Well Posed PNP

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I present a version of PNP in which Maxwell's version of the continuity equation for charge[1] is used so the resulting flux equation for the flux $\mathbf{J}$ of charge (i.e., of total electric current) always involves the permittivity (i.e., dielectric coefficient).

$$\nabla \cdot \mathbf{J} + \frac{\partial \rho}{\partial t} = \nabla \cdot \left(\mathbf{J} + \frac{\partial \mathbf{D}}{\partial t} \right) \qquad = 0;$$
$$\nabla \cdot \mathbf{J} + \frac{\partial \rho}{\partial t} = \nabla \cdot \left(\mathbf{J} + \frac{\partial \left(\varepsilon \mathbf{E} \right)}{\partial t} \right) = 0 \tag{1}$$

This is eq. 6.4 of Jackson, p. 238, expanded, see p. 154. I follow Jackson's notation exactly and use ε for the permittivity (that has units. It is not the dielectric 'constant').

The variable ρ is the net charge, related to the concentration of ions through

$$\rho = \sum_{i=1}^{N} z_i F c_i \tag{2}$$

where I use chemical units (Faradays) because we are dealing with a macroscopic system.

Now we introduce the Nernst Planck equations.

$$\mathbf{J}_i = -D_i \left(\nabla c_i - \frac{F}{RT} z_i c_i \nabla \phi \right); \quad i = 1, \ldots N \tag{3}$$

I use the diffusion coefficient and not mobility to avoid the confusion between the two definitions of mobility (absolute and electrical) in the literature. Obviously if the Einstein approximation fails and enough information is available to distinguish mobility from diffusion coefficient, the mobility should be used explicitly, and the choice of definition should be made explicitly.

Now, we sum over all the ions to get total flux of charge

$$\mathbf{J} = \sum_{i=1}^{N} \mathbf{J}_i = \sum_{i=1}^{N} \left(-D_i \nabla c_i - \frac{F}{RT} z_i c_i \nabla \phi \right) \tag{4}$$

and the Maxwell Continuity equation (1) gives the equation for continuity of electric charge, i.e., current

$$\nabla \cdot \mathbf{J} = \nabla \cdot \left[\sum_{i=1}^{N} \left(-D_i \nabla c_i - \frac{F}{RT} z_i c_i \nabla \phi \right) \right] = -\frac{\partial \left(\varepsilon \mathbf{E} \right)}{\partial t} = \frac{\partial \left(\varepsilon \nabla \phi \right)}{\partial t} \tag{5}$$

I leave the permittivity inside the brackets so we never forget the assumption that is involved in moving it outside!

[1] See p. 238 of J. D. Jackson, *Classical Electrodynamics*, Third Edition (1999), attached to this document.

Note the different form of the continuity of mass for each species

$$\nabla \cdot \mathbf{J}_i + \frac{\partial c_i}{\partial t} = 0 \tag{6}$$

or for the total mass. This is not equivalent to the Maxwell continuity equation. It does not involve the permittivity or Maxwell's essential step replacing $\mathbf{J}$ by $\mathbf{J} + \partial \mathbf{D} / \partial t$ (unnumbered equation between 6.4 and 6.5 in Jackson, p. 238)

$$\sum_{i=1}^{N} \left(\nabla \cdot \mathbf{J}_i \right) + \sum_{i=1}^{N} \frac{\partial c_i}{\partial t} = 0 \tag{7}$$

It is clear that we will get different results if we use the set of equations shown in eq. (6) (which does not depend on the permittivity at all, for example) or if we use a subset of the equations shown in eq. (6) and the Maxwell Continuity equation (1), i.e., eq. (5). One formulation depends on permittivity and the other does not, so they cannot be equal for all values of permittivity!

The issue is resolved when we realize that to make the system well posed (i.e., to reach steady state when concentrations and potentials on the boundaries are constants independent of time), we must relax our boundary conditions on concentration. We must allow one of the concentrations c_m (say) to 'float', i.e., to be determined by the rest of the problem. We introduce an artificial additional pathway for this ion we call the leak pathway, e.g., an $\left(N+1\right)^{th}$ flux equation added to the set described in eq. (3). We have two flux equations for the same ionic species, one the real one and the other the leak. We choose parameters for the leak so the system is not perturbed in the time domain we study. The leak ensures that at infinite time the system will be stable.

<u>Set Of Equations</u> are then

(1) The Maxwell Continuity Equation for the total flux of charge

$$\nabla \cdot \mathbf{J} = \nabla \cdot \left[\sum_{i=1}^{N} \left(-D_i \nabla c_i - \frac{F}{RT} z_i c_i \nabla \phi \right) \right] = -\frac{\partial \left(\varepsilon \mathbf{E} \right)}{\partial t} = \frac{\partial \left(\varepsilon \nabla \phi \right)}{\partial t}$$

(2) The mass continuity equations for the (mass) flux of $N-1$ species, the set

$$\mathbf{J}_i = -D_i \left(\nabla c_i - \frac{F}{RT} z_i c_i \nabla \phi \right); \quad i = 1, \ldots N-1; \quad \text{ion } m \text{ is excluded}$$

(3) Dirichlet boundary conditions on the concentrations of $N-1$ species, ion is excluded, imposed at time zero, and maintained from then on.

(4) Some initial condition on ion *m* which is not maintained in time so the system starts in a well-defined state of perfect electrical neutrality. That is to say, the concentration of the special ion c_m would be chosen so the sum (including) $\sum_{i=1}^{N+1} z_i c_i = 0$ at $t = 0$.

In this document do not discuss the stray and ‘membrane’ capacitances in the setup. That goes as I wrote earlier and can be added if there is some reason I do not perceive right now.

Note the discussion of capacitance to ground (found in earlier versions of this paper) has been replaced by (what I hope) is an exact mathematical statement of the role of permittivity, arising from polarization (see p. 152-154 of Jackson).

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