Supplementary Information

Quantification of Cation-Cation, Anion-Anion and Cation-Anion Correlations in Li Salt / Glyme Mixtures by combining Very-low-frequency Impedance Spectroscopy with Diffusion and Electrophoretic NMR

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Experimental Data of Diffusion NMR and Electrophoretic NMR for the different LiFSI / G4 mixtures

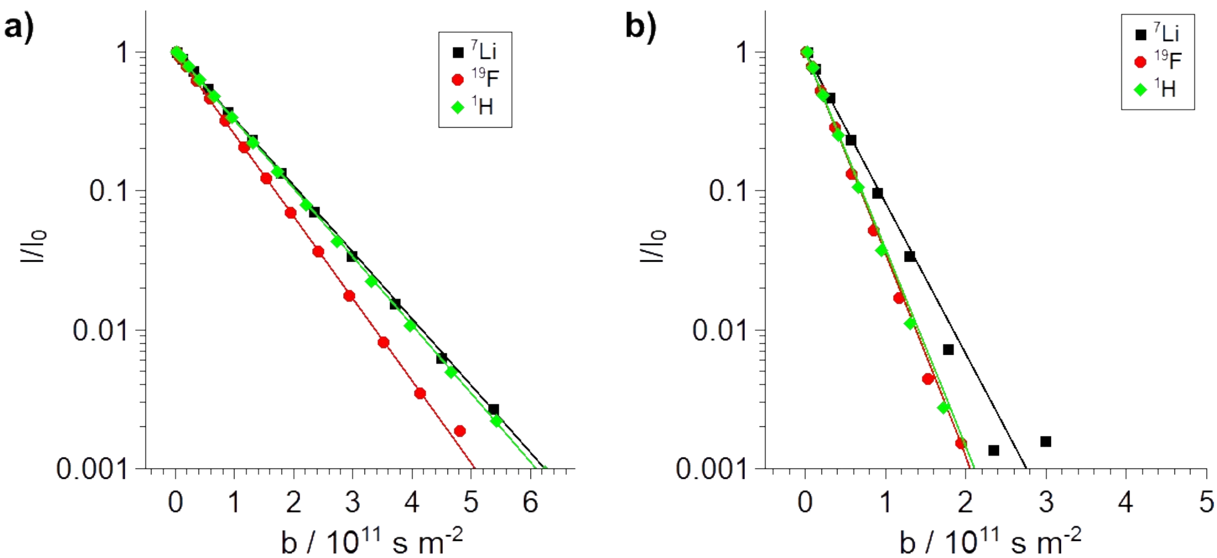

Figure S1: Signal attenuation I/I_0 observed in ^{1}H, ^{7}Li and ^{19}F PFG-NMR experiments a) for the LiFSI / G4 1:1 mixture and b) for the LiFSI / G4 1:2 mixture.

The data of the ^{7}Li and ^{1}H signal exhibit the same slope for the LiFSI / G4 1:1 mixture (Fig. S1a), whereas the slopes differ for the LiFSI / G4 1:2 mixture (Fig. S1b). Thus, the self-diffusion coefficients of ^{7}Li and ^{1}H for the LiFSI / G4 1:1 are identical. For the LiFSI / G4 1:2 mixture the

G4 diffusion coefficient is a fast exchange average of G4 coordinated to Li, and free G4, thus it differs from the diffusion coefficient of the Li^+ ion.

