**CENTER FOR ACCELERATING MATERIALS MODELING**

**PROGRESS REPORT: THIRD QUARTER FY2013**

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**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 KTa1-xNbxO3 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 Third Quarter FY2013**

During the third quarter of FY2013 work has taken place in all 3 of the threads in the CAMM seed project, with the work on the third thread starting during this quarter.

At the end of the second quarter FY2013 the work in the first thread revolved around the choice of refinement strategy being used. At that time there appeared to be difficulties using the Levenberg-Marquardt method because of problems with taking the derivatives of parameters describing the force fields used in the MD simulations. As a consequence we were experimenting with using a (derivative free) Genetic method. Early in the third quarter we made a number of changes to the way that the derivatives were being handled in the framework which made the Levenberg-Marquardt method rapidly converge to a reliable solution. For cases where the initial force field models only need a small amount of refinement this Levenberg-Marquardt method is highly preferred because of its speed of convergence. However the work on the Genetic method was not wasted because we will be able to use this for cases where we are not initially close to the solution.

Following this initial progress in the third quarter a number of developments have followed in relation to the framework development. In the first and second quarters we have been testing the CAMM framework using NDAV’s small development cluster – chadwick, but now we have extended the framework to submit simulation jobs to the *hopper.nersc.gov* Cray supercomputer at NERSC (National Energy Research Scientific Computing Center), Lawrence Berkeley Laboratory. We have also procured, using the equipment funding in CAMM, a server *camm.sns.gov* that will act as the login node for users to make use of the CAMM framework/software.

We have also sought to broaden the use of the CAMM framework by reaching out to 3 SNS user groups whose work could benefit from the developments that CAMM has so far made with the framework. These groups were chosen because the simulations related to their research are an incremental extension of the test simulations that were performed in the first and second quarters. The users also represent a spectrum of simulation background ranging from the expert to those who have never used simulation before. These 3 projects are discussed in more detail later in the report.

The second and third threads of the CAMM seed project involve integrating into the CAMM framework more advanced MD simulations. The second thread is a project to study polymer electrolytes, in this case polyethylene oxide – acrylic acid in the presence of LiCl, which involves the incorporation of coarse grained simulations in the CAMM framework. This project will begin integration during the fourth quarter of FY2013. Work has progressed on this thread during the third quarter by performing some preliminary calculations. The third thread involves the use of ab-initio MD for the study of phonon anharmonicity, work on this thread was only begun at the end of the third quarter FY2013.

**Personnel Working in CAMM**

The personnel, ORNL staff and post-docs, working on CAMM in the third quarter of FY2013 are as envisaged in the seed proposal. Those working on the CAMM framework, and projects with SNS users, are Mark Hagen (PI), Jose Borreguero, Vickie Lynch and Andrei Savici. Galen Shipman (Co-PI) is working on the integration with the supercomputer facilities, NERSC and OLCF. The project on the polyethylene oxide-acrylic acid system in the second thread is being carried out by Bobby Sumpter (Co-PI) and Monojoy Goswami from the Center for Nanophase Materials science (CNMS).

The project on using ab-initio MD to study the electron-phonon coupling in ferroelectric oxide perovskites KTa1-xNbxO3 (and BaTiO3) is being carried out by Olivier Delaire (Co-PI) and Jiawang Hong from Materials Science and Technology Division (MSTD). As envisaged in the original seed proposal this third thread only began work in the third quarter of FY2013. Jiawang Hong, who had previously worked at Rutgers University with Prof. David Vanderbilt on “First principles studies of ferroelectrics and related materials”, joined ORNL on 28th May to work on this part of the CAMM seed project.

**Detailed Descriptions of Progress in Threads One, Two and Three of CAMM**

The following sections give descriptions of the work done in thread one – the development of the refinement software and workflows, and the SNS user projects, (sections 1.0 → 1.3); in thread two – the simulations of the Polyethylene Oxide-Acrylic Acid system; and in thread three the simulations of the electron-phonon coupling and soft modes in ferroelectrics.

