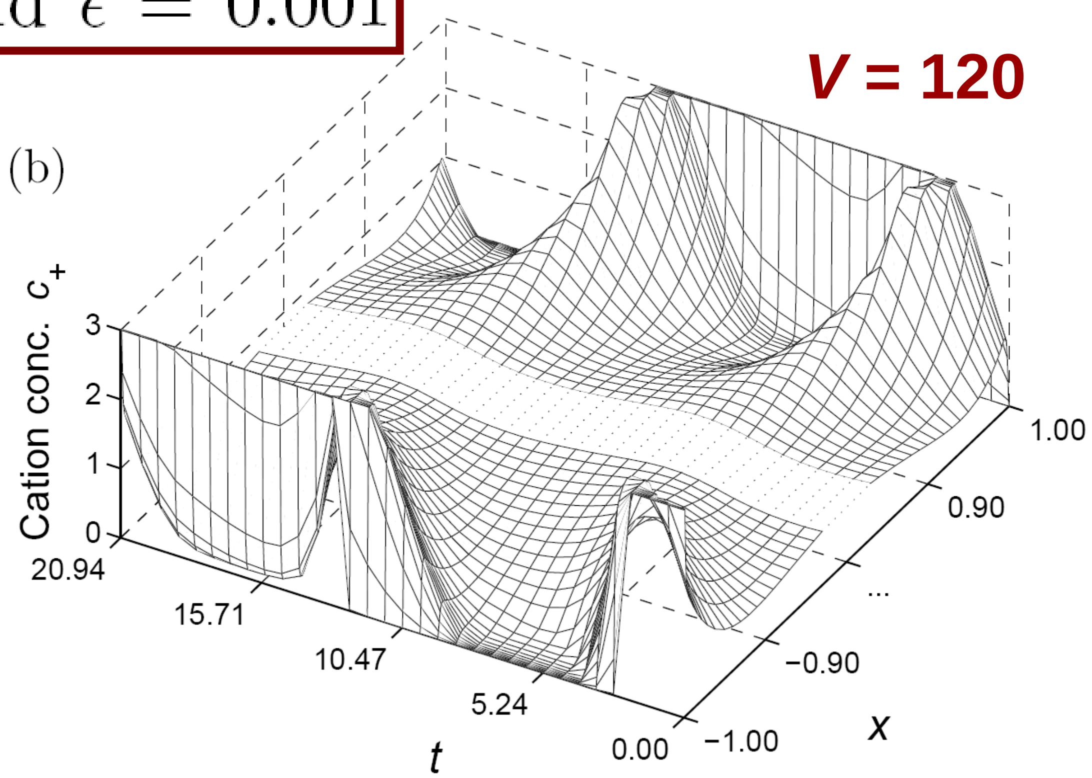
V = 30

(b)



V = 120

(b)