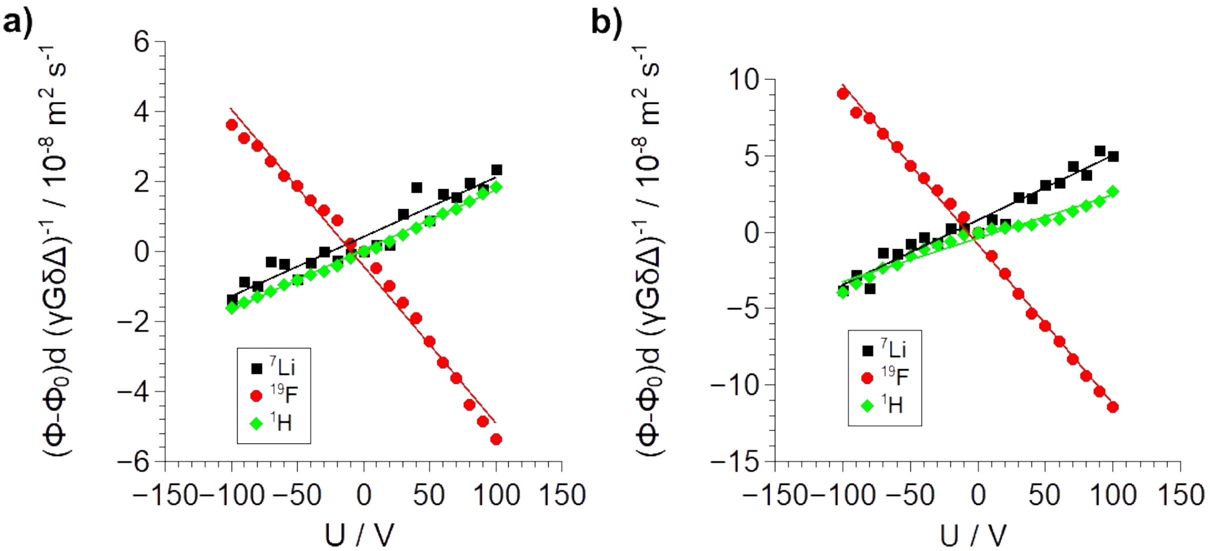

Figure S2: Voltage U dependent reduced phase shift values $(\phi-\phi_0)d\gamma^{-1}G^{-1}\delta^{-1}\Delta^{-1}$ observed via ^{1}H, ^{7}Li and ^{19}F eNMR a) for the LiFSI / G4 1:1 mixture and b) for the LiFSI / G4 1:2 mixture.

The observed ^{1}H phase shift values and their slope describe the G4 movement, exhibiting the same slope and mobility as ^{7}Li for the LiFSI / G4 1:1 mixture (Fig. S2a). This is in agreement with the observation of identical diffusion coefficients. For the LiFSI / G4 1:2 mixture (Fig. S2b) a deviation for the slopes can be observed, which is again a consequence of the fast exchange average giving the G4 mobility.

Thermodynamic factor for the LiTFSI / G4 1:1 mixture and different LiFSI / G4 mixtures

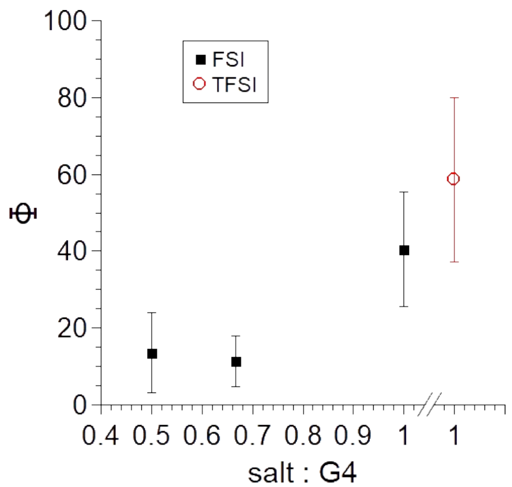

Figure S3: Thermodynamic factors for the different electrolyte mixtures.

Derivation of Eqs. [35a-c]

We start with Eqs. [33a], [33b], [34a], and [34b]:

$$\frac{1}{1+k}\left[\sum_{i=1}^{N/2}\left(\Delta x_i^+\right)\right]+\frac{k}{1+k}\left[\sum_{i=1}^{N/2}\left(\Delta x_i^-\right)\right]=A\cdot x_0\cdot\sqrt{N} \quad \textbf{[33a]}$$

$$\sum_{i=1}^{N/2}\left(\Delta x_i^+\right)-\sum_{i=1}^{N/2}\left(\Delta x_i^-\right)=B\cdot x_0\cdot\sqrt{N} \quad \textbf{[33b]}$$

$$\Delta x_i^+ = x_0\cdot\left(g_i+a_i^+\cdot A+b_i^+\cdot B\right) \quad \textbf{[34a]}$$

$$\Delta x_i^- = x_0\cdot\left(g_i+a_i^-\cdot A+b_i^-\cdot B\right) \quad \textbf{[34b]}$$

First, Eqs. [34a] and [34b] are inserted into Eq. [33a] resulting in:

$$\frac{1}{1+k}\sum_{i=1}^{N/2}\left[x_0\cdot\left(g_i+a_i^+\cdot A+b_i^+\cdot B\right)\right]+\frac{k}{1+k}\sum_{i=1}^{N/2}\left[x_0\cdot\left(g_i+a_i^-\cdot A+b_i^-\cdot B\right)\right] = A\cdot x_0\cdot\sqrt{N} \quad \textbf{[S1]}$$

Since g_i denotes a displacement distribution function with mean $\overline{g_i}=0$ (averaged over all ions), Eq. [S1] can be rewritten as:

$$\frac{1}{1+k}\left[\sum_{i=1}^{N/2}\left(a_i^+\cdot A\right)+\sum_{i=1}^{N/2}\left(b_i^+\cdot B\right)\right]+\frac{k}{1+k}\left[\sum_{i=1}^{N/2}\left(a_i^-\cdot A\right)+\sum_{i=1}^{N/2}\left(b_i^-\cdot B\right)\right]=A\cdot\sqrt{N} \quad \textbf{[S2]}$$

