

学位論文要約

Spatial-Decomposition Analysis of Electrical Conductivity in Concentrated Ionic Systems (濃厚イオン系における電気伝導度の空間分割解析)

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Introduction

The electrical conductivity is a key quantity of ionic systems, especially in the development of electric cells. It quantifies how easily the electric current is induced in the system, and is governed by the dynamics of ionic species. At low concentration, the movement of each ion may be considered uncorrelated; the electrical conductivity is determined by the Nernst-Einstein equation. At medium to high concentrations, in contrast, the cross correlation between ions can become significant. The formation and decay of aggregated ions play influential roles in the transport phenomena in electrolyte solution. The aggregation effects are often taken into account by assuming the presence of such species as dimer, trimer, and so on. These species are transient with finite lifetimes, though. There needs a bridge, therefore, between the concept of aggregation and the correlated motions of ions in direct connection to the electrical conductivity at medium to high concentration of ionic systems.

A New Analysis Framework

Based on the Green-Kubo formula, we propose a new analysis framework to incorporate the concept of ion aggregation and the correlated motions between ions to the electrical conductivity. The conductivity is decomposed into the contributions from the ionic species in the system to enable the determination of the transport number, and is further expressed as a sum of the autocorrelation term of the Nernst-Einstein form and the cross-correlation term describing the two-body motions of ions. The spatial decomposition is then conducted for the cross-correlation term by formulating an integral expression over the ion-pair distance to bridge the static picture of ion pairing and the dynamic picture of correlated motions. With the spatially-decomposed Green-Kubo formula, the extent of localization of the ion-pair contribution to the electrical conductivity can be examined by introducing a cutoff to the spatial integration in the formula.

Application to Concentrated Ionic Systems

The framework is applied to 1 *m* NaCl aqueous solution and [C₄mim][NTf₂] (1-*n*-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) ionic liquid system with molecular dynamics simulations. The computed electrical conductivities and the transport numbers of both systems are in fair agreement with the experimental values. The correlation time for the NaCl system is an order of magnitude smaller than for the ionic liquid system, while the conductivity for the former is an order of magnitude larger than for the latter. The contribution from cross-correlation term to the conductivity is found to cancel the autocorrelation term by 40% and 20% for the NaCl and ionic liquid systems, respectively. By spatial decomposition, the cross-correlation term is decomposed into an integral of the product of the radial distribution and the spatially-decomposed velocity correlation. From the radial distribution function, we see that for the NaCl system strong pairing occurs within several angstroms, and that for the ionic liquid system a typical long-range layer structure is observed spanning over several nanometers. The spatially-decomposed velocity correlation shows that the strong correlation for both systems occurs within the first coordination shell and that the counter-ion pair has stronger correlation than the like-ion pair. By integrating the spatially-decomposed velocity correlation with respect to time, we can estimate how much an ion pair would contribute to the conductivity if they are separated by a given distance initially. It is found that the contribution from the ion pair with small distance is comparable to that from the self-diffusion motion. At large distance, the ion pair contribution becomes similar among all the ionic-species pairs. A cutoff radius was further introduced to the spatial integral in the spatially-decomposed Green-Kubo formula to investigate the extent of localization of the ion-pair contribution to the electrical conductivity. The ion-pair contribution is found to be localized within the first coordination shell for the NaCl system, and not localized with an oscillation extending over nanometers for the ionic liquid system.

Being able to observe the spatial and cross correlations concurrently bridges the physical and chemical viewpoints on the electrical conductivity; the former is based on the Green-Kubo formula and is developed in the time domain, while the latter adopts the concept of ion pair defined in terms of distance, *i.e.*, in the space domain. This analysis framework can be applied to more complex systems such as Li⁺ and Na⁺ solvated in ionic liquid and mixtures of ionic liquids, which can be of use in practice for development of electric cells.