Dynamic Theory of Type 3 Liquid Junction Potentials: Formation of Multi-Layer Liquid Junctions - Supporting Information.

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A: THE ITERATIVE NEWTON-RAPHSON METHOD

The iterative Newton-Raphson method is a standard numerical procedure for solving a system of coupled non-linear simultaneous. The n equations are written in an homogeneous form:

$$f_n(x_0, x_1, ..., x_n) = 0 \tag{1}$$

Let $\vec{x}$ be the vector containing the unkonowns x_0 to x_n; let $\vec{f}(\vec{x})$ be the vector containing the functions f_0 to f_n; and let $\vec{u}$ be the vector containing the differences between $\vec{x}$ at consecutive iterations, such that

$$\vec{u} = \vec{x}_{z+1} - \vec{x}_z \tag{2}$$

In the simple Newton-Raphson method, the Taylor series of a function about a trial solution x_0 is considered:

$$f(x) \approx f(x_0) + (x - x_0)f'(x_0) = 0 \tag{3}$$

and hence the solution x may be derived from successive iterations of the form:

$$x_{z+1} = x_z - \frac{f(x_z)}{f'(x_z)} \tag{4}$$

For a function of multiple variables, a trial vector $\vec{x}_0$ may be altered similarly:

$$f(\vec{x}) \approx f(\vec{x}_0) + \sum_n (x_n - x_{n,0}) \frac{\partial f(\vec{x}_0)}{\partial x_n} \tag{5}$$

and hence, defining $u_n = x_n - x_{n,0}$

$$\sum_n u_n \frac{\partial f(\vec{x}_0)}{\partial x_n} = -f(\vec{x}_0) \tag{6}$$

Where there are n simultaneous equations associated with the n variables, this may be extended, such that for each variable m:

$$\sum_n u_n \frac{\partial f_m(\vec{x}_0)}{\partial x_n} = -f_m(\vec{x}_0) \tag{7}$$

which may be expressed for the vectors $\vec{u}$ and $\vec{f}$ in the matrix form:

$$\vec{J}(\vec{x}_0)\vec{u} = -\vec{f}(\vec{x}_0) \tag{8}$$

Where $\vec{J}$ is the Jacobian matrix, being the n x n square matrix for mhich the element J_{mn} is described:

$$J_{mn} = \frac{\partial f_m}{\partial x_n} \tag{9}$$

i.e. equation 8 is a matrix equation of the form:

$$\begin{pmatrix} \frac{\partial f_0}{\partial x_0} & \frac{\partial f_0}{\partial x_1} & \frac{\partial f_0}{\partial x_2} & \cdots & \frac{\partial f_0}{\partial x_n} \\ \frac{\partial f_1}{\partial x_0} & \frac{\partial f_1}{\partial x_1} & \frac{\partial f_1}{\partial x_2} & \cdots & \frac{\partial f_1}{\partial x_n} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \frac{\partial f_n}{\partial x_0} & \frac{\partial f_n}{\partial x_1} & \frac{\partial f_n}{\partial x_2} & \cdots & \frac{\partial f_n}{\partial x_n} \end{pmatrix} \begin{pmatrix} (x_0 - x_{0,0}) \\ (x_1 - x_{1,0}) \\ \vdots \\ (x_n - x_{n,0}) \end{pmatrix} = \begin{pmatrix} -\vec{f}_0(\vec{x}_0) \\ -\vec{f}_1(\vec{x}_0) \\ \vdots \\ -\vec{f}_n(\vec{x}_0) \end{pmatrix} \tag{10}$$

This equation is solved iteratively and $\vec{x}$ is augmented by $\vec{u}$, until all values u_0 to u_n are less than a characteristic parameter ϵ, at which point $\vec{x}$ is taken as the trial vector for the next timstep. The equation can be solved by an adapted Thomas Algorithm method (LU decomposition followed by back substitution) as the Jacobian is a diagonal matrix with a minimum of fifteen non-zero diagonals for a Type 3 LJP simulation when unknowns x_n are appropriately ordered (e.g. $c_{\mathrm{A},0}$, $c_{\mathrm{X},0}$, ϕ_0, $c_{\mathrm{B},0}$, $c_{\mathrm{Y},0}$, $c_{\mathrm{A},1}$, $c_{\mathrm{X},1}$, ϕ_1, etc).