From Eq. [S2] it follows that:

$$\frac{1}{1+k}\left[\sum_{i=1}^{N/2}\left(b_i^+\right)\right]+\frac{k}{1+k}\left[\sum_{i=1}^{N/2}\left(b_i^-\right)\right]=0 \quad \textbf{[S3]}$$

$$\frac{1}{1+k}\left[\sum_{i=1}^{N/2}\left(a_i^+\right)\right]+\frac{k}{1+k}\left[\sum_{i=1}^{N/2}\left(a_i^-\right)\right]=\sqrt{N} \quad \textbf{[S4]}$$

Next, we insert Eqs. [34a] and [34b] into Eq. [33b]:

$$\sum_{i=1}^{N/2}\left[x_0\cdot\left(g_i+a_i^+\cdot A+b_i^+\cdot B\right)\right]-\sum_{i=1}^{N/2}\left[x_0\cdot\left(g_i+a_i^-\cdot A+b_i^-\cdot B\right)\right]=B\cdot x_0\cdot\sqrt{N} \quad \textbf{[S5]}$$

With $\overline{g_i} = 0$, Eq. [S5] can be rewritten as:

$$\sum_{i=1}^{N/2}\left(a_i^+ \cdot A\right) + \sum_{i=1}^{N/2}\left(b_i^+ \cdot B\right) - \sum_{i=1}^{N/2}\left(a_i^- \cdot A\right) - \sum_{i=1}^{N/2}\left(b_i^- \cdot B\right) = B \cdot \sqrt{N} \quad \textbf{[S6]}$$

From Eq. [S6], it follows that:

$$\sum_{i=1}^{N/2}\left(a_i^+\right) - \sum_{i=1}^{N/2}\left(a_i^-\right) = 0 \quad \Rightarrow \quad \sum_{i=1}^{N/2}\left(a_i^+\right) = \sum_{i=1}^{N/2}\left(a_i^-\right) \quad \textbf{[S7]}$$

$$\sum_{i=1}^{N/2}\left(b_i^+\right) - \sum_{i=1}^{N/2}\left(b_i^-\right) = \sqrt{N} \quad \textbf{[S8]}$$

Now, insertion of Eq. [S7] into Eq. [S4] leads to:

$$\frac{1}{1+k}\left[\sum_{i=1}^{N/2}\left(a_i^+\right)\right] + \frac{k}{1+k}\left[\sum_{i=1}^{N/2}\left(a_i^+\right)\right] = \sum_{i=1}^{N/2}\left(a_i^+\right) = \sqrt{N} \quad \textbf{[S9]}$$

The same is valid for $\sum_{i=1}^{N/2}\left(a_i^-\right)$, thus Eq. [35a] can be written as:

$$\sum_{i=1}^{N/2}\left(a_i^+\right) = \sum_{i=1}^{N/2}\left(a_i^-\right) = \sqrt{N} \quad \textbf{[35a]}$$

Next, we rewrite Eq. [S8] as:

$$\sum_{i=1}^{N/2}\left(b_i^-\right) = \sum_{i=1}^{N/2}\left(b_i^+\right) - \sqrt{N} \quad \textbf{[S10]}$$

and we insert Eq. [S10] into Eq. [S3]:

$$\frac{1}{1+k}\left[\sum_{i=1}^{N/2}\left(b_i^+\right)\right] + \frac{k}{1+k}\left[\sum_{i=1}^{N/2}\left(b_i^+\right) - \sqrt{N}\right] = 0 \quad \textbf{[S11]}$$

From Eq. [S11], we obtain Eq. [35b]:

$$\sum_{i=1}^{N/2}\left(b_i^+\right) = \frac{k}{1+k} \cdot \sqrt{N} \quad \textbf{[35b]}$$

Finally, Eq. [35b] is inserted into Eq. [S10] leading to Eq. [35c].

$$\sum_{i=1}^{N/2}\left(b_i^-\right) = \frac{k}{1+k}\cdot\sqrt{N} - \sqrt{N} = -\frac{1}{1+k}\cdot\sqrt{N} \qquad \textbf{[35c]}$$

Derivation of σ_+^{self} – Eq. [36a]

We start with inserting Eq. [34a] into Eq. [S12]:

$$\Delta x_i^+ = x_0\cdot\left(g_i + a_i^+\cdot A + b_i^+\cdot B\right) \qquad \textbf{[34a]}$$

$$\sigma_+^{self} = \frac{e^2}{2Vk_BT\Delta t}\left\langle\sum_{i=1}^{N/2}\left(\Delta x_i^+\right)^2\right\rangle = \frac{e^2}{2Vk_BT\Delta t}\cdot\left\langle\sum_{i=1}^{N/2}\left[x_0\cdot\left(g_i + a_i^+\cdot A + b_i^+\cdot B\right)\right]^2\right\rangle \qquad \textbf{[S12]}$$

