Derivation

$\phi_j(r) = \dfrac{q_j}{4\pi\varepsilon\varepsilon_0 r}$, $\quad \phi_j'' = \phi_j + \phi_j'$, $\quad \nabla^2 \phi_j''(r) = -\dfrac{\rho_j(r)}{\varepsilon\varepsilon_0}$,

$\cancel{\rho_j = \sum_i e\exp(-q_i \phi_j''(r)/kT)}$ $\qquad \rho_j = N_i \exp(-q_i \phi_j''(r)/kT)$

Assuming the ionic atmosphere is averaged cloud of continuous charge density:

$\rho_j(r) = \sum_i n_i q_i \exp(-q_i \phi_j''(r)/kT)$

$$\Rightarrow \nabla^2 \phi_j''(r) = -\frac{\sum_i n_i q_i \exp(-q_i \phi_j''(r)/kT)}{\varepsilon\varepsilon_0}$$

Expanding exponential: $\nabla^2 \phi_j''(r) = -\dfrac{\sum_i [n_i q_i - (n_i q_i^2 \phi_j''(r))/kT + \dots]}{\varepsilon\varepsilon_0}$

Since solution electrically neutral: $\sum_i n_i q_i = 0$

$$\Rightarrow \nabla^2 \phi_j''(r) = \frac{\sum_i \left(\frac{n_i q_i^2 \phi_j''(r)}{kT}\right)}{\varepsilon\varepsilon_0}$$

$$= \frac{e^2}{\varepsilon\varepsilon_0 kT}\left(\sum_i n_i z_i^2\right)\phi_j''(r)$$

$\Rightarrow \nabla^2 \phi_j''(r) = \alpha^2 \phi_j''(r)$ with $\alpha^2 = \dfrac{e^2}{\varepsilon\varepsilon_0 kT}\sum_i n_i z_i^2$

$$\Rightarrow \nabla^2 \phi_j''(r) - \alpha^2 \phi_j''(r) = 0$$

In spherical coordinates: $\nabla^2 \phi_j''(r) = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right)\phi_j'' + \frac{1}{r^2 \sin^2\phi}\frac{\partial^2}{\partial \theta^2}\phi_j'' + \frac{1}{r^2 \sin\phi}\frac{\partial}{\partial \phi}\left(\sin\phi \frac{\partial}{\partial \phi}\right)$

There is no dependence on θ or ϕ (as we've assumed full spherical symmetry); $\nabla^2 \phi_j''(r) = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right)\phi_j''(r)$

$$= \frac{1}{r^2}\left(r^2 \frac{\partial^2}{\partial r^2} + 2r\frac{\partial}{\partial r}\right)\phi_j''(r)$$

$$= \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right)\phi_j''(r)$$

$$\Rightarrow \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \alpha^2\right)\phi_j''(r) = 0$$

Assume $\phi_j''(r) = \frac{1}{r}u(r)$:

$$\Rightarrow \frac{\partial^2}{\partial r^2}\left(\frac{u(r)}{r}\right) + \frac{2}{r}\frac{\partial}{\partial r}\left(\frac{u(r)}{r}\right) - \frac{\alpha^2 u(r)}{r} = 0$$

$$\Rightarrow \frac{\partial}{\partial r}\left(-\frac{u(r)}{r^2} + \frac{\frac{\partial u}{\partial r}}{r}\right) + \frac{2}{r}\left(-\frac{u(r)}{r^2} + \frac{\frac{\partial u}{\partial r}}{r}\right) - \frac{\alpha^2 u(r)}{r} = 0$$

$$\Rightarrow \cancel{\frac{2u(r)}{r^3}} - \cancel{\frac{\frac{\partial u}{\partial r}}{r^2}} - \cancel{\frac{\frac{\partial u}{\partial r}}{r^2}} + \frac{\frac{\partial^2 u}{\partial r^2}}{r} - \cancel{\frac{2u(r)}{r^3}} + \cancel{\frac{2\frac{\partial u}{\partial r}}{r^2}} - \frac{\alpha^2 u(r)}{r} = 0$$

$$\Rightarrow \frac{1}{r}\frac{\partial^2 u}{\partial r^2} - \frac{\alpha^2}{r}u(r) = 0$$

Setting up A.E.: $\frac{1}{r}y^2 - \frac{\alpha^2}{r} = 0$

$\Rightarrow y = \frac{\pm\sqrt{-4\left(\frac{1}{r}\right)\left(-\frac{\alpha^2}{r}\right)}}{\frac{2}{r}} = \frac{\pm\sqrt{\frac{4\alpha^2}{r^2}}}{\frac{2}{r}} = \frac{\pm\frac{2\alpha}{r}}{\frac{2}{r}} = \pm\alpha$

~~$\Rightarrow u(r) = Ce^{\alpha r} + De^{-\alpha r}$~~ $\Rightarrow u(r) = C\exp(\alpha r) + D\exp(-\alpha r)$

$\Rightarrow \phi_j''(r) = \frac{C\exp(\alpha r)}{r} + \frac{D\exp(-\alpha r)}{r}$

As $r \to \infty$, $\phi_j''(r) \to 0 \Rightarrow C = 0$

$\Rightarrow \phi_j''(r) = \frac{D\exp(-\alpha r)}{r}$

$\Rightarrow \frac{D\exp(-\alpha r)}{r} = \frac{q_j}{4\pi\varepsilon\varepsilon_0 r} + \phi_j'(r)$

Assume that ions have diameter β: $\frac{D\exp(-\alpha\beta)}{\beta} = \frac{q_j}{4\pi\varepsilon\varepsilon_0\beta} + \phi_j'(\beta)$

