Molecular Simulation of Ionic Liquids: From Molecular Interactions to Transport Properties

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Introduction

Current commercial electrical storage devices are restricted by a limiting operational temperature between -20C° and 60C°, despite the need for high-temperature batteries in fields like energy production and automobile creation. [1] This limitation is particularly apparent in lithium-ion batteries, where its volatile and flammable components, such as carbonate-based electrolytes, lead to thermal runway in which the release of heat can trigger subsequent unsafe reactions.[2]
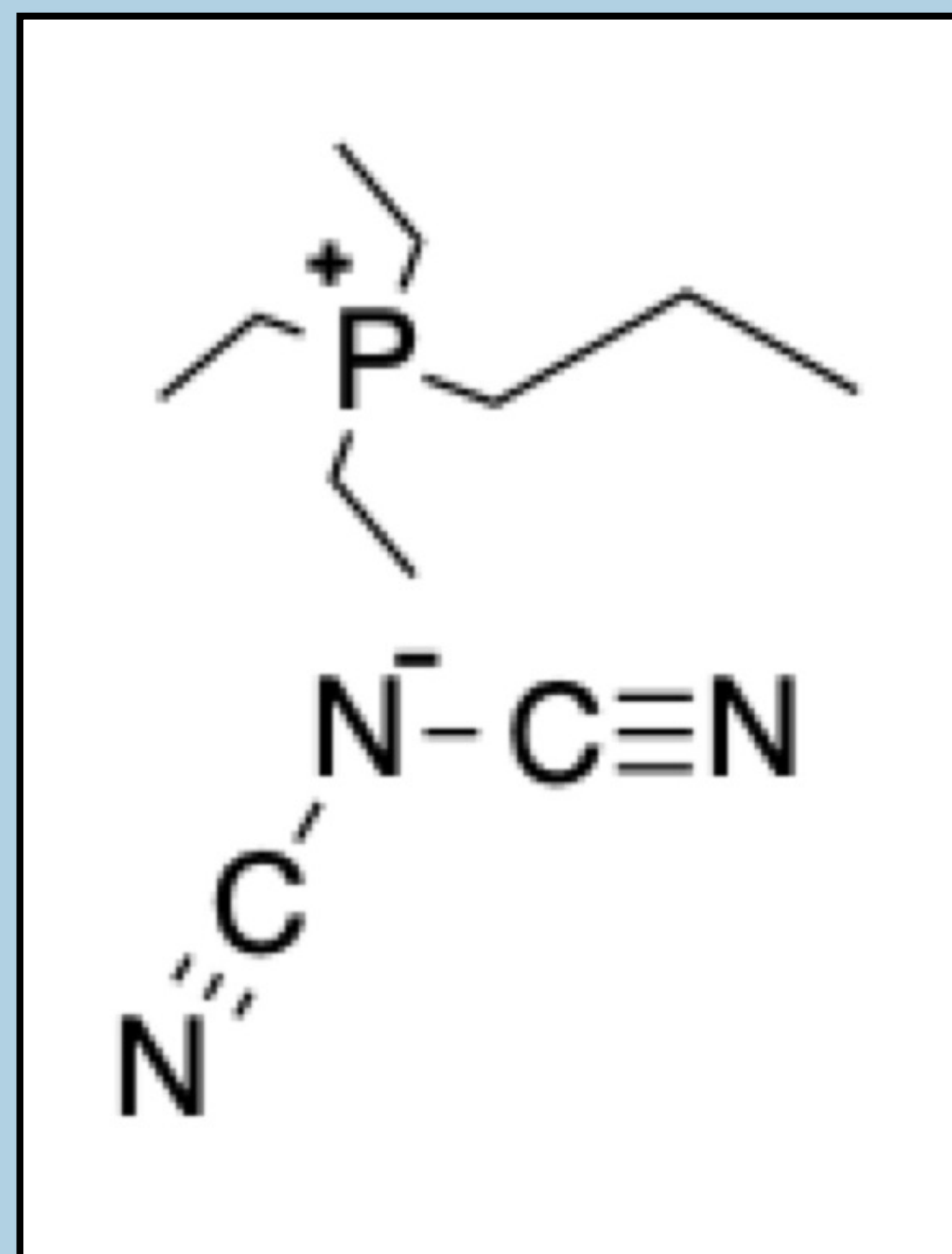

Figure 1. Triethyl-propyl-phosphonium Dicyanamide (P111-DCA).

