CENTER FOR ACCELERATING MATERIALS MODELING

PROGRESS REPORT: SECOND QUARTER FY2013

PI: MARK HAGEN

Background and Overview

The goal for CAMM in FY2013 is to develop the software infrastructure that will enable the refinement of parameters in the force fields (potentials) used in Molecular Dynamics (MD) simulations by comparison with experimental neutron scattering data. In order to achieve this goal the work of CAMM in FY2013 is divided into 3 initial threads that will combine together later in the FY to demonstrate that the goal has been achieved.

The first thread is the development of the refinement software and the workflows for performing the MD simulations as part of the refinement process. This work is being undertaken by staff from Neutron Data Analysis and Visualization (NDAV) group in Neutron Sciences Directorate (NScD) and staff from Computing and Computational Sciences Directorate (CCSD).

The second thread is a science demonstration project that involves the simulation of the polyethylene oxide-acrylic acid system which is being undertaken by staff from the Center for Nanophase Materials Science (CNMS).

The third and final thread is the science demonstration project to simulate phonons in the ferroelectric $KTa_{1-x}Nb_xO_3$ oxide perovskite using a variation of ab-initio molecular dynamics. This work is being undertaken by staff from Materials Science and Technology Division (MSTD) in Physical Sciences Directorate.

Summary of Work in Second Quarter FY2013

In the second quarter of FY2013 work in all 3 of the threads has progressed on schedule, with the aim to merge threads (i) and (ii) in the third quarter of FY2013 and at the same time to start work on the third thread in the third quarter.

The development of the refinement software has progressed in the second quarter with testing and development of the refinement framework prototyped at the end of the first quarter. This work has used the experimental data on aqueous LiCl that had previously been measured on the BASIS spectrometer at the SNS and which we had (in the first quarter) refined manually to find the best fit parameters. During the second quarter we have had the refinement framework running in an automated mode and developed software to both improve the strategy of the fitting process and to organize file input and output. The largest amount of work has however been on understanding what the best optimization method to use is. Initially the Levenberg-Marquardt method was used but because of problems with, we believe, calculating derivatives from the MD simulations this method did not iterate well to the solution. However use of a Genetic Algorithm did find the appropriate solution and we have developed a hybrid method which overall uses a Genetic Algorithm but which uses a Levenberg-Marquardt method for some of the parameters.

The work in the second thread has continued with examination of the equilibration time for the simulations of the ionomer system PEO-AA leading to simulations showing the time dependence from which the intermediate structure factor I(Q,t) will be calculated. At the end of the second quarter this work is about to come together with the first thread whereby we will be able to compute neutron and x-ray structure factors S(Q) and S(Q,E).

During the second quarter of FY2013 the progress in the third thread, for simulations of phonons in the ferroelectric $KTa_{1-x}Nb_xO_3$ oxide perovskite, has been to identify, a highly qualified post-doctoral researcher to work on this thread, and appropriate experimental data on $KTa_{1-x}Nb_xO_3$ which can be used in the refinement. A post-doctoral researcher will start work at ORNL on May 28th and experimental data taken on the HYSPEC beam line at SNS will be used for the initial refinement.

Personnel Working in CAMM

All of the personnel, ORNL staff and post-docs, who worked on CAMM in the second quarter of FY2013 are as envisaged in the seed proposal. Personnel from NDAV are Mark Hagen (PI), Jose Borreguero, who is working on the molecular dynamics and Andrei Savici, who is working on the code for the neutron scattering corrections. Personnel from CCSD are Galen Shipman (Co-PI) and Vickie Lynch, who is working on the Dakota and Kepler software. Personnel from CNMS are Bobby Sumpter and Monojoy Goswami who are working on the LAMMPS simulations of the polyethylene oxide-acrylic acid system.

Olivier Delaire from MSTD, who is the lead for the sub-project on the simulation of the phonons in ferroelectric $KTa_{1-x}Nb_xO_3$ oxide perovskites has been involved in planning meetings and has also lead the search for a post-doctoral researcher for this sub-project during the second quarter of FY2013. As envisaged in the seed proposal the work on this sub-project will commence in the third quarter of FY2013. A highly qualified candidate, Jiawang Hong, was identified and accepted the offer of the position. His start to work date at ORNL is 28th May. He has previously worked at Rutgers University with Prof. David Vanderbilt on “First principles studies of ferroelectrics and related materials” and in the Center for Ferroics at the University of Cambridge, U.K. with Prof. James F. Scott.

