Well Posed PNP

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Here is 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., flux of total electric current) always involves the permittivity (i.e., dielectric coefficient).

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

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 we 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

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

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

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!

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

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

and the different form for the continuity equation of total 'mass'.

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

The mass continuity equations are ***not*** equivalent to the Maxwell continuity equation. They do not involve the permittivity ε.

Maxwell's 'essential step' (language from Jackson, p. 238) replaced $\mathbf{J}$ by $\mathbf{J} + \partial \mathbf{D} / \partial t$. The essential step introduces the permittivity as described in the unnumbered equation between 6.4 and 6.5 in Jackson, p. 238. It is clear that we will get different results if we use the set of equations shown in eq. (6) (that does not depend on the permittivity at all, for example) or if we use the Maxwell Continuity equation (1) and a subset of the equations shown in eq. (6) and, i.e., eq. (5). One formulation depends on permittivity and the other does not, so they cannot be equal for all values of permittivity!

This apparent paradoxical situation 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

$$\nabla \cdot \mathbf{J} = \nabla \cdot \left[\sum_{i=1}^{N} \left(-D_i \nabla c_i - \frac{F}{RT} z_i c_i \nabla \phi \right) \right] = -\frac{\partial \left(\varepsilon \mathbf{E} \right)}{\partial t} = \frac{\partial \left(\varepsilon \nabla \phi \right)}{\partial t} \tag{8}$$

(2) The mass continuity equations for the (mass) flux of $N-1$ species. This set excludes ion m:

$$\mathbf{J}_i = -D_i \left(\nabla c_i - \frac{F}{RT} z_i c_i \nabla \phi \right); \quad i = 1, \ldots N-1; \qquad \text{ion } m \text{ is excluded} \tag{9}$$

(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 of charges (including *m*) would be zero, i.e., $\sum_{i=1}^{N+1} z_i c_i = 0$ 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). The electricians' formulation of 'capacitance to ground' used in my previous discussion is easy to understand from eq. (1).

$$\nabla \cdot \mathbf{J} = -\nabla \cdot \left(\frac{\partial \left(\nabla \phi \right)}{\partial t} \right) \tag{10}$$

suggesting a formula close to the electricians' capacitance to ground idea

$$\mathbf{J} = -\frac{\partial \left(\nabla \phi \right)}{\partial t} \tag{11}$$

as well as the strange looking formulae. I suspect something is here that I do not understand.

$$\nabla \cdot \mathbf{J} = -\nabla \cdot \left(\frac{\partial \left(\nabla \phi \right)}{\partial t} \right); \quad \nabla \cdot \mathbf{J} = -\frac{\partial}{\partial t} \nabla^2 \phi; \quad \nabla \cdot \mathbf{J} = -\nabla^2 \left(\frac{\partial \phi}{\partial t} \right) \tag{12}$$

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