**1.0 Development of the Refinement Software and Workflows**

CAMM staff: Vickie Lynch, Jose Borreguero, Mark Hagen, Andrei Savici, Galen Shipman

At the outset of the third quarter FY2013 a number of improvements were made to the calculation of the derivatives provided to DAKOTA [1] for the refinement of the simulation model which lead to the Levenberg-Marquardt optimization method provided in DAKOTA working very well for our test case, a NAMD model for aqueous LiCl compared to experimental data taken on the BASIS beam line at SNS. Starting from the value predicted by the three point charge model for purer water [2], the Levenberg-Marquardt converged in two to three iterations to the best fit value that we had found from our manual fitting in the first quarter FY2013. The optimized model results are shown in figure 1.

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| Q5.png | Q7.png |
| Figure 1: Experimental data at wavevectors Q=0.5, 0.7, and 0.9 Å-1 from an experiment on aqueous LiCL carried out on the BASIS spectrometer at SNS compared to results from an optimized NAMD simulation. | Q9.png |

We note that each “iteration” in the refinement consists of submitting (2 x np + 1) simulations to the supercomputer/cluster performing the simulations and then submitting (2 x np + 1) calculations of the dynamic structure factor S(**Q**,E) from the simulation trajectories where np is the number of variable parameters in the force field model. If the capacity of the supercomputer/cluster is able to run these simulations simultaneously then the results will only take as long as one simulation.

The submission of these remote jobs is controlled by the Kepler [3] workflow (see figure 2 for a view of a few levels of the workflow and figure 3 for a view of the graphical user interface). The testing in quarter’s one and two FY2013 was done on a 192 core cluster at the SNS, *chadwick.sns.gov*, however we have now rerun the same simulations remotely on the Hopper (Cray XE6) supercomputer at NERSC from the same Kepler workflow running on a workstation *camm-test.sns.gov* at the SNS, and obtained the same optimized results. We are currently working with staff from the OLCF to obtain an approved cyber-security plan that would allow us to do the same to the Titan (Cray XK7) supercomputer at Oak Ridge National Laboratory.

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| Figure 2: Kepler workflow used to submit remote jobs, check ActiveMQ queues, and calculate goodness of fit using input parameters from Dakota. | kepler_gui.png  Figure 3: Graphical User interface of Kepler workflow for simulations. |

We have also modified the workflow so that the ActiveMQ messaging system now controls the interactions between Dakota and Kepler. This will allow us to display a live progress report on the refinement for CAMM users. We have also converted our codes so that the output is in an HDF5 (NeXus) output format that contains meta-data describing the relevant simulation and experimental parameters. This will allow the simulation files to be catalogued in the same way that the SNS experimental data is catalogued.

In the third quarter we also procured a server computer, *camm.sns.gov,* that will act as the login node for users of the CAMM software. It will run the DAKOTA and Kepler workflows, while the simulation jobs will be submitted to the clusters and supercomputers. This server arrived at the end of the third quarter.

* 1. **Octa-Methyl-Silsesquioxane**

SNS Users: Michael Crawford (Dupont) and Niina Jalarvo (Julich) – BASIS and CNCS experiments  
CAMM contacts: Jose Borreguero and Mark Hagen

Polyhedral oligomeric silsesquioxanes (POSS) are silicon-based molecules with a backbone consisting of a cage-like structure that can be decorated with a variety of functional groups. Due to this variability, POSS molecules have found applications as support and specialized environments for catalysis, as semiconductors or insulators, and as impurities to modulate the rheology properties of polymeric materials. MePOSS contains methyl groups that decorate the backbone of the molecule. In addition to being employed as a workbench in the study of POSS systems, MePOSS has found applications in the modulation of the hydrophobicity and plasticity properties of polymeric materials.

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| An AMBER [3] force-field has been adopted for the simulation of MePOSS. This force-field has been previously used in simulations comparing to structural data from ion mobility mass spectroscopy experiments [4].We determined to refine this force-field against quasi-elastic dynamical data taken from a powder sample at the BASIS beamline at SNS. In particular, we sought to refine the potential energy barrier parameter regulating the rate of methyl group rotation around the Si-C bond. | (a) | (b)  C:\Documents and Settings\Jose Borreguero\My Documents\presentations or reports\BSS_presentation.pptx\Figures\mercury_3x3x3.png |
| Figure 4. MePOSS, (a) single molecule and (b) crystal | |

Preliminary fits of the dynamical incoherent structure factor using a single-molecule system (Figure 4a) indicate that the energy barrier parameter in this force-field has been overstated by 37% (Figure 5).