As an alternative to traditional lithium-ion batteries, **Room Temperature Ionic Liquids(RTILs)** exhibit promise in expanding the optimal temperature operation range for batteries above 60C° for use in commercial, high temperature applications. This is a result of RTILs properties of being nonvolatile, nonflammable, and both thermally and electrochemically stable. [3] However so, the exact mechanisms for factors contributing to these properties within RTILs are not well understood. To this end, we simulate different cation-anion pairs used to create these RTILs to observe changes in conductivity to determine factors which have a positive correlation with conductivity to develop new RTILs.

Computational Methods

MD Simulations were set up under the **LAMMPS** software package to allow for polarizability, and further visualized using **Visual Molecular Dynamics(VMD)**.

Long REMD simulations (~35ns) will be used to provide the initial conditions for the single trajectory MD runs to compute ionic liquid transport properties, specifically conductivity.

From this, 5000 individual trajectories per temperature will be used to obtain time-averaged charge-flux correlation functions, which can be later used to calculate conductivity following the Green-Kubo formula [4]:

$$\sigma = \frac{1}{3k_bTV}\int_0^\infty dt\langle J(t).J(0)\rangle$$

where KB is the Boltzmann constant, T is the temperature, V is the system volume, t is the time and J is the charge current defined as:

$$J(t) = \sum_i q_i v_i(t)$$

where q_i and v_i are the charge and velocity respectively of the ith ion particle.

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References

[1] Ma, S., Jiang, M., Tao, P., Song, C., Wu, J., Wang, J., Deng, T., & Shang, W. (2018). Temperature effect and thermal impact in lithium-ion batteries: A Review. *Progress in Natural Science: Materials International, 28*(6), 653–666. https://doi.org/10.1016/j.pnsc.2018.11.002
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Future Work

- Refine the salted Ionic Liquids parameters to produce a more realistic model of its properties
- Extend analysis of computed properties to include viscosity and pair distribution functions to gain a better understanding of the structure-function relationships in Ionic Liquids
- Understanding what is causing predicted conductivities to be higher than experimental conductivities
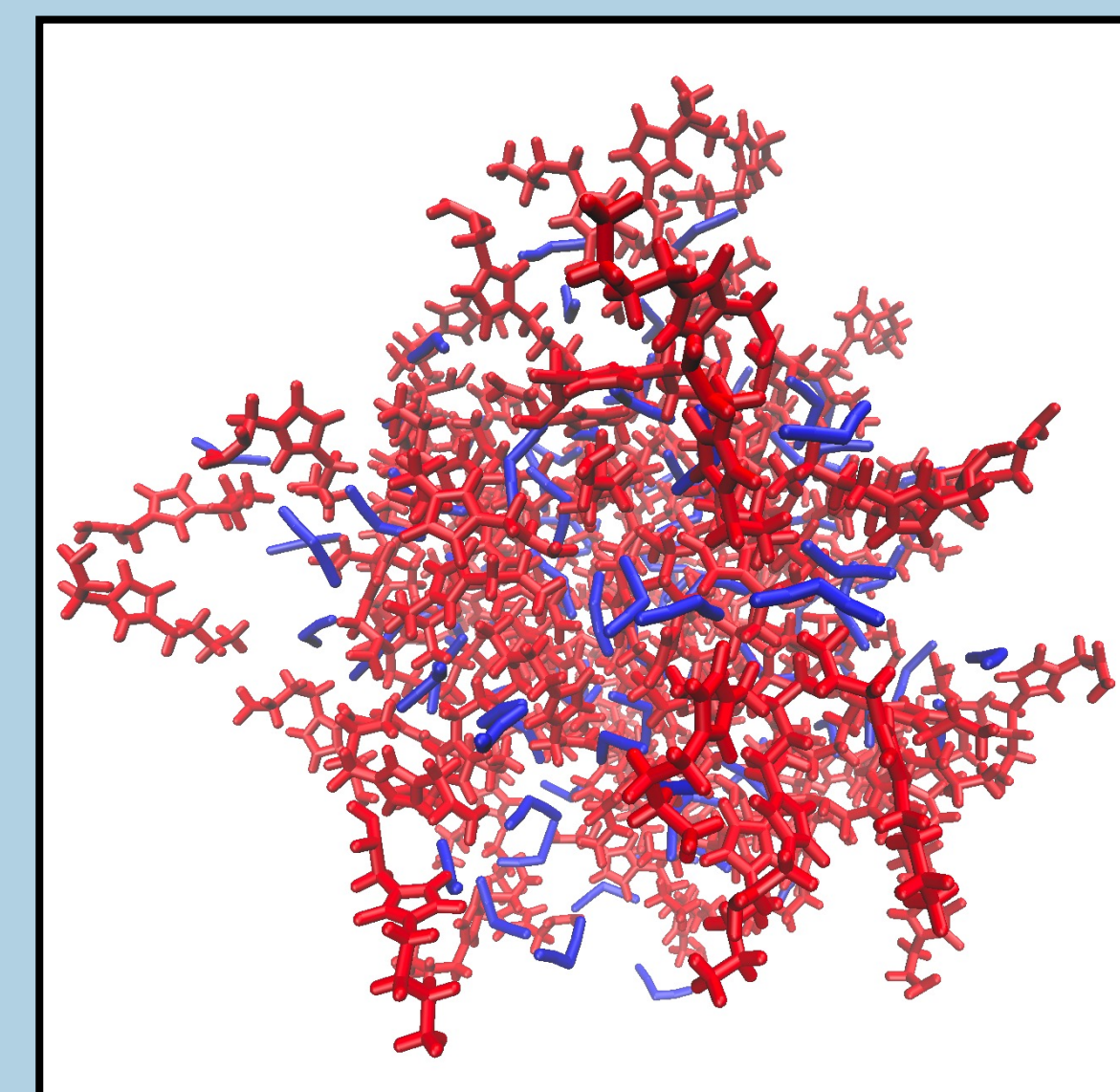
Correlation Functions