Anticipated Work in Third Quarter FY2013

In the third quarter of FY2013 we anticipate being able to deploy the refinement framework developed in thread one for use in modeling systems similar to aqueous LiCl, i.e. those that can be modeled with an MD package such as NAMD. This presumes that the optimization methods being developed at the end of the second quarter of FY2013 prove successful

We also anticipate that the process of merging the work on the second thread into the refinement framework will be well under way with significant testing taking place.

For the third thread, the science demonstration project on ferroelectric $KTa_{1-x}Nb_xO_3$ oxide perovskites, we anticipate to have initial simulation codes identified and under test by the end of the quarter..

Detailed Descriptions of Progress in Threads One, Two and Three

The following three sections give descriptions of the work done in thread one – the development of the refinement software and workflows, in thread two – the simulations of the Polyethylene Oxide-Acrylic Acid system, and an overview of the work that will be starting in thread three in the third quarter of FY2013.

Development of the Refinement Software and Workflows

At the end of the first quarter of FY2013 we had (i) performed "manual" fits of Molecular Dynamics (MD) simulations performed using the NAMD software to experimental data taken on the BASIS backscattering spectrometer at SNS and (ii) constructed a prototype of the refinement framework using the DAKOTA toolkit [1] for optimization, and the Kepler scientific workflow management package [2]. From a high level view the automated refinement framework involves running a sequential loop of programs;

1. DAKOTA to predict new parameters for the next iteration of the refinement.
2. NAMD to perform the MD simulations using the new parameters.
3. SASSENA to perform the weighted Fourier transform of the atomic position and velocity time trajectories from NAMD.
4. Various codes to account for instrumental artifacts in the data; folding with the instrument resolution function, background scattering, elastic line scattering from the sample can and small offsets in the energy scale due to sample size/positioning.
5. Evaluation of the cost function (the weighted least squares) between the experimental and simulation data sets and return the result to DAKOTA ready for the next iteration.

The overall management of submitting and sequencing these programs is done with Kepler. It is worth noting that the programs, in general, take very different amounts of computer time and require quite different resources in order to run. For example the MD simulations will run for 10's of minutes to hours to possibly days and will need to be run on high performance clusters or supercomputers, while the cost function evaluation and the actual prediction of the new parameters by DAKOTA will take only seconds and can be run on a single processor on a workstation. Thus the Kepler framework, which itself only requires seconds of cpu-time, runs on a workstation from which it submits, and monitors, the performance/progress of the other programs. This requires Kepler to have authentication to submit (and monitor) jobs and also have robustness of operation (e.g. if the computers reboot Kepler needs to restart from the appropriate point). The advantage of using Kepler is that it was specifically designed to do this type of work [2] with the Jaguar (now Titan) supercomputer as one of its specific targets.

In the second quarter of FY2013 the work in this thread has been dominated by developing and testing the framework for the refinement framework so that it can run successfully in a semi-automated way. This work has both in a computational sense, for the efficient processing by, and ease of use of, the framework, and also in understanding the best method to use to perform the refinement.

In terms of the efficient running of the refinement it is important that when DAKOTA is searching parameter space it does not unnecessarily run the MD simulation. This could occur when DAKOTA is varying other parameters, such as those describing the elastic line for the sample can, or when the parameters DAKOTA suggests for the simulation are the same as those that have been previously run. As a consequence a piece of refinement strategy software was developed to trap these instances and re-use simulations that had previously been run rather than repeating them.

We have also developed software to manage the input and output from the different programs. The format in which parameters are input and output from DAKOTA is, of course, different to that which NAMD uses for input and output. Furthermore the input and output for the various MD codes currently available, (e.g. NAMD, LAMMPS, etc.) are different to each other. Thus we have taken a template approach, whereby we produce (by hand) a template of the standard input/output for each of these MD codes and have developed software that can (generally) use a template to convert input/output for an MD program to the DAKOTA input/output.

