Role of atomic level simulation in development of batteries

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Abstract

Unlike modeling at other levels as described in this workshop, the role of modeling at the atomic level has its main usefulness in the selection and design of materials for high performance batteries. We describe recent progress in studies of transport mechanisms of lithium in polymer electrolytes which suggest new approaches to the search for electrolytes with higher conductivity.
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1. Introduction

In the workshop for which these are the proceedings, the emphasis was on models of operating batteries for use in vehicle design and the like. In such work, the role of simulation of materials and interfaces at the atomic level has a somewhat indirect role. Primarily, such microscopic simulation has been useful in the development of materials for new, improved batteries. A widely cited example is the work of Ceder et al. [1] which predicted on the basis of first principles electronic structure calculations that substituting aluminum for cobalt in the cathode material Li_xCoO_2 would lower its cost increasing the available voltage. This result was unexpected on the basis of chemical intuition, but confirmed by later experiments.

It may be useful in the light of the diversity of the audience in the workshop (possibly mirrored in the readership of these proceedings) to briefly review the methodologies available for simulation of materials at the atomic level and their respective strengths and weaknesses. One may think in terms of an often cited map of the range of time and space coordinates which may be probed by the various methods, of which one version is reproduced below (Fig. 1).

At the shortest length and time scales (labeled QC in the diagram) one can solve the full Schroedinger equation (in some approximation) for all the electrons or for all the conduction electrons. This is the level at which the Ceder group was working. The calculations are sometimes called ab initio and 'first principles' and are associated with methods including Hartree Fock and density functional

theory for solving the Schroedinger equation. These calculations are now quite routine in many cases, but the challenge in many applications is to connect them to the larger scales of engineering interest. In most cases, temperature does not enter these calculations and the results can be said to apply to zero temperature systems.

This is not as much of a disadvantage as it might at first appear because the characteristic energy scale of electronic structure in solids is of the order of an electron volt which is approximately 10^4 K so that room temperature can for some purposes be regarded as very low in as far as electronic structure is concerned. In an extension of first principles methods, 'direct dynamics' methods have been developed in which the atoms are moved along a Born–Oppenheimer surface while the electronic structure and the resulting atomic forces are continuously recalculated. These methods are very promising, but also very computationally demanding and they have not been much used so far in applications of interest for battery materials. This whole class of first principles methods is usually restricted to systems of order 10^2 atoms (which can be periodically continued in a solid).

In the present paper, we discuss application of molecular dynamics (MD in the diagram) to studies of polymer electrolytes. Molecular dynamics simulates the motion of atoms using classical equations of motion (Newton's laws) and works at larger length and time scales than first principles methods. Because the atoms have finite kinetic energy during the simulation, simulations at finite temperature are easily done. To link molecular dynamics to the underlying quantum mechanical origin of the forces, several methods can be used. (Sometimes this link is not made and empirical force fields are used.) In the work discussed here, this link was made by using forces in the classical

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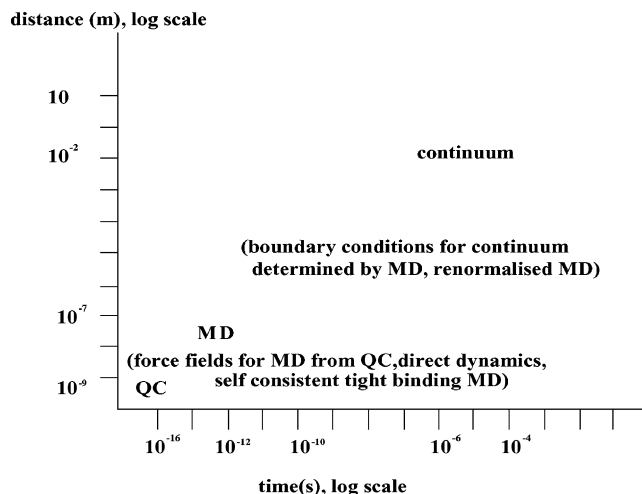**distance (m), log scale**

Fig. 1. Computational length and time scales.

equations of motion which were determined from first principles electronic structure calculations on small clusters of atoms. The first principles calculations were mainly done by the group of our collaborator, Larry Curtiss, at Argonne. The advantage of molecular dynamics is that it can simulate larger systems: easily up to 10^3 atoms and up to 10^6 atoms in some cases. Nevertheless, it is difficult for molecular dynamics simulate the very large space and time scales (up to hundreds of nanometers over times up to hundreds of nanoseconds) which are of interest.