Figure 2. Snapshot of P111 (red) and DCA (blue) IL trajectory.

- Figure 3 and 4 show a comparison between the charge flux correlation functions between the different temperatures of the unsalted Ionic Liquids

- Charge flux correlation function approaches 0 as time increases, indicating 1 picosecond is sufficient for estimating conductivity. (See fig. 2 and fig.3)
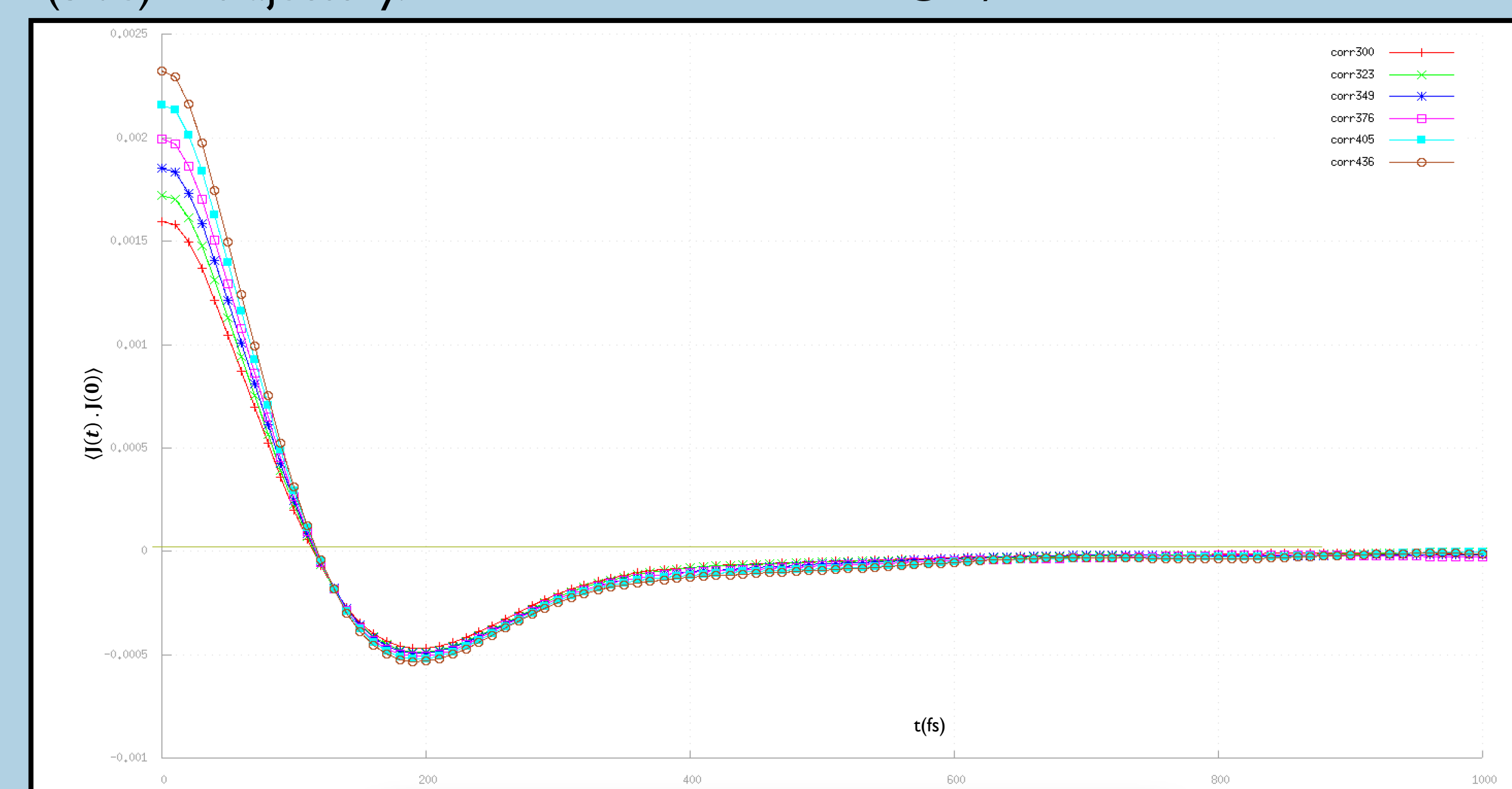