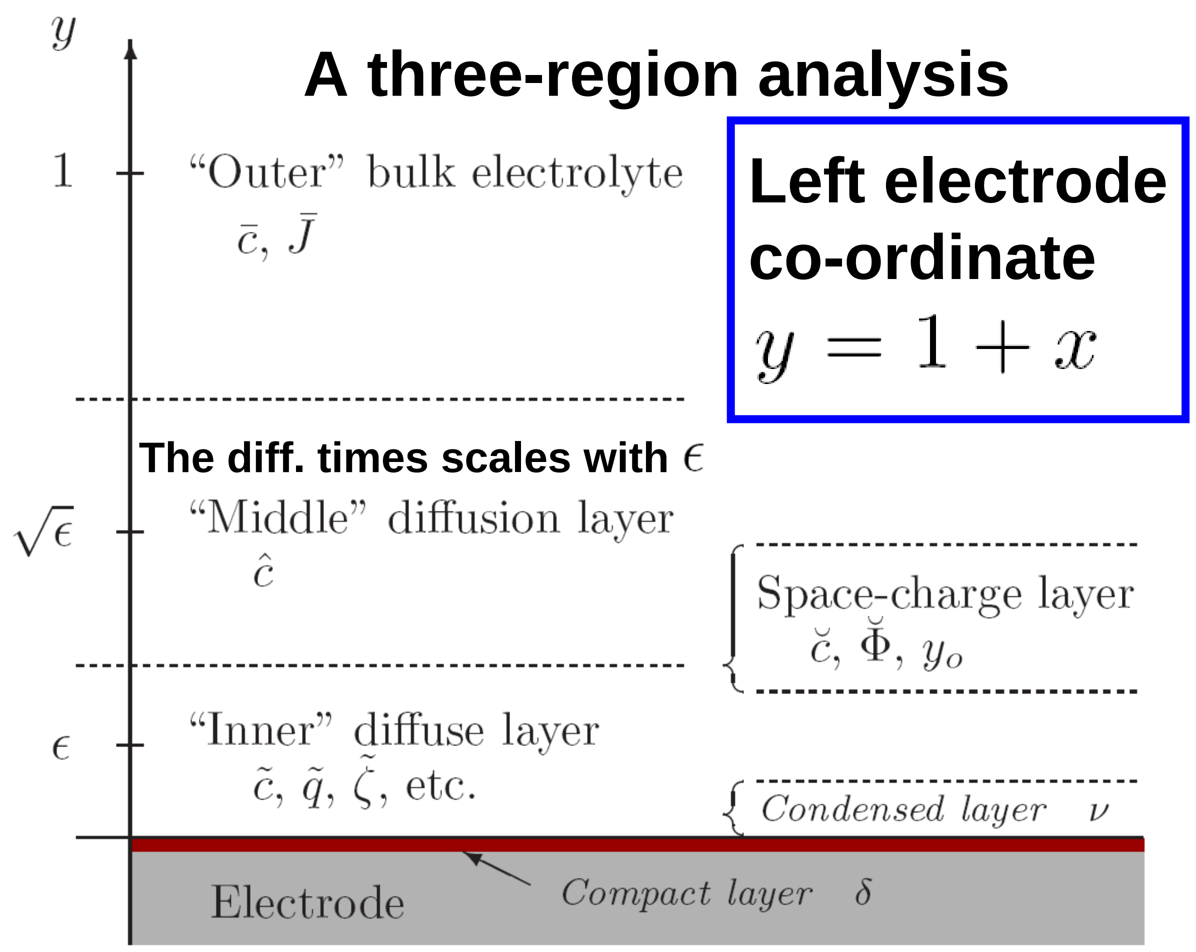


Asymptotic boundary-layer analysis

Regular power series expansion

$$c = c^{(0)} + \epsilon c^{(1)} + \epsilon^2 c^{(2)} + \dots$$

A three-region analysis



Left electrode co-ordinate

$$y = 1 + x$$

1) Quasi-electroneutral bulk:

$$\bar{\phi} = -\frac{\bar{J}(t)}{\bar{c}_o} x \qquad \bar{c}_+ = \bar{c}_- = \bar{c}$$

2) Oscillating diffusion layer:

$$\partial_t \hat{c} = \partial_{\hat{y}}^2 \hat{c} \quad \text{where} \quad \hat{y} = y/\sqrt{\epsilon}$$

$$\hat{\rho} = -\epsilon \partial_{\hat{y}}^2 \hat{\psi} = -\epsilon^{3/2} \frac{\bar{J} \partial_{\hat{y}} \hat{c}}{\hat{c}^2}$$

due to variations in the conductivity (conc. polarization effects): $-\frac{1}{\sqrt{\epsilon}} \partial_{\hat{y}} \hat{\psi} = \bar{J} \left(\frac{1}{\hat{c}} - \frac{1}{\bar{c}} \right)$

Matching (1) & (2): $\lim_{\hat{y} \to \infty} \hat{c} \; = \; \lim_{y \to 0} \bar{c} \; = \; \bar{c}_o$