Assuming there is continuity between ϕ_j'' and its 1st derivative, and that ϕ_j' is constant: $\frac{d}{d\beta}(\phi_j'') = -\frac{D\exp(-\alpha\beta)}{\beta^2} - \frac{\alpha D\exp(-\alpha\beta)}{\beta} = -\frac{q_j}{4\pi\varepsilon\varepsilon_0\beta^2}$

$\Rightarrow D\left(\frac{-\exp(-\alpha\beta) - \alpha\beta\exp(-\alpha\beta)}{\beta^2}\right) = -\frac{q_j}{4\pi\varepsilon\varepsilon_0\beta^2}$

$\Rightarrow D\exp(-\alpha\beta)\left(\frac{1+\alpha\beta}{\beta^2}\right) = \frac{q_j}{4\pi\varepsilon\varepsilon_0\beta^2}$

$\Rightarrow D\exp(-\alpha\beta) = \frac{q_j}{4\pi\varepsilon\varepsilon_0}\frac{1}{1+\alpha\beta}$

$\Rightarrow D = \frac{q_j}{4\pi\varepsilon\varepsilon_0} \frac{\exp(\alpha\beta)}{1+\alpha\beta}$

$\Rightarrow \Phi_j''(r) = \frac{q_j}{4\pi\varepsilon\varepsilon_0} \frac{\exp(\alpha\beta)}{1+\alpha\beta} \frac{\exp(-\alpha r)}{r}$

$\Rightarrow \frac{q_j}{4\pi\varepsilon\varepsilon_0} \frac{\exp(\alpha\beta)}{1+\alpha\beta} \frac{\exp(-\alpha r)}{r} = \frac{q_j}{4\pi\varepsilon\varepsilon_0 r} + \Phi_j'$

Assuming $r = \beta$; $\Phi_j' = \frac{q_j}{4\pi\varepsilon\varepsilon_0} \frac{\exp(\alpha\beta)}{1+\alpha\beta} \frac{\exp(-\alpha\beta)}{\beta} - \frac{q_j}{4\pi\varepsilon\varepsilon_0\beta}$

$\Phi_j' = \frac{q_j}{4\pi\varepsilon\varepsilon_0\beta}\left(\frac{\exp(\alpha\beta)\exp(-\alpha\beta)}{1+\alpha\beta} - 1\right)$

$= \frac{q_j}{4\pi\varepsilon\varepsilon_0\beta}\left(\frac{1-1-\alpha\beta}{1+\alpha\beta}\right) = -\frac{q_j}{4\pi\varepsilon\varepsilon_0} \frac{\alpha}{1+\alpha\beta}$

$\Rightarrow U_j = -\frac{q_j^2}{4\pi\varepsilon\varepsilon_0} \frac{\alpha}{1+\alpha\beta}$

$\Rightarrow G = \frac{1}{2}\left(-\frac{e^2}{4\pi\varepsilon\varepsilon_0} \frac{\alpha}{1+\alpha\beta}\right) \sum_i n_i z_i^2 = -\frac{e^2}{8\pi\varepsilon\varepsilon_0} \frac{\alpha}{1+\alpha\beta} \sum_i n_i z_i^2$

Also, $G = 2nRT \log_e \gamma_\pm$

Let $I = \frac{1}{2}\sum_i n_i z_i^2$. Then $I = \frac{1}{2N}\sum_i n_i z_i^2$

$\Rightarrow \alpha^2 = \frac{e^2}{\varepsilon\varepsilon_0 kT} \sum_i n_i z_i^2 = \frac{2Ne^2 I}{\varepsilon\varepsilon_0 kT}$

$$\Rightarrow 2nRT\log_e\gamma_\pm = -\frac{e^2}{8\pi\varepsilon\varepsilon_0}\frac{\left(\frac{2Ne^2}{\varepsilon\varepsilon_0 kT}\right)^{\frac{1}{2}}\sqrt{I}}{1+\beta\left(\frac{2Ne^2}{\varepsilon\varepsilon_0 kT}\right)^{1/2}\sqrt{I}}\sum_i n_i z_i^2$$

Letting $A = \frac{e^2 B}{2.303\times 8\pi\varepsilon\varepsilon_0 kT}$ and $B = \left(\frac{2e^2N}{\varepsilon\varepsilon_0 kT}\right)^{1/2}$;

$$2nRT\log_e\gamma_\pm = \frac{-2.303\,A\sqrt{I}}{1+\beta B\sqrt{I}}\sum_i n_i z_i^2\,kT$$

Using log rules: ~~$\log_x$~~ $\log_{10}\gamma_\pm = \frac{\log_e\gamma_\pm}{\log_e 10}$

$$\Rightarrow \log_e\gamma_\pm = 2.303\log_{10}\gamma_\pm = \log_e 10\log_{10}\gamma_\pm$$

$$\Rightarrow 2nRT\log_{10}\gamma_\pm = -A\frac{\sqrt{I}}{1+\beta B\sqrt{I}}\sum_i n_i z_i^2\,kT$$

Since solution symmetrical: $2nRT\log_{10}\gamma_\pm = \frac{-kTA\sqrt{I}}{1+\beta B\sqrt{I}}Nz_i^2\times 2$

(i.e. equal concentrations of each ion)

Using ideal gas law: ~~$NKT = NKT = P$~~ $PV = nRT = NkT$;

$$2NkT\log_{10}\gamma_\pm = -Az_i^2\frac{\sqrt{I}}{1+\beta B\sqrt{I}}2NkT$$

$$\Rightarrow \log_{10}\gamma_\pm = -Az_i^2\frac{\sqrt{I}}{1+\beta B\sqrt{I}}$$