We report recent results of molecular dynamics studies of electrolytes based on polyethylene oxide (PEO) because of the extensive experimental information [2] which is avail-

able about it and also because electrolytes similar to PEO remain the technical choice for lithium polymer battery applications. The main purpose of these investigations is to understand the mechanism of lithium transport in polyethylene oxide. The ionic conductivity of the electrolyte is too low for practical lithium polymer batteries and this is a serious obstacle to technical progress in design of this class of batteries. It is hoped that a clearer understanding of the atomic mechanism of ion transport will guide design of better electrolyte design to alleviate this problem. Previous simulation work on polymer electrolytes based on PEO, mainly containing iodide salts, has been reported and with different approaches to the modeling of the amorphous state [3–8]. We built the molecular dynamics model for the polymer [9] and the ions in it in collaboration with quantum chemist Larry Curtiss, who provided force fields for our models as described above. We are also collaborating with the neutron scattering group of Marie-Louise Saboungi and David Price of Argonne and have used their data to validate and refine our simulation model of the polymer.

In our method of producing a model of the amorphous polymer we 'polymerize' a model of the monomeric liquid dimethyl ether computationally. We published comparisons between our molecular dynamics model and the results of elastic neutron measurements on the neat polymer by our collaborators [11]. We show an example of a more refined version of this comparison in Fig. 2. This figure shows a weighted radial distribution function, which measures the local structure of the polymer. (See [10,11] for detailed definitions.) The results depend on some details of the calculations, such as whether we run a simulation at constant
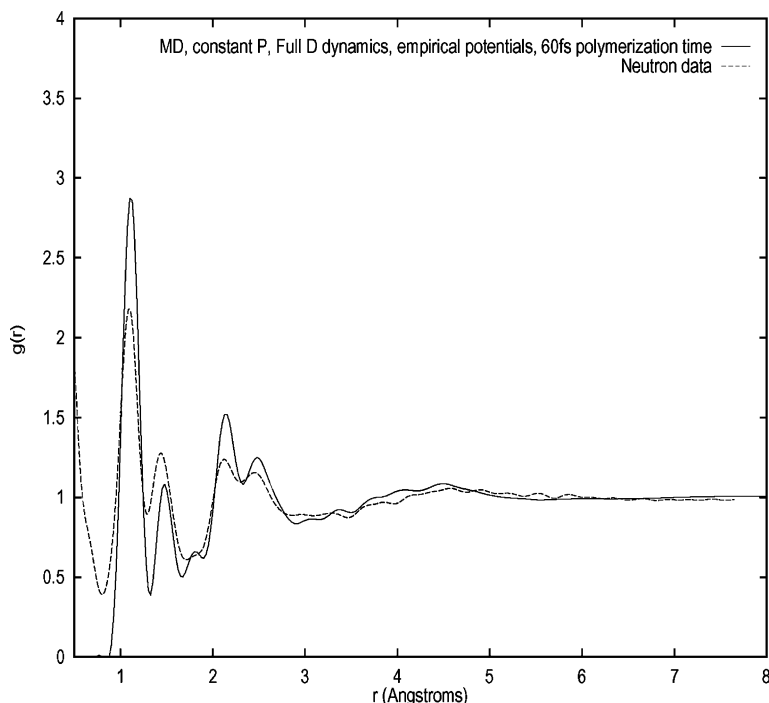

Fig. 2. Weighted radial distribution function calculated from the model compared with experimental neutron scattering results (dashes).

pressure or constant volume and on the method of including the hydrogen atoms in the model. Generally, the comparison shows reasonably good agreement of the calculations with the experimental results, though the simulations generally tend to exhibit sharper structural features than those found in the experimental data.

We studied the structure of isolated lithium and perchlorate ions in the polymer as well [12]. The isolated lithium ion is coordinated by six oxygen atoms from the polymer in the model. This appears to be consistent with recent neutron results.

