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1 ABSTRACT

In this paper we describe a multi-scale approach to ion migration processes, which involves a bridging from the atomic scale to the macroscopic scale. To this end, the diffusion coefficient of a material i.e. a macroscopic physical quantity, will be appropriately determined from molecular dynamics simulations on the microscale. This way, performance predictions become possible prior to material synthesis. However, standard methods produce in general wrong results for ensemble setups which correspond to battery or capacitor applications.

We introduce a novel method to derive correct values also for such problems. These values are then used in a macroscopic system of partial differential equation (Poisson-Nernst-Planck system) for the numerical simulation of ion migration in a battery.

2 INTRODUCTION

Batteries are important for a variety of mobile electronic devices. Moreover, future electric cars need efficient and lightweight batteries. Therefore, there is a great demand for new and improved types of batteries, which in turn requires improved and novel materials.

Batteries work due to ion migration between electrodes. Important topics include the increase of charge capacity, the maximally allowed current and a high (cycle) life time. Additional challenges are present for materials which undergo substantial volume changes depending on temperature or intercalation. Simulations are an important tool to better understand the processes in existing batteries and to derive new batteries which may be based on novel materials. To address these issues, it is necessary that basic material properties can be predicted and their respective influence on the battery performance can be evaluated.

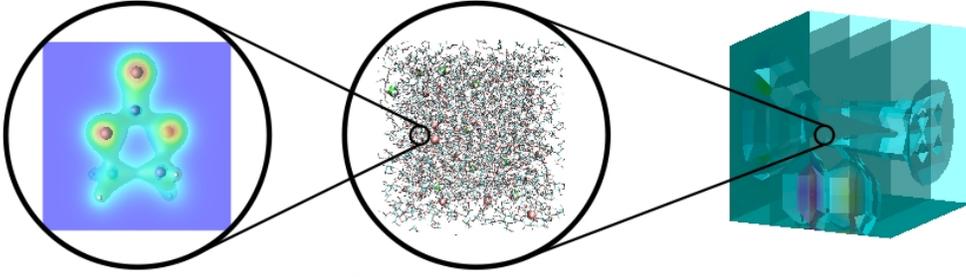


Figure 1: Scheme of the scales in material design. From left to right: electron density of Ethylene Carbonate (EC), and BF_4 ions in EC, ion concentration in a battery cell demonstrator.

We use molecular dynamics to investigate the influence of defects and artificial nanostructures on electrode and separator materials. The microscopic particle behavior is then scaled up to macroscopic values such as chemical potential, volume changes, diffusion coefficients, etc. In this paper we present an improved method for the derivation of diffusion values. These values are then fed to the time dependent Poisson-Nernst-Planck equations in three dimensions, which in turn are numerically solved by an adaptive finite element method. In this context, special challenges appear with the strong non-linear coupling of the ions' electric field with the ions' charge concentration. We treat this non-linearity by a Quasi-Newton iteration with adaptive direction- and step-size-control.

3 THEORY

For the molecular dynamic problem on the microscale we make use of the TREMOLO-X software package, a joint development at the University of Bonn and Fraunhofer SCAI, for details see [5] and the web page www.tremolo-x.com.

The quantity of primary interest is the diffusion coefficient of the charged ions within the electrolyte or the electrodes. Standard techniques to derive this value from molecular dynamics simulations are based on the Einstein relation or a Green-Kubo relation, i.e. the velocity auto correlation (VAC).

Here, let $\vec{x}_p(t)$ be the position of particle p at time t , let n be the number of particles, and let $\langle \rangle$ denote the averaging operator. Then, we define the mean square distance

$$\langle \tilde{L}^2(t) \rangle = \frac{1}{n} \sum_{p=1}^n (x_p(t) - x_p(t_0))^2 \quad (1)$$

In case the system is in an equilibrium state, this is equivalent to the Green-Kubo relation

$$\langle \tilde{L}^2(t) \rangle = \int_{t_0}^t \int_{t_0}^t \langle v_p(\tau) v_p(\tau') \rangle d\tau' d\tau \quad (2)$$

where $\vec{v}_p(t)$ is the velocity of particle p at time t , see [4]. However, in an active battery or capacitor, ions are in general in flux due to an external electrochemical potential and a corresponding non-zero convection; thus the system is no longer in equilibrium. As a consequence, the two traditional prediction methods (1) and (2) for diffusion fail and become divergent.