Here, the brackets $\langle\cdots\rangle$ denote the ensemble average. In the following, we assume that center-of-mass and dipole fluctuations are uncorrelated, implying that $\langle AB\rangle = \langle A\rangle\cdot\langle B\rangle = 0$. With $\overline{g_i} = 0$, $\langle A\rangle = 0$ and $\langle B\rangle = 0$, it follows that:

$$\sigma_+^{self} = \frac{e^2\cdot(x_0)^2}{2Vk_BT\Delta t}\cdot\left\langle\sum_{i=1}^{N/2}(g_i)^2 + \sum_{i=1}^{N/2}\left(a_i^+\cdot A\right)^2 + \sum_{i=1}^{N/2}\left(b_i^+\cdot B\right)^2\right\rangle \qquad \textbf{[S13]}$$

With $\overline{(g_i)^2} = 1$ and thus the sum $\sum_{i=1}^{N/2}(g_i)^2$ being identical to $N/2$, Eq. [S13] can be written as:

$$\sigma_+^{self} = \frac{e^2\cdot(x_0)^2}{2Vk_BT\Delta t}\cdot\left[\frac{N}{2} + \sum_{i=1}^{N/2}\left(a_i^+\right)^2\cdot\langle A^2\rangle + \sum_{i=1}^{N/2}\left(b_i^+\right)^2\cdot\langle B^2\rangle\right] \qquad \textbf{[S14]}$$

With the number density $N_v = \frac{N/2}{V}$ and the prefactor $\sigma_0 = \frac{N_v\cdot e^2\cdot(x_0)^2}{2\cdot k_B\cdot T\cdot\Delta t}$, we finally obtain Eq. [36a]:

$$\sigma_{+}^{self} = \sigma_0 \cdot \left(1 + \frac{\sum_{i=1}^{N/2} \left(a_i^+\right)^2}{\frac{N}{2}} \cdot \langle A^2 \rangle + \frac{\sum_{i=1}^{N/2} \left(b_i^+\right)^2}{\frac{N}{2}} \langle B^2 \rangle \right) \quad \textbf{[36a]}$$

Derivation of σ_{++} – Eq. [36b]

We start with inserting Eq. [34a] into Eq. [31a], giving [S15].

$$\Delta x_i^+ = x_0 \cdot \left(g_i + a_i^+ \cdot A + b_i^+ \cdot B\right) \quad \textbf{[34a]}$$

$$\sigma_{++} = \frac{e^2}{2Vk_BT\Delta t} \left\langle \left(\sum_{i=1}^{N/2} \Delta x_i^+ \right)^2 \right\rangle \quad \textbf{[31a]}$$

$$\sigma_{++} = \frac{e^2}{2Vk_BT\Delta t} \cdot \left\langle \left(\sum_{i=1}^{N/2} \left[x_0 \cdot \left(g_i + a_i^+ \cdot A + b_i^+ \cdot B\right) \right] \right)^2 \right\rangle \quad \textbf{[S15]}$$

Since $\overline{g_i} = 0$, the sum $\left[\sum_{i=1}^{N/2} g_i \right]^2$ cancels, and Eq. [S16] is obtained.

$$\sigma_{++} = \frac{e^2 \cdot (x_0)^2}{2Vk_BT\Delta t} \cdot \left\langle \left(\sum_{i=1}^{N/2} \left(a_i^+ \cdot A\right) + \sum_{i=1}^{N/2} \left(b_i^+ \cdot B\right) \right)^2 \right\rangle \quad \textbf{[S16]}$$

With Eqs. [35a] and [35b], this results in:

$$\sigma_{++} = \frac{e^2 \cdot (x_0)^2}{2Vk_BT\Delta t} \cdot \left\langle \left(\sqrt{N} \cdot A + \frac{k}{1+k} \cdot \sqrt{N} \cdot B \right)^2 \right\rangle \quad \textbf{[S17]}$$

With $\langle AB \rangle = \langle A \rangle \cdot \langle B \rangle = 0$, this leads to Eq. [36b]:

$$\sigma_{++} = \frac{e^2 \cdot (x_0)^2}{2Vk_BT\Delta t} \cdot \left(N\langle A^2 \rangle + N\frac{k^2}{(1+k)^2} \langle B^2 \rangle \right) = \sigma_0 \cdot \left(2\langle A^2 \rangle + 2\frac{k^2}{(1+k)^2} \langle B^2 \rangle \right) \quad \textbf{[36b]}$$

Derivation of $\sigma^{distinct}_{++}$ – Eq. [36c]

