CENTER FOR ACCELERATING MATERIALS MODELING

PROGRESS REPORT: FIRST 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 $KTa_{1-x}Nb_xO_3$ 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 1st Quarter FY2013

The Center for Accelerating Materials Modeling from SNS Data (CAMM) began work at the start of the first quarter FY2013. In the first quarter the following has been completed.

A design was developed for version 1.0 of the workflow involving the interaction of the refinement software package (Dakota[1]) with the codes for the molecular dynamics (MD) simulations and the calculation of the dynamic structure factor for the neutron scattering. It was decided to use the Kepler[2] scientific workflow management package (developed in research sponsored by the Office of Advanced Scientific Computing Research) to manage the workflow of submitting and monitoring the computing jobs for the various MD simulations and neutron scattering calculations. Initial tests have been successfully performed using Dakaota and Kepler together.

In order to carry out tests of the Dakota/Kepler software a 'quick' (10's of minutes rather than many hours) simulation case was identified. The case chosen was that of quasi-elastic neutron scattering data measured on the BASIS backscattering spectrometer at SNS from an aqueous LiCl sample. Simulations of the LiCl solution were performed using the NAMD program and compared to the experimental data to refine a value for the electric dipole moment of the water molecules in the presence of the ions.

For the science demonstration sub-project on polyethylene oxide-acrylic acid initial molecular dynamics simulations have been performed to determine the initial equilibration conditions of the model which will need to be performed as a precursor to the refinement against experimental data.

The science demonstration sub-project on ferroelectric $KTa_{1-x}Nb_xO_3$ oxide perovskites does not start until the third quarter of FY2013. In preparation for the start of this work a post-doctoral position to work on at the ab-initio molecular dynamics calculations was advertised and 3 qualified candidates were identified. Interviews for these candidates will take place at the start of January 2013. This is on-track to make an appointment and start the sub-project on schedule in the third quarter of FY2013.

In preparation for the two science sub-projects a successful request was made for a Directors Discretionary award of 4 million cpu-hours on the computers of the Oak Ridge Leadership Facility (OLCF). This, combined with the time that NDAV has on the NERSC computing facility will ensure that sufficient computational time is available.

Staff from CAMM attended the 2-day kick-off meeting of the Nanoporous Materials Genome Center (NMGC) at the University of Minnesota-Minneapolis. They presented the concept of CAMM at this meeting and held discussions on possible future areas of collaboration between CAMM and NMGC.

Personnel Working in CAMM

All of the personnel, ORNL staff and post-docs, 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 in the search for a post-doctoral candidate for this sub-project. As envisaged in the seed proposal the work on this sub-project will commence in the third quarter of FY2013, when an extra member of personnel, the post-doc for this sub-project, will join CAMM.

Publications and Presentations

Papers:
M. Goswami and Bobby G. Sumpter, *Phys. Rev. Lett*. (Under review)
[Note, a part of the work reported in this paper is part of the CAMM effort and an appropriate acknowledgement has been included.]

Invited talks:
M. Hagen, *Integrating Materials Modeling and Simulation with Neutron Scattering*
Presented at the International Symposium on Neutron Scattering, Mumbai, India, January 2013
[This talk included material on the role of, and initial development work of, CAMM.]

Presentations:
Talk and poster, M.Hagen and J. Borreguero, *CAMM Seed Project: Force Field Refinement by Iterative Fitting to Neutron Scattering Data*, Presented at the kick-off meeting for the Nanoporous Materials Genome Center, University of Minnesota-Minneapolis, November 2012

Outreach and Collaborations

In November 2012 Mark Hagen and Jose Borreguero from CAMM attended the 2 day kick-off meeting for the Nanoporous Materials Genome Center (NMGC) at the University of Minnesota-Minneapolis. The kick-off meeting was chaired by Laura Gagliardi, PI for the NMGC, and Mark Pederson, Program Manager for Theoretical and Computational Chemistry in Chemical Sciences, Geosciences and Biosciences Division of BES. Similarly to CAMM the NMGC was proposed in response to the *Predictive Theory and Modeling* call in May 2012.

In brief the goal for NMGC is to be able computationally design structures for Metal-Organic Frameworks (MOFs) and to compute their properties as reliably and accurately as is possible. One of the most important aspects for the reliable computation of properties is the development of appropriate force fields for MD simulations and a lot of time was spent on discussing this at the kick-off meeting. The presentation by Hagen and Borreguero on the goal of CAMM, to refine MD force field potentials from quasi-elastic and inelastic neutron scattering data, was therefore extremely opportune. At the kick-off meeting some experimental data on quasi-elastic neutron scattering studies of MOF's on the CNCS beam line at SNS was presented.