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| **(a)** | **(b)** |
| Figure 5. Preliminary fits of calculated quasi-elastic incoherent structure factor derived from molecular dynamics simulations against data taken from powder micro-crystal sample at the BASIS beamline. (a) Fit with the original force-field (K=0.11). (b) Fit after potential has been refined (K=0.07). | |

Since the simulated system is composed of a single-molecule, we plan to build a crystalline system that will assess the relevance of confined diffusion of the MePOSS (Figure 4b), an effect which was neglected in the single-molecule approximation.

**1.2 The Boson Peak in Poly-Glutamic Acid Polymers**

SNS Users: Jonathan Nickels and Stefania Perticaroli (University of Tennessee – Knoxville) – CNCS experiments  
CAMM contacts: Jose Borreguero and Mark Hagen

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| The boson peak (BP) is an excess of low energy excitations beyond those observed in crystalline materials, and a ubiquitous phenomenon of systems endowed with a rugged energy landscape. The BP has been observed in inelastic neutron scattering data taken from proteins, glasses and amorphous solids, its prominent feature being a local maximum of the dynamic structure factor in the 2-7 meV energy transfer range. One hypothesis states that the BP arises from collective motions of atoms with damped resonances at frequencies in the acoustic range [5]. These types of resonances are both governed by the strength of the interactions between neighboring atoms as well as by their connectivity or topology. In a crystal, the topology is fully specified by the particular crystal symmetry but in an amorphous solid the description of the topology is dependent on the probed length-scale. The poly-Glutamic acid polymer (pE) is an excellent system to study the role of the topology in the determination of the BP because its topology can be altered with variations of the pH, while the chemical composition remains constant. | Figure 6. pE polymer chain solvated in water. Only the center of mass of the water molecules is displayed (red dots) to allow visualization of the polymer chain. |

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| (a) | (b) |
| Figure 7. Dynamical structure factors of the single pE polymer chain. (a) Intermediate structure factor I(Q,t) showing a decay in the nano-second time scale with superimposed oscillations in the pico-second time scale. (b) structure factor S(Q,E) showing a broad boson peak in the 1-9meV range. | |

We aim to obtain a pE melt system that will faithfully reproduce the BP observed in inelastic neutron scattering experiments taken at the CNCS beamline of SNS. As a first step, we have built a single pE chain 482-monomers long solvated in water (Figure 6) with the CHARMM force-field, and calculated its inelastic incoherent structure factor. Oscillations superimposed on the decaying intermediate structure factor I(Q,t) are readily observable in the pico-second time-scale (Figure 7a). These oscillations result in a broad BP in the 1-9meV range (Figure 7b). Having observed a BP in our simulations, our future goals include the generation of a pE melt system as well as the identification of the force-field parameters that will give rise to a change in the topology of the simulated system with changes in the environment.

**1.3 Water Adsorption to Barite Surfaces**

SNS user: Andrew Stack, Chemical Sciences Division, ORNL – BASIS experiment  
CAMM contacts: Jose Borreguero and Mark Hagen

Experimental determination of water exchange rates with mineral surfaces are difficult to obtain, often yielding ambiguous results [6], yet these rates are fundamental in the understanding of related processes such as mineral dissolution and growth. The aim is to reproduce the quasielastic neutron scattering experiments taken from Barite (BaSO4) samples at the BASIS beamline. The simulated system is composed of a Barite cube solvated with water molecules on two opposite sides, and simulated with a LAMMPS force-field (Figure 8a). It should be noted that Andrew Stack is an experienced user of MD simulation and already had LAMMPS results that could be used.

The fit of the simulated structure factor to experimental data at room temperatures is excellent (Figure 8b). This validation of the simulated system allows us to address the wealth of atomistic information provided by the simulation in order to present a detailed picture of water adsorption, such as the distribution of residence times by the water molecules on the mineral surface. Our next goal is to expand the fit to encompass a wide range of temperatures and in this way being able to describe the thermal activation of water desorption.