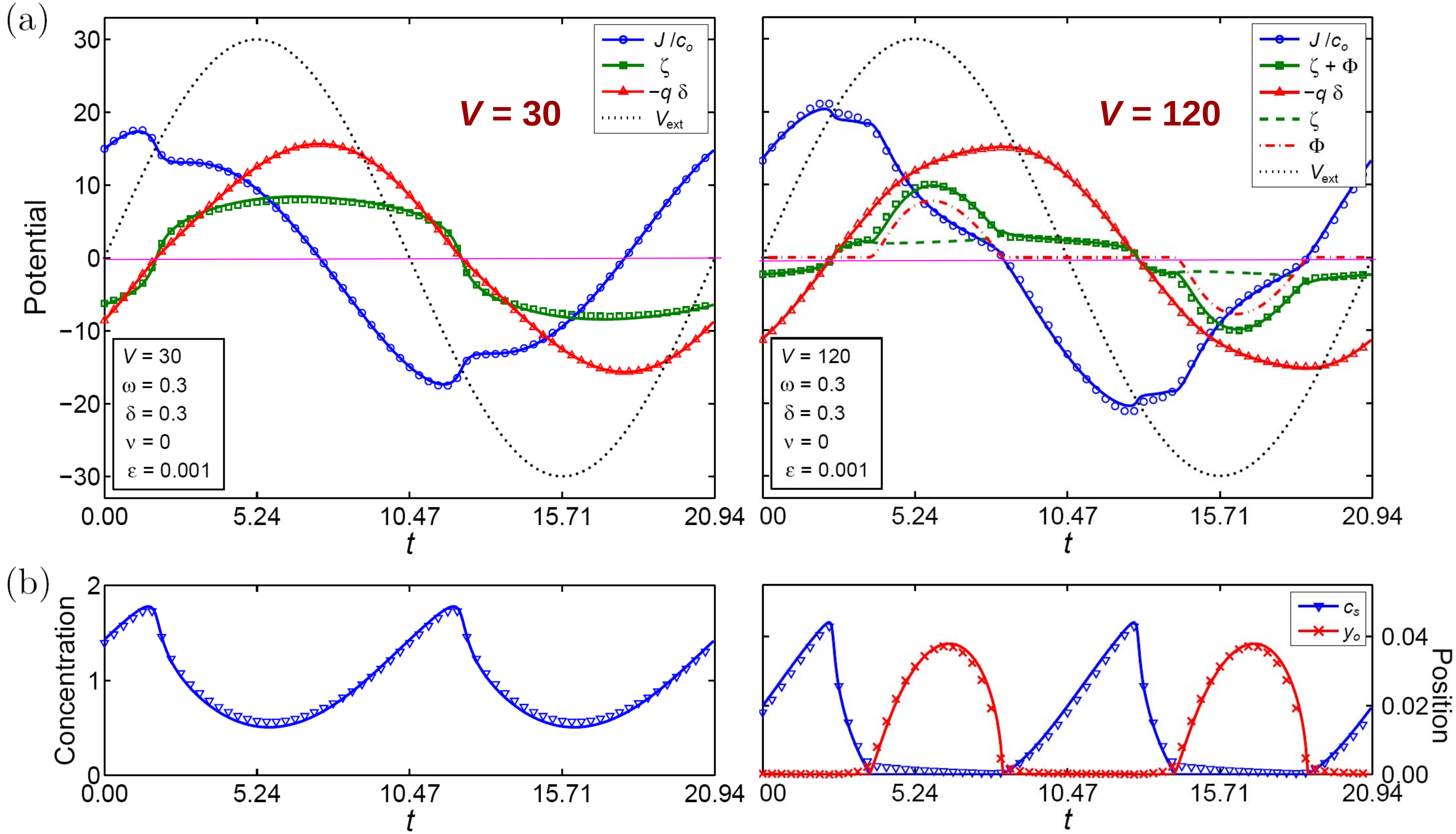
3) Quasi-equilibrium double layer:

$$\tilde{\psi} = 4 \tanh^{-1} \left[\tanh(\tilde{\zeta}/4) e^{-\sqrt{\hat{c}_s}\, \tilde{y}} \right]$$

Matching (2) & (3): $-\frac{1}{\sqrt{\epsilon}} \lim_{\hat{y} \to 0} \partial_{\hat{y}} \hat{c} = \lim_{\hat{y} \to 0} \hat{F} = \tilde{F}_o$