As well as the parameter input/output we have also developed code that writes (i) the output files for the intermediate scattering function I(Q,t), (ii) the dynamic structure factor S(Q,E), and (iii) the dynamic structure factor with the instrumental artifacts taken into account, as HDF5 (Hierarchical Data Format) files in the same format as the experimental reduced data files produced by the MANTID data reduction program at the SNS. Thus it is easy to plot the fit results against the experimental data using the MANTID software package used for data reduction at the SNS.

In this last respect we have engaged our colleagues in NDAV who work on the MANTID and ADARA projects, providing them with details on the structure of the CAMM framework and requesting that the necessary components be added to the MANTID, ICAT and Active MQ software in the SNS data reduction and management software suite to integrate the CAMM refinement framework. Specifically in MANTID a user interface to load, and allow user friendly manipulation of, the CAMM results files is required. The file locations and metadata for the SNS experimental raw and reduced data files are currently catalogued using the ICAT software. The same cataloguing needs to be carried out for the simulation data files generated by the CAMM refinement framework. Finally, in the ADARA structure for data streaming and post-acquisition processing the Active MQ software is used to capture and report the status of the processing to the user via a web interface. A similar capture and reporting of the status is required for the programs in the CAMM refinement framework and this should be done in the same way.

While the work on MANTID, ICAT and Active MQ is outside the scope of CAMM it has been important to instigate the start of this work by our NDAV colleagues in the second quarter of FY2013. This is because, at the current rate of progress, it is plausible to envisage that the CAMM refinement framework could be deployed later in the third quarter of FY2013 as an analysis tool for cases similar to that of aqueous LiCl that are studied on the BASIS and CNCS spectrometers at SNS. While the research work of CAMM will concentrate in the third quarter on tackling the more advanced simulation problems that form threads (ii) and (iii) the deployment of CAMM software which could be used as an analysis tool leading to publications, with the appropriate accreditation to the CAMM project, would be a significant step.

While the computational operation of the CAMM refinement framework can be automated it is unlikely to be a tool that can be routinely used by an uninitiated user. Apart from the automated fitting there are a number of other steps to the overall process. Firstly the initial construction of the atomistic model, whether it is for a liquid, polymer, protein etc., is not trivial and requires skill. Secondly there is an initial scaling of the simulation size and time that needs to be performed. In order to obtain a physically reliable starting configuration for the MD the model needs to be equilibrated for an amount of simulation time during which, depending upon the ensemble type, energy or temperature, are maintained. Apart from ensuring that the model will be equilibrated it is also necessary to ensure that its size is large enough to reproduce the wavevector dependence of the neutron scattering and that it run time (after equilibration) is long enough to capture all of the energy dependence. However it is important also not to choose too large a model since the MD run time scales with sample size, e.g. doubling the linear dimension of the model will lead to at least an 8x increase in run time, and the MD simulation will be run many times during the fitting process. When the fitting process is completed however there will need to be further investigation of the size and time scaling to ensure that the final parameters obtained from the fitting do not depend on model size or the length of the MD run time.

As well as developing the code for steps 1 through 5 in the loop for the refinement framework we have also investigated the optimum method for DAKOTA to use to perform the refinement. Initially we used the conventional methodology used in most fitting programs for neutron scattering data analysis, the Levenberg-Marquardt method. In this method one computes the cost function (the sum of least squares) and then (usually

numerically) the derivatives of the cost function with respect to the parameters. These derivatives are then used to compute a weighted gradient and the next set of parameters estimated by projecting along the gradient.

This method works very well when one is fitting to a continuous (analytic) function where the derivatives can be accurately calculated. It works very well for adjusting the parameters describing the corrections for the instrumental measurement artifacts. However when trying to optimize the parameters in the MD simulation the method did not seem to iterate the parameters, instead it just seemed to keep the parameters constant even though it was obvious that there were better parameters nearby. After some investigation we determined that this was because the numerical derivatives were not accurate enough due fluctuations in the MD simulation. The MD simulation is, of course, averaging over phase space and when the results are examined in detail one can see the effects of these fluctuations. We investigated whether this could be mitigated by using a larger sample size and/or longer runs, and whether it depended upon the ensemble choice, NVE or NPT. In the end however we concluded that a derivative based method was not appropriate for optimizing the simulation parameters.