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| (a) | (b)  C:\Users\h3n\Documents\MGI-PI Meeting\Andrew Stack\fit_Qintegrated_logY.jpeg |
| Figure 8. Water adsoption to BaSO4. (a) Water molecules adsorbed to two opposite sides of a BaSO4 cube. (b) Fit of the simulated incoherent structure factor of the water molecules to QENS experiments. | |

**2.0 Coarse grained simulations of polymer electrolyte Polyethylene Oxide-Acrylic Acid**

CAMM staff: Bobby Sumpter and Monojoy Goswami

Polymer electrolyte batteries are considered to be the next generation power sources for portable electronics. In this project we wish to understand the charge and counter ion transfer in polymer electrolyte batteries which is responsible for higher current density. Polymer electrolyte batteries also show a lower heat generation compared to organic Li-ion batteries that are available currently. The material that is used for this purpose is also known as ionomer electrolyte for the very low charge density on the backbone of the polymer chain.

We have performed coarse-grain Molecular Dynamics (MD) simulations, in which sections of the polymer are modeled as “units”, to understand the effect of dielectric constant on the microphase separation of, and counter ion transport of, ionomer electrolytes. We have mainly focused on charge dynamics of precisely placed model ionomers. At low dielectric constant, due to strong Coulomb interactions between the charges and counter ions, percolated structures have been observed in our small-scale MD simulations. These structures eventually affect the counter ion dynamics, by dramatically slowing down the counter ion motion in the strongly correlated agglomerate. The counter ions gain entropy by continuous collisions within the cluster that leads to ballistic hopping of the counter ions through the ionic channels, a process that is dependent on dielectric constant. These preliminary results can connect the dots between structural inhomogeneity and counter ion hopping in ionomer electrolytes at a molecular level thereby help design better materials for future technologies.

We would like to use quasi-elastic neutron scattering to examine the dynamics of the polymer and counter ions. In order to do this there are two possible approaches. One approach is to modify the code in the CAMM framework that performs the Fourier transform of the MD trajectories to incorporate the coarse grained “units” rather than using individual atoms. This has great advantages in terms of speed of performance, because the coarse grained simulations are much faster. The second approach is to perform an all atom simulation, in which case the Fourier transform for the neutron scattering law is exactly correct. The disadvantage of all atom simulations of such a large system is that the computation time will be large.

In practice we need to do both approaches to demonstrate that results using the coarse grained simulation are equivalent to the all atom simulation. We would use the CAMM framework refinement with the coarse grained simulations to refine against the experimental data, and at the end of the refinement revert to an all atom simulation to verify that the results are the same. In the third quarter of FY2013 we have been constructing a

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| fully atomistic model of polyethylene (PE) oxide polymers in a highly concentrated solution and then replaced the -oxygen- with acrylic acid (AA) monomer for input to LAMMPS. We have equilibrated the structures to a melt state. There are certain numerical/physics issues in the fully atomistic model that needs to be addressed before a conclusive result can be obtained.  In order to give ourselves confidence that the results will be comparable to quasi-elastic neutron scattering experiments we have performed the Fourier transforms for the Li counter-ions in order to demonstrate that the energy scales are correct. These results are shown in Figure 9. | C:\Users\h3n\Documents\MGI-PI Meeting\Bobby Sumpter\monojoy_SQE.jpeg  Figure 9: Weighted Fourier transform of  the Li counter ion motions |