We start with

$$\sigma^{distinct}_{++} = \sigma_{++} - \sigma^{self}_{+} \quad \textbf{[S18]}$$

derived from Eq. [20] and insert Eqs. [36a] and [36b]:

$$\sigma^{distinct}_{++} = \sigma_0 \cdot \left[2\langle A^2 \rangle + 2\frac{k^2}{(1+k)^2}\langle B^2 \rangle - \left(1 + \frac{\sum_{i=1}^{N/2} \left(a^{+}_{i}\right)^2}{\frac{N}{2}} \cdot \langle A^2 \rangle + \frac{\sum_{i=1}^{N/2} \left(b^{+}_{i}\right)^2}{\frac{N}{2}} \langle B^2 \rangle \right) \right] \quad \textbf{[S19]}$$

After resorting the terms, Eq. [36c] is obtained.

$$\sigma^{distinct}_{++} = \sigma_0 \cdot \left[-1 + \left(2 - \frac{\sum_{i=1}^{N/2} \left(a^{+}_{i}\right)^2}{\frac{N}{2}} \right) \langle A^2 \rangle + \left(2\frac{k^2}{(1+k)^2} - \frac{\sum_{i=1}^{N/2} \left(b^{+}_{i}\right)^2}{\frac{N}{2}} \right) \langle B^2 \rangle \right] \quad \textbf{[36c]}$$

Derivation of σ^{self}_{-} – Eq. [36d]

Analoguous to the derivation of σ_{+}^{self}, insertion of

$$\Delta x_i^- = x_0 \cdot \left(g_i + a_i^- \cdot A + b_i^- \cdot B\right) \qquad \textbf{[34b]}$$

Into

$$\sigma_{-}^{self} = \frac{e^2}{2Vk_BT\Delta t}\left\langle \sum_{i=1}^{N/2} \left(\Delta x_i^-\right)^2 \right\rangle \qquad \textbf{[S20]}$$

gives Eq. [36d]:

$$\sigma_{-}^{self} = \sigma_0 \cdot \left(1 + \frac{\sum_{i=1}^{N/2} \left(a_i^-\right)^2}{\frac{N}{2}} \cdot \left\langle A^2 \right\rangle + \frac{\sum_{i=1}^{N/2} \left(b_i^-\right)^2}{\frac{N}{2}} \left\langle B^2 \right\rangle \right) \qquad \textbf{[36d]}$$

Derivation of σ_{--} – Eq. [36e]

Insertion of Eqs. [34b], [35a] and [35c] into

$$\sigma_{--} = \frac{e^2}{2Vk_BT\Delta t}\left\langle \left(\sum_{i=1}^{N/2} \Delta x_i^-\right)^2 \right\rangle \qquad \textbf{[31b]}$$

results in Eq. [36e]:

$$\sigma_{--} = \sigma_0 \cdot \left(2\left\langle A^2 \right\rangle + 2\frac{1}{(1+k)^2}\left\langle B^2 \right\rangle\right) \qquad \textbf{[36e]}$$

Derivation of $\sigma_{--}^{distinct}$ – Eq. [36f]

Insertion of Eqs. [36d] and [36e] into

$$\sigma_{--}^{distinct} = \sigma_{--} - \sigma_{-}^{self} \qquad \textbf{[S21]}$$

derived from Eq. [21] and resorting the terms results in Eq. [36f]:

$$\sigma_{--}^{distinct} = \sigma_0 \cdot \left[-1 + \left(2 - \frac{\sum_{i=1}^{N/2} \left(a_i^-\right)^2}{\frac{N}{2}} \right) \langle A^2 \rangle + \left(2\frac{1}{(1+k)^2} - \frac{\sum_{i=1}^{N/2} \left(b_i^-\right)^2}{\frac{N}{2}} \right) \langle B^2 \rangle \right] \quad \textbf{[36f]}$$

Derivation of σ_{+-} – Eq. [36g]

Insertion of Eqs. [34a] and [34b] into Eq. [31c]

$$\sigma_{+-} = \frac{e^2}{2Vk_BT\Delta t} \left\langle \left(\sum_{i=1}^{N/2} \Delta x_i^+ \right) \cdot \left(\sum_{i=1}^{N/2} \Delta x_i^- \right) \right\rangle \quad \textbf{[31c]}$$

gives:

$$\sigma_{+-} = \frac{e^2}{2Vk_BT\Delta t} \cdot \left\langle \left(\sum_{i=1}^{N/2} \left[x_0 \cdot \left(g_i + a_i^+ \cdot A + b_i^+ \cdot B \right) \right] \right) \cdot \left(\sum_{i=1}^{N/2} \left[x_0 \cdot \left(g_i + a_i^- \cdot A + b_i^- \cdot B \right) \right] \right) \right\rangle \quad \textbf{[S22]}$$

With $\overline{g_i} = 0$, this transforms into:

$$\sigma_{+-} = \frac{e^2 \cdot (x_0)^2}{2Vk_BT\Delta t} \cdot \left\langle \left(\sum_{i=1}^{N/2} \left(a_i^+ \cdot A + b_i^+ \cdot B \right) \right) \cdot \left(\sum_{i=1}^{N/2} \left(a_i^- \cdot A + b_i^- \cdot B \right) \right) \right\rangle \quad \textbf{[S23]}$$