The reason for this failure becomes apparent once we take a closer look at the formula for ion flux on the particle level. Let Ω be the domain of the system in question, let $B_d(\vec{x})$ be a sphere of diameter around point \vec{x} , let \vec{x}_p denote the location and \vec{v}_p the velocity of particle p and, finally, let $\delta(\vec{x})$ be the three-dimensional delta distribution. Then, the flux of particles can be written as

$$\begin{aligned}
\vec{J} &= \frac{1}{|B_r(x)|} \int_{B_r(x)} \sum_{p: x_p \in \Omega} \delta(x - x_p) \frac{\partial \vec{x}_p}{\partial t} dx \\
&= \frac{1}{|B_r(x)|} \int_{B_r(x)} \sum_{p: x_p \in \Omega} \delta(x - x_p) \vec{v}_p dx \\
&= \frac{1}{|B_r(x)|} \int_{B_r(x)} \sum_{p: x_p \in \Omega} \delta(x - x_p) (\vec{v}_p - \langle v \rangle + \langle v \rangle) dx \\
&= \underbrace{\frac{1}{|B_r(x)|} \int_{B_r(x)} \sum_{p: x_p \in \Omega} \delta(x - x_p) (\vec{v}_p - \langle v \rangle) dx}_{\text{diffusion}} \\
&\quad + \underbrace{\frac{1}{|B_r(x)|} \int_{B_r(x)} \sum_{p: x_p \in \Omega} \delta(x - x_p) \langle v \rangle dx}_{\text{convection}}.
\end{aligned}$$

This separation into a diffusive and convective part is not taken into account by the traditional formulae (1) and (2), which therefore may fail. Thus a new method is required which is able to predict the correct value of pure diffusion also for the non-equilibrium case. The idea is to remove – or more accurately to disregard – the contribution of the convection while computing the displacement of the particles. For reasons of brevity we will not give the complete derivation here, but point the reader to [9]. There, one can also find a derivation of the splitting of convection and diffusion for the continuous Nernst-Planck equation, which shows that the micro and the macro-scale behave equivalently and the results are indeed transferable.

Here, we only present the resulting, corrected formula for the mean square displacement (MSD) based Einstein relation for diffusion, i.e.

$$\langle L^2(t) \rangle = \frac{1}{n} \sum_{i=0}^n (x_p(t) - x_p(t_0) - \langle x(t) - x(t_0) \rangle)^2. \quad (3)$$

This value can then be used to compute the actual diffusion coefficient

$$D = \frac{\langle L^2(t) \rangle}{6 \cdot (t - t_0)}$$

While the original formulae (1) and (2) are analytically equivalent in the infinite limit, the derivation of the integral in the expression (2) has a much stricter requirement of the equilibrium in the ensemble. As a consequence, the instability of approach (2) in the case of an external field cannot be removed in the same way as it can be done for (1) by (3). In the next sections, we consider the MSD based method (3) more closely.

4 RESULTS

4.1 Benchmarking of the corrected diffusion method

First, we perform benchmark tests with a unit-reduced Lennard-Jones fluid, following the setup of [8] and compare the numerical results. Simulations were carried out for reduced densities 0.6 and 0.8, and, for each density, at temperatures 1.2 and 3.0 (all in reduced units). After an initial relaxation for 1000 time units, the MD simulation using the NVE ensemble was first carried out for 500 time units. Then, the measurement process was started. It was successively restarted after 4000 time units.

For systems without external forces, both methods (1) and (3) result in nearly identical values (see figure 2), which match the results from [8]. However, in the presence of an external field, the conventional method (1) yields completely different results (with a computed diffusion coefficient that exceeds the valid one by several multiples and finally diverges, compare figure 3), while the improved new approach (3) still gives the correct result.

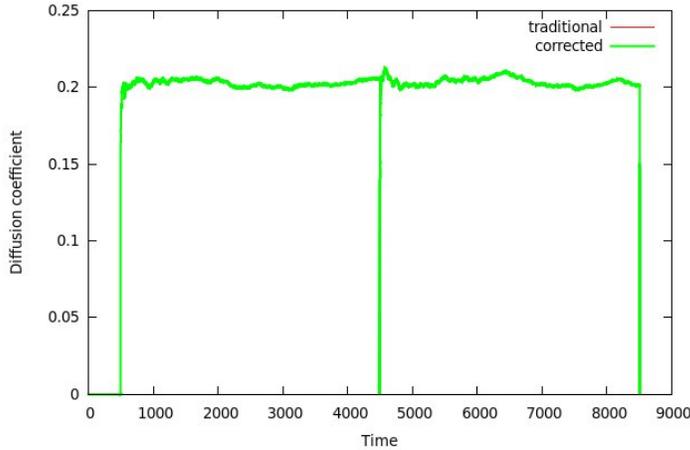


Figure 2: Comparison of the traditional (1) and the corrected (3) method for the classical equilibrium case. The computed values are nearly identical.

