

The nonlinear Poisson–Boltzmann equation

SPITZER¹ has reminded us that the nonlinear Poisson–Boltzmann equation (NPBE) contains a logical inconsistency. An early incisive analysis of this inconsistency was given by Onsager² 50 years ago. Unhappily, more recently, a considerable confusion^{1,3} has accrued concerning the nature and consequences of the inconsistency. Spitzer's¹ statement that "the NPBE violates the important electrostatic theorem of additivity of electrostatic potentials" is simply incorrect, and his recommendation that "the linearization of the NPBE is desirable, in principle" is entirely inappropriate.

First we consider the nature of the inconsistency. Onsager² was concerned with the microscopic NPBE as it is used to describe the potential generated by a single ion in solution that is screened by the response to it of all the other ions in the electrolyte. As Onsager makes clear, the inconsistency derives from the replacement of the potential of mean force, $w_i(r)$, in the correct Boltzmann relation (his equation (21); ref. 2), by the simpler electrostatic potential energy $e_i\psi_j(r)$ to obtain what is finally an inconsistent Boltzmann relation (his equation (13); ref. 2). The replacement is made in order to write a one-particle NPBE. Note that neither the Poisson equation nor the superposition theorem of electrostatics as such is germane to the inconsistency studied by Onsager. The confusion is compounded by a supposed connection of the linear superposition of electrostatic potentials to a linear dependence of space charge ρ on potential ψ (refs 1,3). In actuality, the linear superposition theorem of electrostatics⁴ holds for an arbitrary distribution of space charge $\rho(r)$. Thus, in the analogue to the NPBE appropriate to Fermi–Dirac statistics, namely, the Thomas–Fermi equation⁵, $\rho \propto \psi^{3/2}$. For space-charge-limited currents in a planar vacuum diode⁶, $\rho \propto \psi^{-1/2}$; in the analogous solid-state diode⁷, $\rho \propto \psi^{-1/3}$, and so on.

We next take up the consequences of the inconsistency. As noted above, the inconsistency refers directly to the microscopic NPBE. However, it is important to note that most of the literature on the NPBE since World War II, including the Spitzer letter¹, is not concerned with this equation but rather with the macroscopic NPBE. This latter equation describes the spatial dependence of the average potential generated by relatively large, charged surface(s) in contact with the electrolyte. This local average potential is what remains after all microscopic fluctuations have been averaged out. For the macroscopic NPBE a new phenomenon comes into play when linearization finally fails (that is, at high surface-charge concentrations), which is the formation of a counterion condensate close to the surface⁸.

Fixman⁹, in a theoretical study of the problem within the framework of statistical mechanics, pointed out that substantial errors deep in the condensate lead to far smaller errors outside the condensate. He aptly described this phenomenon as "the buffering action of 'the condensed phase'" (ref. 9). This very pronounced decoupling of a large surface charge from the 'distant' bulk electrolyte is also a direct mathematical consequence of the NPBE, as shown for planar geometry by Verwey and Overbeek¹⁰. The buffering action of the condensate, as predicted by the NPBE, is even more striking for cylindrical and spherical geometries, as shown by numerical studies of this equation by Lampert and Martinelli (to be published elsewhere). Fixman's numerical calculations led him to conclude that the NPBE is acceptable⁹ up to local, condensate concentrations as high as 2–3 M, provided that the bulk salt concentration does not exceed ~ 0.1 M, which happens to be, approximately, that for physiological saline. It is also relevant here and perhaps not widely known that some 15 yr after his incisive criticism of the microscopic NPBE, Onsager used the macroscopic NPBE to calculate "The effects of shape on the interaction of colloidal particles"¹¹.

Spitzer¹ alludes to the difficulty of testing experimentally the Gouy–Chapman–Stern (GCS) model for incorporating adsorption into double-layer theory, as constructed with the NPBE. If that is the situation in electrochemistry and colloid chemistry, then matters are improved considerably in biophysical studies of charged phospholipid bilayer membranes immersed in an aqueous solution. McLaughlin *et al.*¹² showed, by adding small concentrations of divalent cations to a host solution of monovalent ions, that the observed shift in membrane potential disagreed strongly with predictions of linearized PB theory, but agreed adequately with GCS theory. In a recent critique of the work of several groups using various experimental techniques, McLaughlin concludes¹³ "that fortunately, the GCS theory appears to be a good first approximation for describing the adsorption of cations to bilayer membranes".

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Homologies in the avian tarsus

MCGOWAN has recently presented evidence from the avian tarsal joint for a wide taxonomic separation between ratite and carinate birds. He implies that the pretibial bone of carinates is formed by ossification of a portion of the cartilaginous precursor of the calcaneum (a "calcaneal spur"), while in ratites the comparable structure is an ascending process of the astragalus. However, the youngest specimen he described was a 12-day-old quail embryo. Examination of a large series of cleared and stained chicken embryos shows that the 7-day-old embryos have separate cartilaginous calcania, astragali and tibiae, but no ascending processes or pretibial bones. Eight-day-old chicken embryos show a separate triangular pretibial chondrification above the calcaneum which does not appear to be part of either the astragalus or the calcaneum. On day 9 the pretibial, astragalar and calcaneal cartilages fuse. The pretibial cartilage appears to fuse with both the calcaneal and astragalar cartilages. Only in the fused state could one mistake the pretibial chondrification for an extension of the calcaneum. By day 17 the pretibial bone (calcaneal spur of McGowan¹) has begun to ossify; at this point it is the only tarsal bone undergoing ossification (Fig. 2b–d of ref. 1). Thus, the pretibial bone is the last carinate tarsal element to chondrify and the first to ossify.

McGowan¹ shows that the first bone to ossify in the tarsal complex of ratites is the "ascending process". We believe that this concordance between the ossification of the ascending process of ratites and the pretibial bone of carinates would be hard to explain if they are not the same bone. This is especially true when we consider that the calcaneum is the last bone to ossify in McGowan's preparations.

McGowan¹ describes the "ascending process" of ratites as an ossification with a disk-like base and separate from the astragalus. He describes an early stage in the development of the distal end of the tibiotarsus as comprising a medial ossification and a lateral cartilaginous area. The lateral cartilaginous area has a dorsal spur which he considers to be "homologous with the precursor of the carinate pretibial bone". The enlargement of the astragalus found in some ratites might be a derived character state related to neoteny. The earlier ossification of the astragular portion of the joint may increase the relative