With $\langle AB \rangle = \langle A \rangle \cdot \langle B \rangle = 0$, this simplifies to:

$$\sigma_{+-} = \frac{e^2 \cdot (x_0)^2}{2Vk_BT\Delta t} \cdot \left[\left(\sum_{i=1}^{N/2} \left(a_i^+ \right) \cdot \sum_{i=1}^{N/2} \left(a_i^- \right) \right) \langle A^2 \rangle + \left(\sum_{i=1}^{N/2} \left(b_i^+ \right) \cdot \sum_{i=1}^{N/2} \left(b_i^- \right) \right) \langle B^2 \rangle \right] \quad \textbf{[S24]}$$

Insertion of Eqs. [35a]-[35c] results in [36g]:

$$\sigma_{+-} = \frac{e^2 \cdot (x_0)^2}{2Vk_BT\Delta t} \cdot \left(N\langle A^2 \rangle - N\frac{k}{(1+k)^2}\langle B^2 \rangle \right) = \sigma_0 \cdot \left(2\langle A^2 \rangle - 2\frac{k}{(1+k)^2}\langle B^2 \rangle \right) \quad \textbf{[36g]}$$

Derivation of σ_{ion} – Eq. [36h]

Insertion of Eqs. [36b], [36e], and [36g] into Eq. [12]

$$\sigma_{ion} = \sigma_{++} + \sigma_{--} - 2\sigma_{+-} \quad \textbf{[12]}$$

results in:

$$\sigma_{ion} = \sigma_0 \cdot \left(2\langle A^2 \rangle + 2\frac{k^2}{(1+k)^2}\langle B^2 \rangle \right) + \sigma_0 \cdot \left(2\langle A^2 \rangle + 2\frac{1}{(1+k)^2}\langle B^2 \rangle \right) - 2\sigma_0 \cdot \left(2\langle A^2 \rangle - 2\frac{k}{(1+k)^2}\langle B^2 \rangle \right) \quad \textbf{[S25]}$$

This simplifies to Eq. [36h]:

$$\sigma_{ion} = \sigma_0 \cdot 2 \cdot \langle B^2 \rangle \quad \textbf{[36h]}$$

Derivation of $t_+^{\mu} \cdot \sigma_{ion}$ – Eq. [37a]

We start with

$$t_+^{\mu} \cdot \sigma_{ion} = \sigma_{++} - \sigma_{+-} \quad \textbf{[S26]}$$

derived from Eq. [14] and insert Eqs. [36b] and [36g]:

$$t_+^{\mu} \cdot \sigma_{ion} = \sigma_0 \cdot \left(2\langle A^2 \rangle + 2\frac{k^2}{(1+k)^2}\langle B^2 \rangle \right) - \sigma_0 \cdot \left(2\langle A^2 \rangle - 2\frac{k}{(1+k)^2}\langle B^2 \rangle \right) = \sigma_0 \cdot 2 \cdot \frac{k}{1+k} \cdot \langle B^2 \rangle \quad \textbf{[37a]}$$

Derivation of $\left(1 - t_+^{\mu}\right) \cdot \sigma_{ion}$ – Eq. [37b]

We start with

$$\left(1-t_{+}^{\mu}\right)\cdot\sigma_{ion}=\sigma_{--}-\sigma_{+-} \quad \textbf{[S27]}$$

and insert Eqs. [36e] and [36g]:

$$\begin{aligned}&\left(1-t_{+}^{\mu}\right)\cdot\sigma_{ion}=\\ &\sigma_0\cdot\left(2\langle A^2\rangle+2\frac{1}{(1+k)^2}\langle B^2\rangle\right)-\sigma_0\cdot\left(2\langle A^2\rangle-2\frac{k}{(1+k)^2}\langle B^2\rangle\right)\\ &=\sigma_0\cdot 2\cdot\frac{1}{1+k}\cdot\langle B^2\rangle\end{aligned} \quad \textbf{[37b]}$$

Derivation of $t_{+}^{abc}\cdot\sigma_{ion}$ – Eq. [39]

We start with

$$t_{+}^{abc}\cdot\sigma_{ion}=\sigma_{++}-\frac{(\sigma_{+-})^2}{\sigma_{--}} \quad \textbf{[S28]}$$

derived from Eq. [13] and insert Eqs. [36b], [36e], and [36g]:

$$t_{+}^{abc}\cdot\sigma_{ion}=\sigma_0\cdot 2\cdot\left[\langle A^2\rangle+\frac{k^2}{(1+k)^2}\langle B^2\rangle-\frac{\left(\langle A^2\rangle-\frac{k}{(1+k)^2}\langle B^2\rangle\right)^2}{\langle A^2\rangle+\frac{1}{(1+k)^2}\langle B^2\rangle}\right] \quad \textbf{[38]}$$