Furthermore, qualitative tests were performed for systems with constant average velocities. There the corrected method proved to be superior to the classical one as well. Note however that such scenarios can in general also be successfully treated with

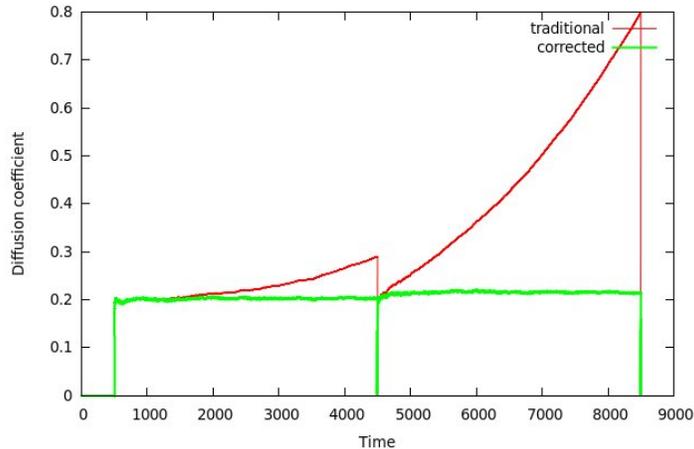


Figure 3: Comparison of the traditional (1) and the corrected (3) method for an applied external field. The traditional computation (1) diverges, whereas the new method (3) gives the proper value.

the traditional method (1) by removing the momentum of the center of mass from the ensemble.

	Traditional method 1		Corrected method 3		Benchmark value
	No force	With force	No force	With force	
Temp 1.2 Den 0.6	0.203	*	0.203	0.203	0.195
Temp 1.2 Den 0.8	-	*	-	0.087	0.084
Temp 3.0 Den 0.6	-	*	-	0.431	0.425
Temp 3.0 Den 0.8	-	*	-	0.232	0.225

Table 1: * These computations showed divergence, compare figure 3. Thus applying averaging would result in meaningless, too large values.

Altogether we see from the results in table 1 that our new method (3) behaves just as good as the classical method (1) for traditional ensembles in simple situations, while it is far superior in the cases where an outer force is in effect or the center of mass is in motion.

4.2 Diffusion of Li^+ in EC

Next we consider dissociated LiBF_4 in an Ethylene Carbonate (EC) solution. Intramolecular forces for EC and were modeled after [3] and [7], respectively. The intermolecular forces were modeled by Lennard-Jones and Coulomb interactions with the parameters in table 2.

molecule	atom	$\sigma/\text{\AA}$	$\epsilon/\frac{\text{kcal}}{\text{mol}}$	q/e
EC	O	2.96	0.210	-0.6452
	OS	3.00	0.170	-0.4684
	C	3.75	0.105	1.0996
	CT	3.5	0.066	0.033
	H1	2.5	0.030	0.1041
Li ⁺	Li	1.46	0.191	1.0
BF ₄ ⁻	B	3.581	0.3975	0.9756
	F	3.118	0.2552	-0.4939

Table 2: Van der Waals parameters and partial charges for EC

The basic system consisted of 2197 EC molecules. Then, for each Li⁺ or BF₄⁻ molecule added, one EC molecule was removed. After the introduction of these extra ions, the corresponding systems were relaxed and then equilibrated in an NPT setting for a temperature of 323K and a pressure of 1 atm. The actual measurement was performed for 147 ps at the end of the simulation. The thermostat was of Nose-Hoover type, the barostat of Parinello type. For further details of the implementation, see [5].

Computations were carried out for different concentrations of LiBF₄ in the electrolyte. In order to have comparability with experimental values, the diffusion of the bound hydrogen atoms was used to express the diffusion coefficient of EC. The results obtained for the diffusion coefficients can be found in table 3.