Therefore we have tested other optimization approaches and determined that a Genetic Algorithm seems to work well to find the optimum simulation parameters. At a high level view a Genetic Algorithm works by carrying out a series of "trials" around the region of the (expected) solution and then breeds the trials to find the optimized fit. While this may at first sound as though it would be slower than Levenberg-Marquardt, since it seems to compute more simulations, the increase in wall clock time is not so great because those simulations can be done simultaneously.

While the Genetic Algorithm works well for the simulation parameters it is not efficient for the instrument parameters. Thus, at the time of writing, we are testing a hybrid method, in which the overall optimization of the simulation parameters is performed by a Genetic Algorithm but within the trial the optimum parameters for the instrument artifacts are determined by a Levenberg-Marquardt optimization. In figure 1 below a plot is shown of some of the LiCl data and fit results.

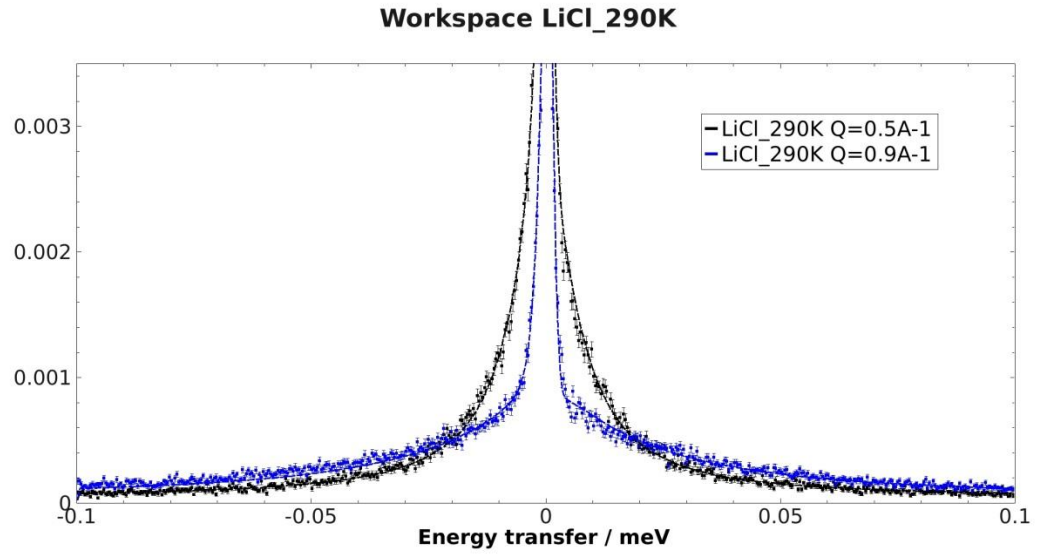

Figure 1: Experimental data at wavevectors Q=0.5 and 0.9 $Å^{-1}$ from an experiment on aqueous LiCl carried out on the BASIS spectrometer at SNS compared to results from a NAMD simulation.

Science project on Polyethylene Oxide-Acrylic Acid

Large-scale molecular dynamics simulations have been used to examine the morphology and dynamics of ionomers containing various charge states and chain lengths [3]. Figures 2-4 summarize some of the results to date. At low dielectric, due to stronger electrostatic interaction strengths, higher agglomeration (right figure) can be observed. The observed structures show layered and percolated morphologies [3]. The mean square displacement (MSD) as a function of time for the counter-ions is shown in Figure 3, indicating a unusual behavior. The slopes show different values for different time regimes and are plotted in Figure 3. At the early and intermediate times, anomalous diffusion followed by normal Fickian diffusion is observed. At longer times, however, the slopes show two values, one near to zero (0.01) and the other ~ 2.0 implying that the counter-ions are almost immobile (0.01) for certain times and then becomes super-diffusive (2.0). This can be explained as follows. The counter-ions, once passed the diffusive regime (equilibrium), stay on the percolated cluster thereby making them immobile for certain time frame. While the counter-ions are at their lowest entropy states with almost zero mobility, they slowly gain energy through collisions that induces thermal activation. These thermally activated counter-ions 'hop' from one site to another. The hopping mechanism can be more precisely explained by calculating the intermediate structure factor, I(Q,t) of the system [4].

The results obtained from these course-grained simulations provide physical insight about this class of polymer electrolytes. A fully atomistic study is underway to account for lengths directly appropriate to experimental measurements.