Using this model we studied ion pairing of lithium perchlorate in PEO [13]. Ion pairing [14–17] is a significant factor limiting ionic conductivity and there is evidence that pairing increases with increasing temperature [18,19] possibly [20,21] because more entropy is available to a pair than to separated ions. To do the pairing study, we calculated the potential of mean force between a lithium and perchlorate ion in the system for several temperatures when a pair of ions is at various separation distances in our model. We found evidence at low ionic concentrations for two minima in the potential of mean force, one at lithium–chlorine separations of 3.5 and about 6.5 Å. We studied the same system with five ion pairs in a system of 216 polymerized monomers and again found two minima at the same separation distances but in this case there is evidence of entropic effects in the binding free energy of the pairs at 3.5 Å. We have been able to deduce the structure of the paired ion complexes. These results on ion pairing, if confirmed by a more detailed analysis of the neutron scattering data, can provide useful guides to design of electrolytes with better conductivity. We are currently extending these studies to other anions, beginning with triflate.

2. Ionic conductivity

We emphasize that the key limitation of the molecular dynamics approach is that the time scales easily accessible to molecular dynamics simulation are in the range 10^{-10} s whereas conductive properties relevant to battery design are associated with time scales of 1 s and longer. Much of the effort in this project has been directed at attempts to deal with this limitation. Basically we have taken three approaches to this problem in the context of the understanding the ionic conductivity of the polymer at low frequencies: we have attempted to accumulate statistics on barrier heights for lithium hopping motions [22], we have attempted to rescale the molecular dynamics to longer times by softening the force field potentials along the polymer backbone [23] and we have employed the parallel replica method of Voter [24], which permits very long simulations to be made by use of parallel processing methods.

All these methods have some advantages and drawbacks. Statistical determination of barrier height distributions is

computationally very expensive and tends to be biased by the implicit model of the lithium hopping mechanism. Temporal rescaling works well as long as no new physics occurs at low frequencies, but it is not clear that this condition is satisfied in the situations of interest. In the present contribution, we will report only results using the Voter parallel replica method [24]. The advantage of this method is that no potential modifications occur (though they do in some of the other Voter methods) and we can increase the temporal range of the simulations (at least in calendar time) by several orders of magnitude. There are still some implicit assumptions concerning the nature of the electrolyte dynamics but these are less restrictive than in the other two methods.

In the simulations reported here, we assume, following Voter (but see below), that the low frequency lithium conductivity is dominated by rare, statistically independent events in which the lithium ions undergo large spatial motions fluctuations in a time short compared to the time between these fluctuations. (Some aspects of this description of the algorithm we have used differ from one which we presented earlier [25].) Thus, the coordinates chosen to define the occurrence of a rare event are the positions of the lithium ions. Also, following Voter, we monitor the changes in the 'quenched' values of these coordinates, obtained by essentially reducing the temperature of the computational sample to zero. The specific algorithm is then as follows:

1. Initiate N copies (sometimes called replicas below) of the simulation cell. (N is the number of processors. In most of our simulations we used $N = 16$ or 20.) In all these copies the atoms have the same positions but they have different initial velocities, all chosen from a Gaussian ensemble consistent with the temperature of the simulation.
2. Simulate the dynamics of each of these copies of the simulation cell using ordinary molecular dynamics methods for a number M of simulation time steps. We chose 1000 time steps, each corresponding to 0.42 fs of real time.
3. Perform a 'quench' of each of the N copies. In a quench a relaxational algorithm is used in which each of the atoms moves the direction of the force on it until a point of local equilibrium is reached.
4. Determine the unweighted sum of the changes in the coordinates of all the lithium atoms in the sample since the last quench.
   4.1 If this is not larger than a fixed critical value, for any replica, go back to step 2 and continue the (finite temperature) simulation for M for steps for each replica of the system.
   4.2 If, for one replica, the sum is larger than the critical value, then run the simulation on this replica at finite temperature for a relaxation time τ. (We used 60,000 times steps in the results reported here.) Reproduce
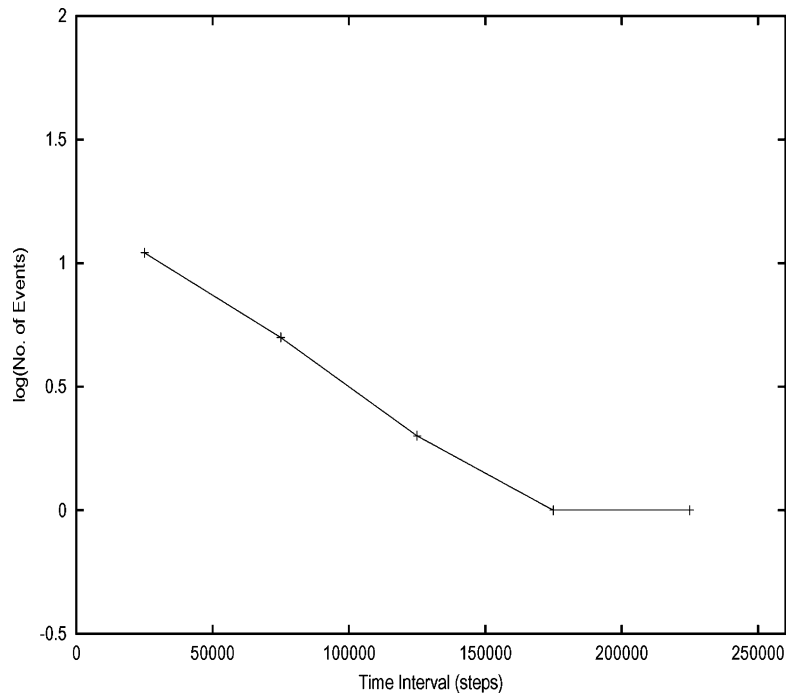
Fig. 3. Distribution of times between 'rare events' associated with large movements of Li ions. One step = 0.42 fs.