# Ions	$D_{EC(H)} \left[10^{-10} \frac{m^2}{s} \right]$	$D_{Li} \left[10^{-10} \frac{m^2}{s} \right]$
6	5.47	0.5
8	3.24	1.65
10	4.56	1.4
12	3.31	0.75
14	3.05	1.16
(average)	3.926	1.092

Table 3: Results for diffusion coefficients of EC and Li⁺

These values are to be compared with results computed by other simulations and found in lab experiments. In the simulation study [10], using the same ions and electrolytes as in this work, a diffusion coefficient for Li⁺ of $4.7 \cdot 10^{-10} \frac{m^2}{s}$ was derived, but no value for EC was given. Furthermore, to the best of our knowledge, no experimental values for exactly the same configuration have been published so far. However, a slightly different setup using the same electrolyte but $N(SO_2CF_3)_2^-$ as a counter-ion was investigated by both, simulation and experiment. Here, the simulation study [2]

produced diffusion coefficients for Li^+ and the EC electrolyte of $2.8 - 2.9 \cdot 10^{-10} \frac{\text{m}^2}{\text{s}}$ and $5.3 - 5.8 \cdot 10^{-10} \frac{\text{m}^2}{\text{s}}$, respectively. Moreover, in experimental work [6] the diffusion coefficients of Li^+ and EC were measured to be $2.1 \cdot 10^{-10} \frac{\text{m}^2}{\text{s}}$ and $4.3 \cdot 10^{-10} \frac{\text{m}^2}{\text{s}}$, respectively. Note that due to the larger counter-ion $N(\text{SO}_2\text{CF}_3)_2^-$, a direct comparison of these values may be questionable. Nevertheless, let us point out that our diffusion coefficient of Li^+ is twice as close to this experimental result as the one derived in [10]. At the same time, a much better result than in [2] is predicted for the diffusion of EC.

5 Going up in scale: Macroscopic ion migration

The derived values can now be fed as input parameters into a macroscopic continuous model for ion migration. To this end, we employ the time-dependent, fully coupled Poisson- Nernst-Planck (PNP) equations

$$\begin{aligned} \frac{\partial c_i}{\partial t} &= \nabla \cdot \left[D_i \left(\nabla c_i + \frac{z_i \cdot e \nabla \Phi}{k_B T} c_i \right) \right] \\ -\Delta \Phi &= \frac{F}{\epsilon_r \epsilon_0} \sum_i z_i c_i(x) \end{aligned}$$

in three dimensions with appropriate boundary conditions.

The PNP equation system is discretized using the finite element library deal.II [1]. In this context, special issues exist with the strong non-linear coupling of the ions' concentration with the ions' electric field. Any explicit treatment will lead to an oscillating behavior in the solution so that, in order to guarantee a numerically stable progression of the solution, all variables must be handled fully implicit. As a result, each time step of the solution requires not only the solution of a single linear equation system, but an iteration of such systems, i.e. a Quasi-Newton method.

As a first test we apply our method to an asymmetric, three-dimensional demonstration case. To this end, we simulate a unit cube containing four distinct subdomains (c.f. figure 5), each of which has its specific nanostructure with appropriately derived diffusion coefficients for both ionic species, which vary independently between $8.3 \cdot 10^{-11}$ and $5.0 \cdot 10^{-9}$. The two ionic species have opposing charges and are initially distributed with constant and equilibrated concentration. Then, an external electric field along the x-axis and a constant current across the y/z-plane boundaries are applied. Thus ion migration takes place accordingly and the distribution changes rapidly, compare figure 5.

6 CONCLUSION

We introduced a new, improved method to measure diffusion in molecular dynamics. It is at least as good as the traditional methods for standard ensembles, but in addition allows for an external force field. This is a prerequisite for any multiscale simulation of ion migration in new battery systems and capacitors. The resulting diffusion coefficients,

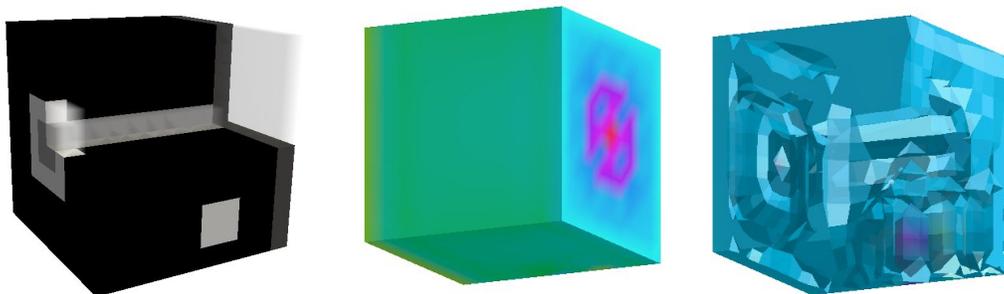


Figure 4: Cut-open unit cube with different diffusion regions, initial isosurfaces of ion concentration and final isosurfaces of ion concentration after 10 time units.

plugged into the Poisson- Nernst-Planck equation, yield improved macroscopic models and there allow for more accurate numerical results.

7 ACKNOWLEDGMENTS

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