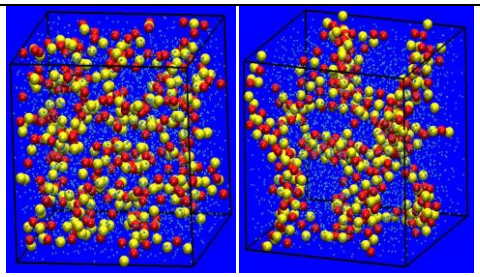

Figure 2: Snapshots of the central simulation box for different dielectric constant. Left figure: ε = 1/2 and right figure: ε = 1/10 The yellow spheres are free counterions and the red spheres are the charged monomeric units. For clarity, the neutral monomer units are represented in tiny cyan spheres. Lower dielectric constant (right figure) show highly percolated charge states.

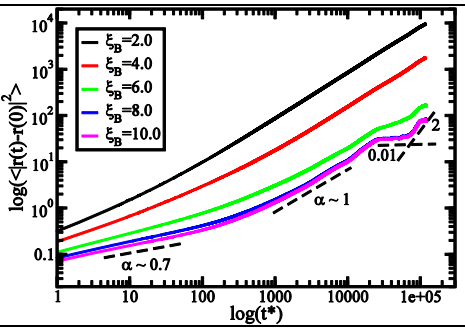

Figure 3: Mean square displacement (MSD) of counterions for different dielectric constant. Slopes at different time segments for low dielectric constant media are shown below the graphs. Slopes α changes from 0.7, 1.0, 0.01 to 2 implying anomalous, diffusive, slow clustered motion and counterion hopping.

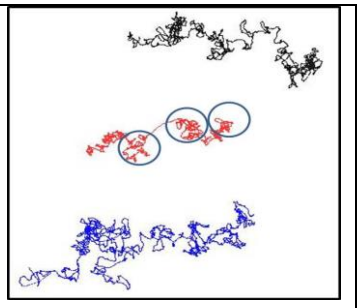

Figure 4: Trajectories for 3 different counterions for high dielectric constants. The counterions stay at the clustered state (shown in circle), then jump to another clustered state for some time before jumping to the next

Electron-phonon coupling and soft phonon mode in Ferroelectric $KTa_{1-x}Nb_xO_3$

The CAMM postdoctoral researcher (Jiawang Hong) will investigate phonons in energy materials, including the effects of anharmonicity, lattice instabilities, and electronic structure, by performing first-principles simulations (ab-initio lattice dynamics and molecular dynamics). Simulations of the perovskite structure ferroelectric oxides $K(Ta,Nb)O_3$ and $BaTiO_3$ will be performed, focusing on the effects of temperature and phase stability under the application of an external electric field. These simulations will be used in theoretical scattering kernels, which will be quantitatively compared to, and refined (using the CAMM refinement framework) against, inelastic neutron scattering measurements performed at the SNS.

$KTaO_3$ is a well-known incipient ferroelectric material (quantum paraelectric), exhibiting anomalous phonon dispersions [5, 6]. By alloying with the high temperature ferroelectric $KNbO_3$ the Curie temperature, and associated structural phase transitions, of $KTa_{1-x}Nb_xO_3$ can be controlled. We have observed anomalous thermal conductivity behavior above the Curie temperature in $KTa_{1-x}Nb_xO_3$ crystals, likely related to the soft phonon mode associated with the ferroelectric instability. In addition, strong electron-phonon interactions are suggested by the significant suppression of the thermal conductivity in semiconducting, Ca-doped materials [7].

For comparison with the simulations we will use experimental data [8] that has been collected using the HYSPEC spectrometer at the SNS. We used an incident energy E_i=25meV (Fermi chopper at 420Hz) in order to investigate the behavior of the soft transverse-optic mode in a single-crystal of $KTa_{1-x}Nb_xO_3$ with nominal composition, x=0.12 at T=300K, and T=120K. The sample was aligned with (h,k,0) as the scattering plane, and data were collected on range of orientations of the crystal in order to map the phonon dispersions, focusing on the transverse optic and acoustic branches along [0,k,0], in the Brillouin zone (200). Figures 5 and 6 show experimental data for S(**Q**,E) at 300 and 120K, respectively. The TA and TO branches are clearly identified, and the soft nature of the TO mode at the (200) zone center is also observed. In addition, the TO branch further softens upon cooling, with a minimum TO phonon E<5meV. This corresponds to a nearly ferroelectric behavior. We plan to measure the behavior of the TO branch across the ferroelectric transition in further experiments.