the atomic positions associated with this replica $N - 1$ times and give the atoms in each of the new replicas different velocities consistent with a Boltzmann distribution. These N replicas now replace the earlier ones. Go to step 2.

Voter shows that one can regard the resulting time sequences as follows: each time that one of the coordinate changes exceeds the critical value (called a rate event) for some replica, concatenate the histories of each of the replicas which did not experience a rare event (in any order) followed by the history of the one replica which experienced a rare event, followed by the history of relaxation (step 4.2) for this replica. (Do not include those histories associated with making the quench.) Add this concatenated history to the history, similarly concatenated between previous rare
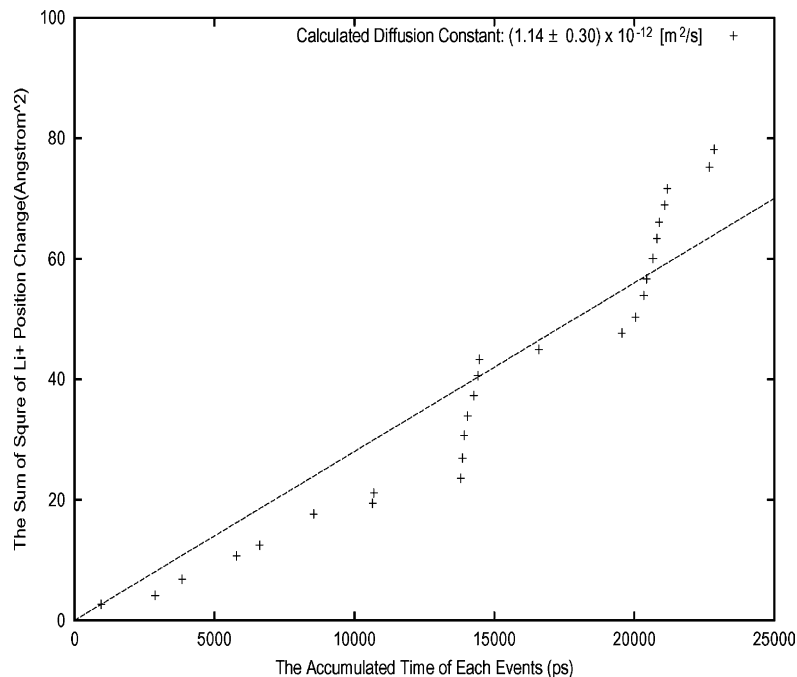

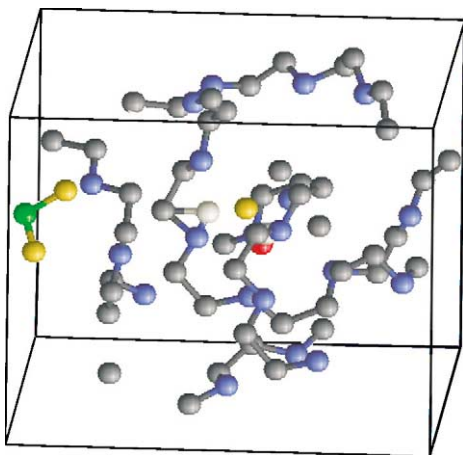Fig. 4. Displacement squared as a function of simulation time.