In the case of $\langle A^2\rangle\ll\frac{k}{(1+k)^2}\langle B^2\rangle$, the term $\langle A^2\rangle^2$ from the expansion of $\left(\langle A^2\rangle-\frac{k}{(1+k)^2}\langle B^2\rangle\right)^2$ can be neglected, resulting in:

$$t_{+}^{abc}\cdot\sigma_{ion}\approx\sigma_0\cdot 2\cdot\left[\langle A^2\rangle+\frac{k^2}{(1+k)^2}\langle B^2\rangle+\frac{\frac{2k}{(1+k)^2}\langle A^2\rangle\langle B^2\rangle-\frac{k^2}{(1+k)^4}\langle B^2\rangle^2}{\langle A^2\rangle+\frac{1}{(1+k)^2}\langle B^2\rangle}\right] \quad \textbf{[S29]}$$

In the right-hand term, the terms $-\frac{k^2}{(1+k)^4}\langle B^2\rangle^2$ and $\frac{1}{(1+k)^2}\langle B^2\rangle$ are factored out in the numerator and in the denominator, respectively:

$$t_{+}^{abc} \cdot \sigma_{ion} \approx \sigma_0 \cdot 2 \cdot \left[\langle A^2 \rangle + \frac{k^2}{(1+k)^2} \langle B^2 \rangle + \frac{\left(1 - \frac{2(1+k)^2}{k} \cdot \frac{\langle A^2 \rangle}{\langle B^2 \rangle}\right)}{\left(1 + (1+k)^2 \cdot \frac{\langle A^2 \rangle}{\langle B^2 \rangle}\right)} \cdot \frac{\left(-\frac{k^2}{(1+k)^4} \langle B^2 \rangle^2\right)}{\left(\frac{1}{(1+k)^2} \langle B^2 \rangle\right)} \right] \quad \textbf{[S30]}$$

$$= \sigma_0 \cdot 2 \cdot \left[\langle A^2 \rangle + \frac{k^2}{(1+k)^2} \langle B^2 \rangle + \frac{\left(1 - \frac{2(1+k)^2}{k} \cdot \frac{\langle A^2 \rangle}{\langle B^2 \rangle}\right)}{\left(1 + (1+k)^2 \cdot \frac{\langle A^2 \rangle}{\langle B^2 \rangle}\right)} \cdot \left(-\frac{k^2}{(1+k)^2} \langle B^2 \rangle\right) \right]$$

Since $\langle A^2 \rangle \ll \langle B^2 \rangle$, we apply the approximation $\frac{1 - x_1}{1 + x_2} \approx 1 - x_1 - x_2$:

$$t_{+}^{abc} \cdot \sigma_{ion} \approx$$

$$\sigma_0 \cdot 2 \cdot \left[\langle A^2 \rangle + \frac{k^2}{(1+k)^2} \langle B^2 \rangle + \left(1 - \frac{2(1+k)^2}{k} \cdot \frac{\langle A^2 \rangle}{\langle B^2 \rangle} - (1+k)^2 \cdot \frac{\langle A^2 \rangle}{\langle B^2 \rangle}\right) \cdot \left(-\frac{k^2}{(1+k)^2} \langle B^2 \rangle\right) \right] \quad \textbf{[S31]}$$

$$= \sigma_0 \cdot 2 \cdot \left[\langle A^2 \rangle + \frac{k^2}{(1+k)^2} \langle B^2 \rangle - \frac{k^2}{(1+k)^2} \langle B^2 \rangle + \frac{2k^2(1+k)^2}{k(1+k)^2} \cdot \frac{\langle A^2 \rangle \langle B^2 \rangle}{\langle B^2 \rangle} + \frac{k^2(1+k)^2}{(1+k)^2} \cdot \frac{\langle A^2 \rangle \langle B^2 \rangle}{\langle B^2 \rangle} \right]$$

$$= \sigma_0 \cdot 2 \cdot \left[\langle A^2 \rangle + 2k \langle A^2 \rangle + k^2 \langle A^2 \rangle \right]$$

Thus, we finally obtain Eq. [39]:

$$t_{+}^{abc} \cdot \sigma_{ion} \approx \sigma_0 \cdot 2 \cdot (1+k)^2 \cdot \langle A^2 \rangle \quad \textbf{[39]}$$

Derivation of $\frac{\sigma_{++}^{distinct}}{\sigma_{+}^{self}}$ – Eq. [40a]

