

EMERGENT BEHAVIOUR IN ELECTRODIFFUSION: PLANCK'S OTHER QUANTA

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(Received July 9, 2013 – Revised August 20, 2013)

A well-established nonlinear continuum model of time-independent electrodiffusion describes the migrational and diffusional transport of two ionic species, with equal and opposite valences, across a liquid junction. The ionic charge densities provide the source for a static electric field, which in turn feeds back on the charges to contribute the migrational component of the ionic transport. Underpinning the model is a form of the second Painlevé ordinary differential equation (PII). When Bäcklund transformations, extended from those known in the context of PII, are applied to an exact solution of the model first found by Planck, a sequence of exact solutions emerges. These are characterized by corresponding ionic flux and current densities that are found to be quantized in a particularly simple way. It is argued here that this flux quantization reflects the underlying quantization of charge at the ionic level: the nonlinear continuum model 'remembers' its discrete roots, leading to this emergent phenomenon.

Keywords: emergent behaviour, nonlinear electrodiffusion, Bäcklund transformations, flux quantization, Painlevé II equation.

PACS Nos: 66.10.-x, 82.39.Wj, 87.10.Ed, 01.65.+g

MSC2010 Codes: 34B60; 34C14; 34B30; 34B15; 76R99

1. Introduction

Many examples are known of simple structures and patterns, now commonly called emergent phenomena, appearing in the analysis of complex, nonlinear systems [1–5]. Two examples are pertinent here. The first is the modeling of the nerve impulse and its propagation by Hodgkin and Huxley [6, 7]. The second is the theory of solitons and their interactions, developed by Seeger et al. for the sine-Gordon equation in the context of crystal dislocations [8], and subsequently by Zabusky and Kruskal for the Korteweg–de Vries equation in the context of waves in various nonlinear dispersive media [9].

Here we present a further case arising in a simple continuum model of steady electrodiffusion, governed by coupled nonlinear ordinary differential equations. It has connections with the two well-known examples cited. Nerve conduction proceeds by processes of electrodiffusion, albeit involving more ionic species than in the case we consider here, and the model we discuss is underpinned by Painlevé's second

nonlinear ordinary differential equation (PII), known to be intimately related by similarity reductions to soliton equations [10].

Since the pioneering works of Nernst [11] and Planck [12], transport of charged ions across liquid junctions has played a fundamental role in a variety of natural systems. Nerve conduction has been mentioned but there are many others [13]. An extension of the Nernst–Planck model [14–16] incorporates the effect of the electric field that develops within a junction in response to diffusional separation of ions carrying different charges. Essential to what follows is the nonlinearity that results as the electric field acts back on the charged ions to contribute a convective component to the ionic transport.

Recent analysis of the model [17–19] has highlighted the role played by the second Painlevé nonlinear differential equation (PII), its exact solutions, and associated Bäcklund transformations [20]. A remarkable phenomenon has emerged in this analysis [19], whereby ionic flux and electric current densities appear with evenly-spaced ‘quantized’ values associated with sequences of solutions of the model, generated by Bäcklund transformations from a given solution.

Our intention here is to show, in the context of sequences of exact rational solutions, that this effect, which has been called [19] “Bäcklund flux-quantization”, is a reflection of the quantization of electric charge at the level of the individual ions involved in transport across the junction.

Thus it can be said that the classical continuum model, through its nonlinear structure, ‘remembers’ its discrete roots, and displays them in this emergent phenomenon.

2. The model

In its simplest form, the extended model deals with steady transport in one dimension of two ionic species carrying equal and opposite charges across a liquid junction occupying $0 \leq x \leq \delta$, between reservoirs of well-stirred ionic solutions occupying $x < 0$ and $x > \delta$. Concentrations of the positively and negatively charged species are modeled as continuous—indeed, once differentiable—functions $c_+(x)$ and $c_-(x)$, respectively.

The governing system of ordinary differential equations (ODEs) is [15]

$$\begin{aligned} c_+'(x) &= (ze/k_B T) E(x) c_+(x) - \Phi_+/D_+, \\ c_-'(x) &= -(ze/k_B T) E(x) c_-(x) - \Phi_-/D_-, \\ E'(x) &= (4\pi ze/\epsilon) [c_+(x) - c_-(x)] \end{aligned} \quad (1)$$

for $0 < x < \delta$. Here Φ_+ , Φ_- denote the steady (constant) flux densities in the $+x$ -direction of the two species, D_+ , D_- their diffusion coefficients, and z their common valence, while $E(x)$ denotes the induced electric field, k_B Boltzmann’s constant, e the electronic charge, ϵ the electric permittivity, and T the ambient absolute temperature within the solution in the junction. An important auxiliary

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