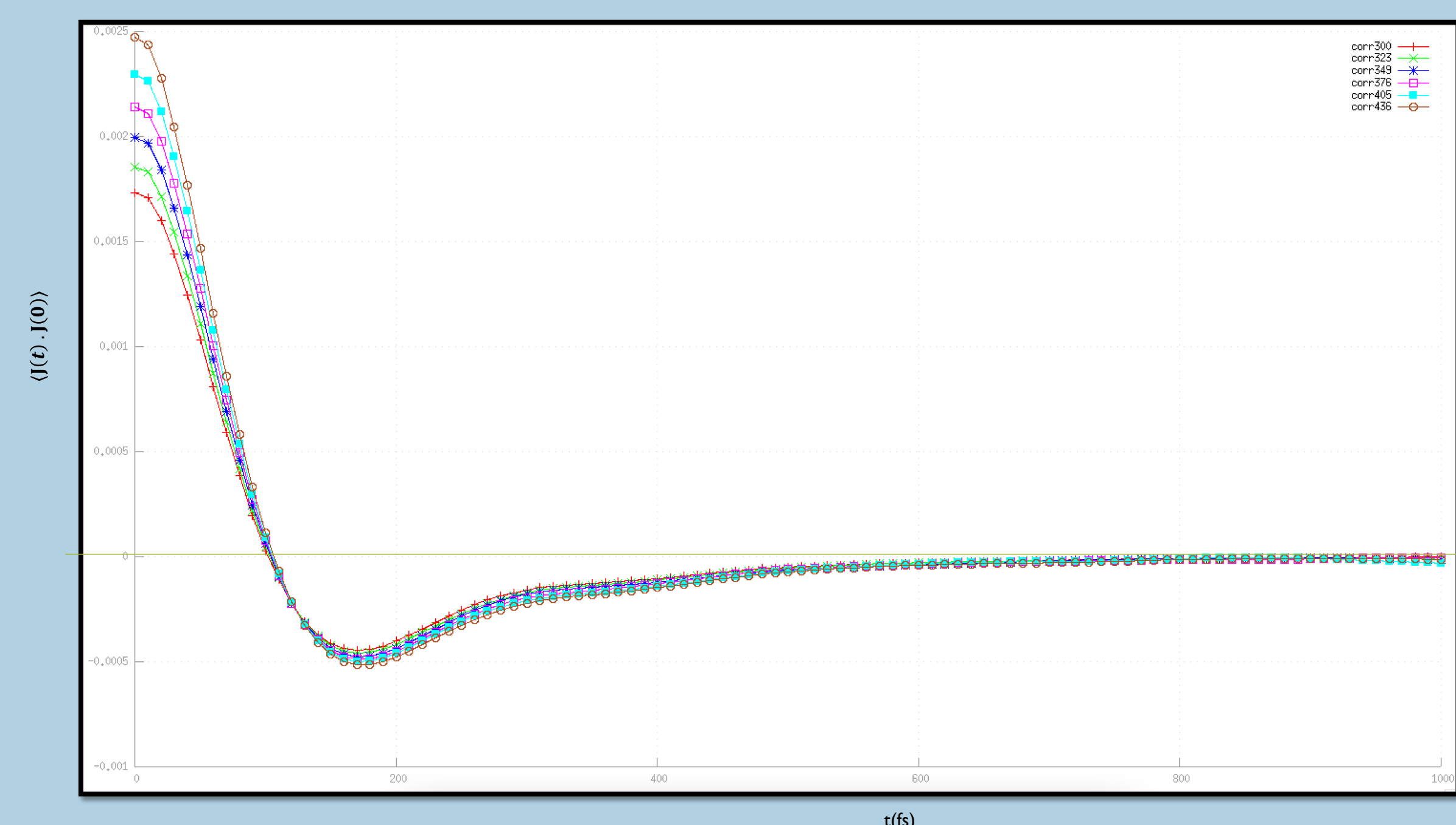**Figure 3.** P111-DCA Charge Flux Correlations across 6 temperatures