We divide Eq. [36c] by Eq. [36a]:

$$\frac{\sigma_{++}^{distinct}}{\sigma_{+}^{self}} = \frac{\sigma_0 \cdot \left[-1 + \left(2 - \frac{\sum_{i=1}^{N/2} \left(a_i^+\right)^2}{\frac{N}{2}} \right) \langle A^2 \rangle + \left(2\frac{k^2}{(1+k)^2} - \frac{\sum_{i=1}^{N/2} \left(b_i^+\right)^2}{\frac{N}{2}} \right) \langle B^2 \rangle \right]}{\sigma_0 \cdot \left(1 + \frac{\sum_{i=1}^{N/2} \left(a_i^+\right)^2}{\frac{N}{2}} \cdot \langle A^2 \rangle + \frac{\sum_{i=1}^{N/2} \left(b_i^+\right)^2}{\frac{N}{2}} \langle B^2 \rangle \right)} \quad \textbf{[S32]}$$

$$= \frac{-1 + 2\langle A^2 \rangle - \frac{\sum_{i=1}^{N/2} \left(a_i^+\right)^2}{\frac{N}{2}} \langle A^2 \rangle + 2\frac{k^2}{(1+k)^2} \langle B^2 \rangle - \frac{\sum_{i=1}^{N/2} \left(b_i^+\right)^2}{\frac{N}{2}} \langle B^2 \rangle}{1 + \frac{\sum_{i=1}^{N/2} \left(a_i^+\right)^2}{\frac{N}{2}} \cdot \langle A^2 \rangle + \frac{\sum_{i=1}^{N/2} \left(b_i^+\right)^2}{\frac{N}{2}} \langle B^2 \rangle}$$

Now we assume that the fluctuations are small so that $\frac{\sum_{i=1}^{N/2} \left(a_i^+\right)^2}{N/2} \cdot \langle A^2 \rangle \ll 1$ and $\frac{\sum_{i=1}^{N/2} \left(b_i^+\right)^2}{N/2} \langle B^2 \rangle \ll 1$. In this case, we can apply the approximation $\frac{1}{1+x} \approx 1 - x,$ resulting in Eq. [40a]:

$$\frac{\sigma_{++}^{distinct}}{\sigma_{+}^{self}} \approx -1 + 2\langle A^2 \rangle + 2\frac{k^2}{(1+k)^2} \langle B^2 \rangle \quad \textbf{[40a]}$$

Derivation of $\frac{\sigma^{distinct}_{--}}{\sigma^{self}_{-}}$ – Eq. [40b]

We divide Eq. [36f] by Eq. [36d]:

$$\frac{\sigma^{distinct}_{--}}{\sigma^{self}_{-}} = \frac{\sigma_0 \cdot \left[-1 + \left(2 - \frac{\sum_{i=1}^{N/2} \left(a^{-}_{i}\right)^2}{\frac{N}{2}} \right) \langle A^2 \rangle + \left(2 \frac{1}{(1+k)^2} - \frac{\sum_{i=1}^{N/2} \left(b^{-}_{i}\right)^2}{\frac{N}{2}} \right) \langle B^2 \rangle \right]}{\sigma_0 \cdot \left(1 + \frac{\sum_{i=1}^{N/2} \left(a^{-}_{i}\right)^2}{\frac{N}{2}} \cdot \langle A^2 \rangle + \frac{\sum_{i=1}^{N/2} \left(b^{-}_{i}\right)^2}{\frac{N}{2}} \langle B^2 \rangle \right)} \quad \textbf{[S33]}$$

$$= \frac{-1 + 2\langle A^2 \rangle - \frac{\sum_{i=1}^{N/2} \left(a^{-}_{i}\right)^2}{\frac{N}{2}} \langle A^2 \rangle + 2 \frac{1}{(1+k)^2} \langle B^2 \rangle - \frac{\sum_{i=1}^{N/2} \left(b^{-}_{i}\right)^2}{\frac{N}{2}} \langle B^2 \rangle}{1 + \frac{\sum_{i=1}^{N/2} \left(a^{-}_{i}\right)^2}{\frac{N}{2}} \cdot \langle A^2 \rangle + \frac{\sum_{i=1}^{N/2} \left(b^{-}_{i}\right)^2}{\frac{N}{2}} \langle B^2 \rangle}$$

Again we assume that the fluctuations are small so that $\frac{\sum_{i=1}^{N/2}\left(a_i^-\right)^2}{N/2}\cdot\left\langle A^2\right\rangle \ll 1$ and $\frac{\sum_{i=1}^{N/2}\left(b_i^-\right)^2}{N/2}\left\langle B^2\right\rangle \ll 1$. In this case, the approximation $\frac{1}{1+x}\approx 1-x$ results in Eq. [40b]:

$$\frac{\sigma_{--}^{distinct}}{\sigma_{-}^{self}} \approx -1+2\left\langle A^2\right\rangle+2\frac{1}{(1+k)^2}\left\langle B^2\right\rangle \qquad \textbf{[40b]}$$