Detailed dynamic response obtained numerically

$$\omega = 0.3,\ \delta = 0.3,\ \nu = 0,\ \text{and}\ \epsilon = 0.001$$

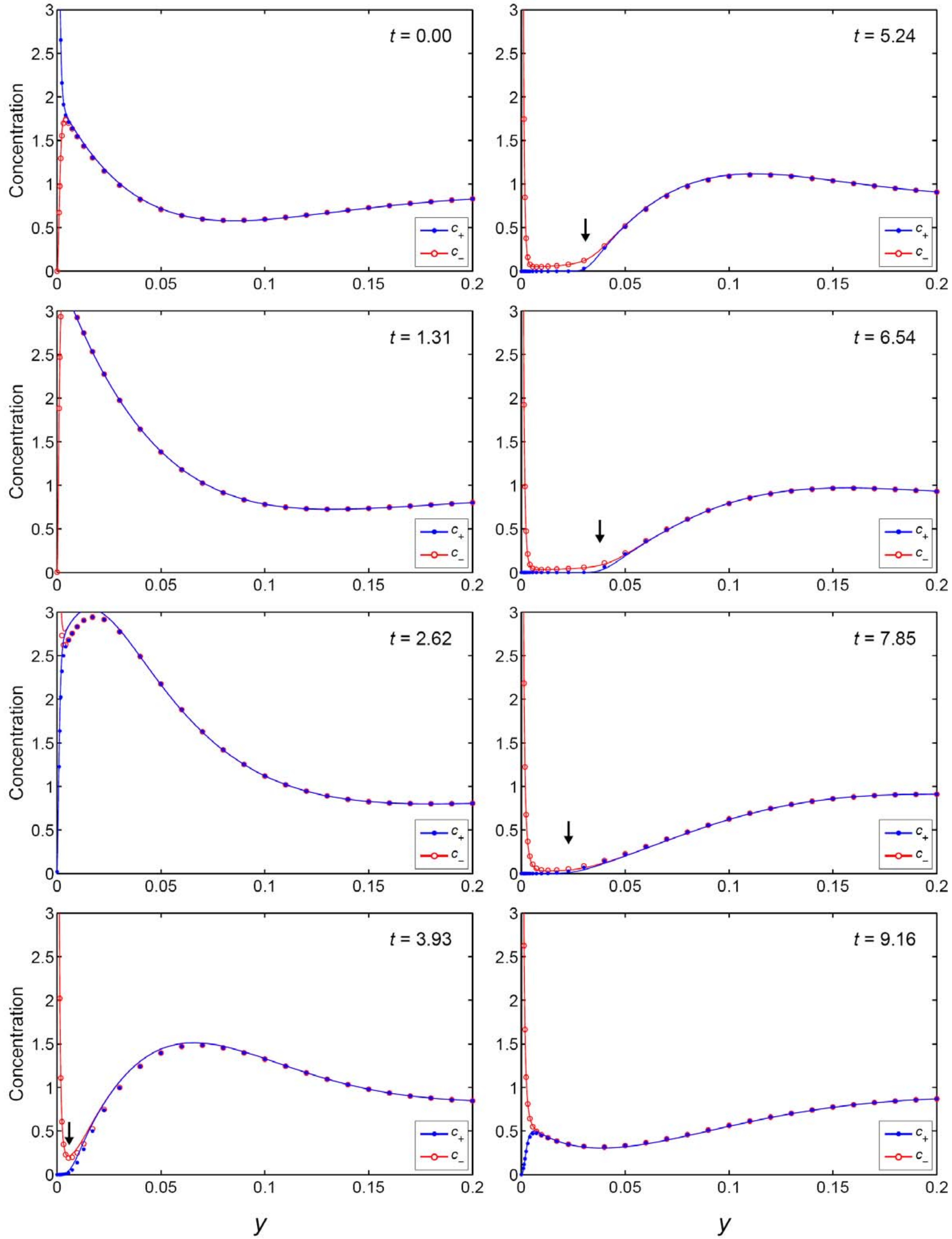


Uniformly valid approximations

$$V = 120, \ \omega = 0.3$$

$$\delta = 0.3, \ \nu = 0 \ \epsilon = 0.001$$

Asymptotic analysis (lines) vs. full numerics (points)



Conclusion

Our original contributions are the solution in the oscillating diffusion layer, controlling the extent of the transient space-charge layer, and the uniformly valid for-mulation of the charge-voltage relation over the transition between quasi-equilibrium and non-equilibrium.

We have compared our asymptotic analysis for the PNP model to a full numerical solution of the PNP equations, and found good qualitative and quantitative agreement.