Figure 4. AC4-DCA Charge Flux Correlations across 6 temperatures
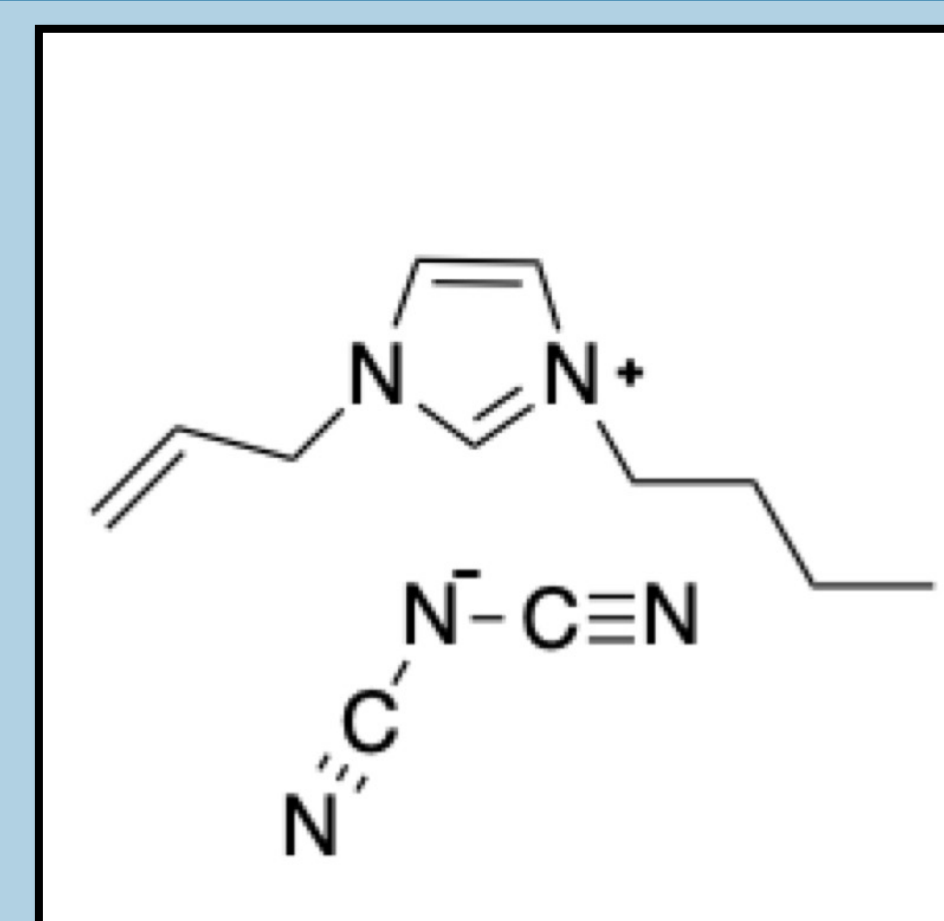
Conductivity