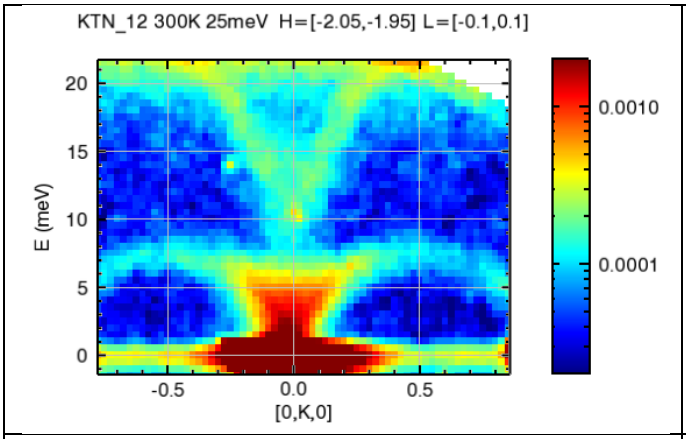

Figure 5: Transverse acoustic and optic phonon branches in KTN12 along [0,k,0] at 300K.

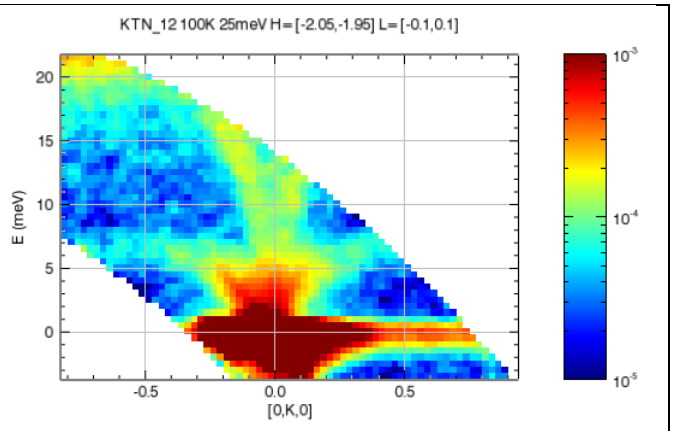

Figure 6: Transverse acoustic and optic phonon branches in KTN12 along [0,k,0] at 120K.

References:

[1] B. M. Adams, W. J. Bohnhoff, K. R. Dalbey, J. P. Eddy, M. S. Eldred, P. D. Hough, S. Lefantzi, L. P. Swiler, and D. M. Vigil, DAKOTA: A Multilevel Parallel Object-Oriented Framework for Design Optimization, Parameter Estimation, Uncertainty Quantification, and Sensitivity Analysis. Version 5.2 User's Manual, Sandia Technical Report SAND2010-2183, updated Nov. 2011.

[2] B. Ludäscher, I. Altintas, C. Berkley, D. Higgins, E. Jaeger, M. Jones, E. A. Lee, J. Tao, and Y. Zhao. Scientific workflow management and the Kepler system. Concurrency and Computation: Practice & Experience, pp. 1039–1065, 2006

[3] M. Goswami and B. G. Sumpter, Appl. Phys. Lett. (Under review).

[4] M. Goswami, J. Borreguero, R. Kumar, B. G. Sumpter, (to be submitted to J. Chem. Phys.)

[5] J.D. Axe, J. Harada, G. Shirane, Phys. Rev. B **1**, 1227 (1970).

[6] E. Farhi, A.K. Tagantsev, R. Currat, B. Hehlen, E. Courtens, and L.A. Boatner, Eur. Phys. J. B **15**, 615 (2000).

[7] W. Siemons, M.A. McGuire, V.R. Cooper, M.D. Biegalski, I.N. Ivanov, G.E. Jellison, L.A. Boatner, B.C. Sales, and H.M. Christen, Advanced Materials **24**, 3965 (2012).

[8] Experimental data is taken from work performed by; Olivier Delaire, Chen Li, Barry Winn, Mark Hagen, Michael Manley, Michael McGuire, Wolter Siemons, Brian Sales and Lynn Boatner