**3.0 Electron-phonon coupling and soft phonon mode in Ferroelectric KTa1-xNbxO3**

CAMM staff: Olivier Delaire and Jiawang Hong

The goal for the 3rd quarter was to identify initial simulation codes and undertake test simulations. The anharmonic lattice dynamics simulation codes used in this project enable the calculation of phonon dispersions at finite temperature, extending the traditional density-functional theory (DFT) simulations of harmonic phonons at zero Kelvin. For demonstration and validation purposes, calculations were performed on the prototypical ferroelectric ABO3 perovskite material BaTiO3, in the high-temperature cubic phase. BaTiO3 was chosen as a first test case because it undergoes the same series of phase transitions as KTa1-xNbxO3upon cooling, while being simpler (no alloying). The high-temperature paraelectric phase is cubic perovskite (T>TC= 400K), successfully transforming upon cooling to a tetragonal phase (280<T<400K), then an orthorhombic phase (180<T<280K), and eventually a rhombohedral phase (T<180K). While the cubic phase is experimentally stable (mechanically and thermodynamically) at elevated temperature, traditional DFT calculations of phonons in the harmonic approximation yield unstable phonon dispersions (represented as negative frequencies in Figure 10a, in agreement with results in the literature, see Figure 10b). With a combination of ab-initio molecular dynamics calculations at finite temperature, and an effective lattice dynamics model capturing anharmonic force-constants, we are able to reproduce the anharmonic stabilization of phonons at finite temperature. This is seen in Figure 10c, where all phonon energies predicted by our anharmonic calculation are positive, and show excellent agreement with reported measurements.

We performed ab-initio MD calculations to obtain the force constants at finite temperature for BTO cubic structures. Calculations were performed on the NERSC supercomputer *hopper.nersc.gov* and on the MSTD blocks of the Oak Ridge Institutional Cluster. We used a 3×3×3 supercell (135 atoms), described with the PBE exchange-correlation functional, as implemented in the VASP software package to obtain the ab-initio MD trajectories. For each temperature, we chose five different volumes in the MD calculations (with 3000 time steps each), in order to obtain the free energy, from which the equilibrium volume was derived. After this procedure, we performed high-accuracy calculation with an energy cutoff of 500 eV for electronic plane-waves, and a Gamma-centered 3×3×3 K-point mesh for the electronic states, with 10000 time steps for MD ion motions. Sampling from the ion trajectory was used to extract both the harmonic and anharmonic components of the interactomic force-constant matrices. Using these force-constants, the finite-temperature phonon dispersions were calculated. In addition, the phonon linewidths and full spectral functions were also calculated (not shown here). Measurements of BaTiO3 on HYSPEC at SNS are scheduled for 1st quarter FY14, and should enable a more detailed comparison with the anharmonic calculations.

In the 4th quarter of FY13, we anticipate that calculations will be performed on KTa1-xNbxO3 (x=0 and 1) in the cubic phase, to determine the relative importance of anharmonicity in stabilizing the phonons, for the two end-members of the alloy. In addition, we will leverage simulation codes enabling the quantitative calculation of the single-crystal dynamical structure factor for phonons, Sph(**Q**,E), directly measured in inelastic neutron scattering experiments, to obtain the anharmonic Sanh(**Q**,E), corresponding to the measurements at high temperatures. Also, we will investigate theoretical approaches enabling the calculation of phonons under an external applied electric field in BaTiO3 (measurements under electric field are scheduled on HYSPEC for 4th quarter of FY13).

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| Figure 10a: Phonon dispersions for cubic BTO at zero Kelvin, harmonic calculation. Soft modes (negative frequencies) confirm that cubic BTO is mechanically unstable at zero K. Our results agree with previous harmonic DFT calculations (1-b). |  | Figure 10b: Previously reported theoretical calculations with harmonic DFT [Ghosez *et al.*, PRB 60, 836 (1999)]. |
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| dispersionex1.eps |  |  |
| Figure 10c: Phonon dispersions for cubic BTO calculated at 440K, taking into account anharmonic effects. Notice the anharmonic stabilization (no negative frequencies), and the good agreement with experimental data [Harada *et al*., PRB 4, 155 (1971)]. |  |  |

**Anticipated Work in Fourth Quarter FY2013**

In the fourth quarter of FY2013 we will develop the user interface for the CAMM framework and continue with the SNS user projects, with the aim of being able to allow the users to run the software themselves from the camm.sns.gov login node. For the second thread, on the polymer electrolyte Polyethylene Oxide – Acrylic Acid we will integrate the coarse grained simulations into the framework and compare the results from the coarse grained and all atom simulations. For the third thread we will continue with the current ab-initio simulations and prepare a strategy to integrate them in the CAMM framework.

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