Fig 5. 1-ally-3-butyl-imidazolium Dicyanamide (AC4Im-DCA)

- The computational conductivities results have a similar trend to that of the experimental results.
- Within the uncertainty of the calculation , the AC4-DCA and P111-DCA have similar conductivities as function of temperature, as seen in Fig. 6.
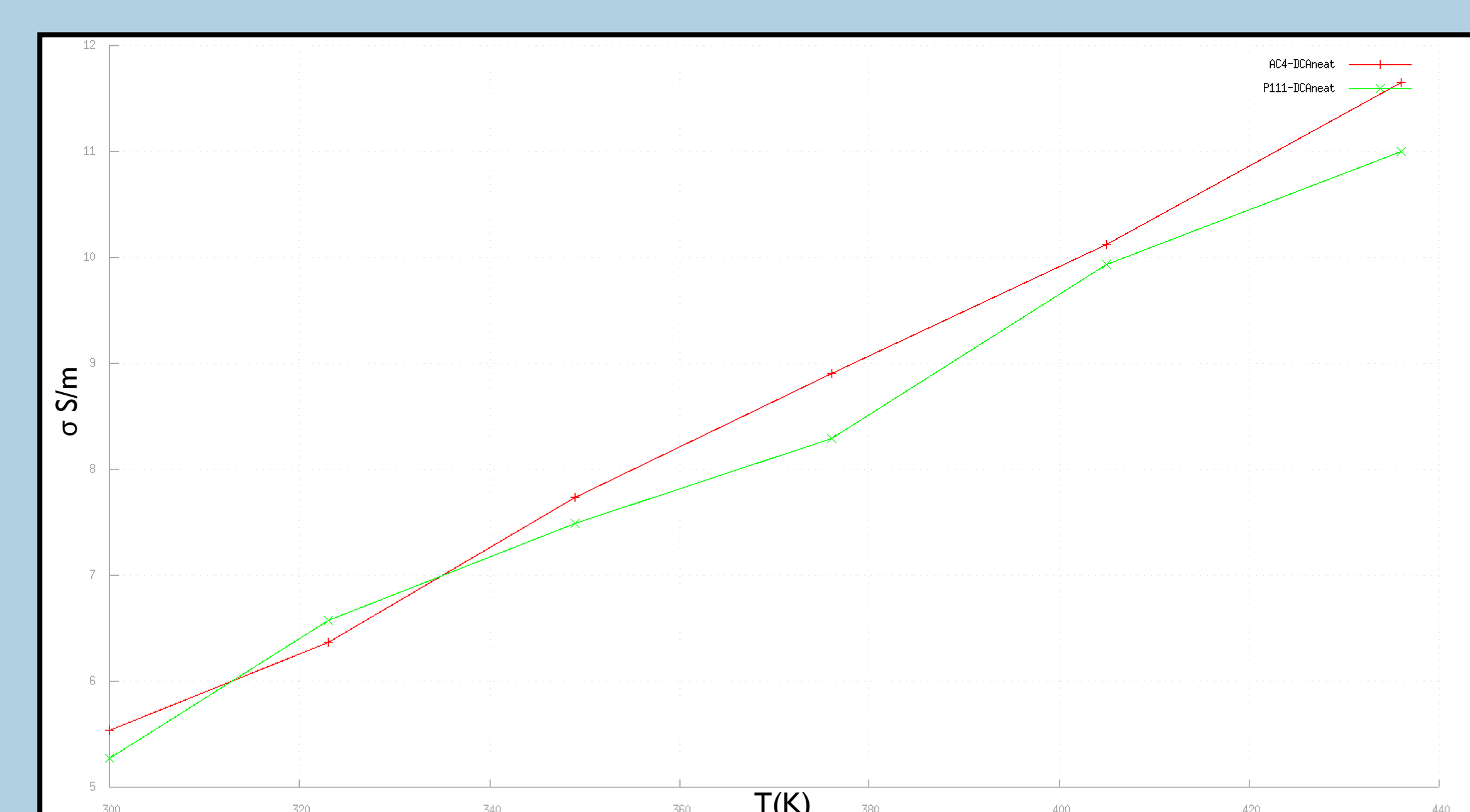

Fig 6. P111-DCAneat Conductivity vs AC4-DCAneat Conductivity