Fig. 5. Local environment of Li ion at the start of a large jump. Blue is oxygen in PEO; gray is carbon in PEO (united atom model); green is chlorine in perchlorate; yellow is oxygen in perelilorate; red is lithium; white spheres indicate initial and final positions of lithium.
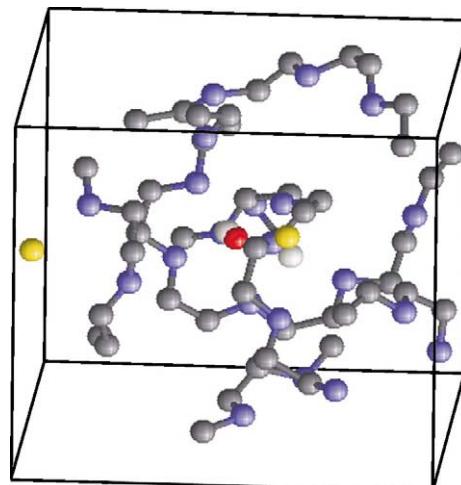

Fig. 7. Local environment of Li ion 0.38 ps after preceding figure.

events. This concatenated history is characteristic of history of the system and can be used to calculate temporal properties of the system at low frequencies. There will be high frequencies signals in this concatenated history which are spurious due to mismatch between the concatenated histories.

In a previous report [25], on our first efforts to implement an algorithm of this type for PEO electrolytes we used a different coordinate to identify rare events and there was evidence in the results that the relaxational time τ in 4.2 was not long enough. To check that the method described here satisfies the assumptions of the Voter replica method, we have calculated the distribution of time separations between rare events, which should be exponential if the method is applicable. We show a characteristic result in Fig. 3 showing that the distribution is very nearly exponential as required.

In Fig. 4, we show the mean square displacement of the lithium ions as a function of time as calculated using this

method. From the slope of a straight line fitted to this data we infer a lithium diffusion constant for our model of PEO of $1.14 \pm 0.20 \times 10^{-12} \, \mathrm{m^2/s}$ at 280 K. This is quite close to measured Li diffusion constants in lithium perchlorate [26].

We have also used these simulations to obtain information about the physical origin of the lithium ion motions. We show some pictures from a movie of one such event in Figs. 5–7. In this particular event, which lasts a time of about 0.4 ps (mean time between events is about one nanosecond), the lithium ion is carried in its lithium solvation cage from an initial position to a position in which it can change some of its solvating oxygens by a torsional motion of one of the polymer chains.

We are currently analyzing several dozen such events and are steadily accumulating more. No definitive statistical conclusions are yet available. We do find that a wide variety of different kinds of motions are associated with the rare, large lithium displacements.
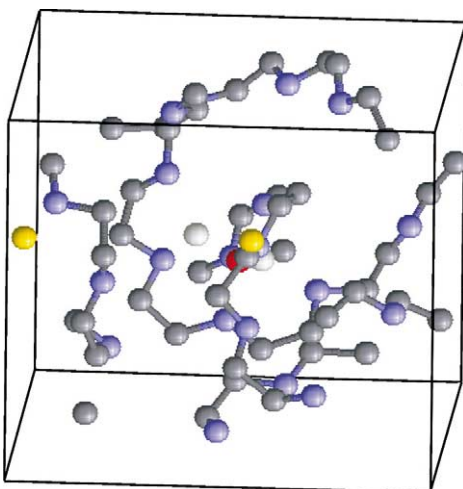
3. Conclusions

We find that our model gives a lithium diffusion constant for lithium perchlorate in PEO which is in rough agreement with experiment. The lithium motions associated with the diffusion are rare events of durations on the order of picoseconds separated by times of the order of nanoseconds. The data accumulated so far are consistent with, but do not yet prove, a picture of the conduction mechanism in which the lithium moves as a passenger of the moving polymer chain, to which it is tightly bound, and the rare events are associated with the fast transfer of the lithium ion to a new solvation cage when this motion occasionally results in the transfer of the lithium to a partially new solvation cage. This picture is qualitatively similar to the Marcus picture of electron transfer in which slow solvent motions (analogous

Fig. 6. Local environment of Li ion 0.21 ps after preceding figure.

to slow polymer motions here) are the rate limiting motions which occasionally bring the atoms into a configuration in which the electron (analogous to a lithium ion here) is quickly transferred. Polymer design based on this qualitative picture has recently yielded some promising improvements in ion conductivity.

Acknowledgements

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