There is a clear opportunity to use the software being developed within CAMM to support NMGC, and Laura Gagliardi has been invited to SNS to discuss how this aspiration to collaborate can be made reality.

Anticipated Work in Second Quarter FY2013

At the start of the second quarter of FY2013 we will work to get the test case of aqueous LiCl solutions running in a fully automated way using Dakota and Kepler to optimize and manage the refinement of the force field against the experimental data from BASIS. This work is expected to be done on the Chadwick cluster used by NDAV for development work. Once this is successful on Chadwick we will transfer the code to run on the Titan supercomputer at OLCF, using this case as a quick test.

We also anticipate the initial equilibrium work for the LAMMPS simulations of polyethylene oxide-acrylic acid will have been completed. It will therefore be possible to adapt the workflows within Dakota and Kepler to assimilate the LAMMPS simulations for this science project and to be testing these by the end of the second quarter.

For the science demonstration project on ferroelectric $KTa_{1-x}Nb_xO_3$ oxide perovskites we anticipate to have made an appointment for the post-doctoral position and to be close to having the successful candidate in place.

Detailed Descriptions of Progress in Threads One and Two

The following two sections give descriptions of the work done in thread one – the development of the refinement software and workflows, and in thread two – the simulations of the Polyethylene Oxide-Acrylic Acid system, respectively.

Development of the Refinement Software and Workflows

For the refinement of the potential in the MD simulations against the neutron scattering experimental data, CAMM will use the Dakota toolkit [1] that has many options for optimization and sensitivity analysis. This software was written to be a flexible, extensible interface between simulation codes and analysis methods from least squares to genetic algorithms. To change the optimization algorithm or sensitivity analysis, the parameters in the Dakota text input file are simply changed. No changes need to be made to the simulation workflow. This is designed to run in parallel and request the cost functions from as many simultaneous simulations as appropriate for the optimization method. For example, methods requiring numerical derivatives will request simultaneous small steps for each parameter and genetic algorithms will calculate the fitness of each child in parallel. The Dakota software keeps a binary restart file of all parameters evaluated which can be used to restart the optimization in case of workstation failure or software crash. Dakota also uses this data to never evaluate the same parameters twice. It just returns the previous fitness if the algorithm requests a repeated evaluation.

For the workflow that calculates the cost function of the simulation results, CAMM will use the Kepler software [2]. The workflow is developed using a graphical user interface (see Figure 1 for an example of the interface), but the run-time engine can execute the workflow saved in an XML file from the command line or the graphical interface. This software has a parallel director and over 350 actors for determining file existence, reading files, doing Boolean switches, executing web services, and running simulations on remote machines. The software just needs one remote job ssh connection for the complete optimization and has the options for using a password, ssh key, or grid certificate.

The initial hardware system that we are using to test the optimization and workflow is an eight core front-end workstation that runs the Dakota and Kepler software and a 192 core cluster called Chadwick that runs the simulation software. Both Dakota and Kepler will be running simultaneously on the front-end and the Kepler workflow will copy results back from Chadwick to be used in the Dakota optimization.

The first, test, optimizations have been successfully run using this test system where the simulation is remotely submitted to Chadwick using Kepler actors and the resulting cost function is written to a file that is copied back to the workstation. Presently we are using an ssh key for the connection between the workstation and Chadwick for our tests, but we have a grid certificate ready for testing when the Globus software is installed on Chadwick. Dakota writes the parameter files for concurrent evaluations and then waits until a file containing the fitness results returns. The optimal values are found using a least squares algorithm. Kepler's simulation workflow checks for when a parameter files exists and creates a unique working directory on Chadwick for each evaluation. The simulation is run as a batch job on Chadwick and then the fitness file is copied from the working directory on Chadwick back to the workstation. Dakota uses these results to decide which parameters to test next. When the maximum number of iterations or the convergence tolerance is reached, Dakota stops the optimization.

A second Kepler workflow has been written to read Dakota's restart file and check if a subset of the parameters has been previously evaluated. In that case, Kepler actors can retrieve simulation files from the working directory on the remote cluster and not have to redo the entire simulation workflow. For example, if the instrument resolution function changes but the simulation parameters do not; previous simulation data can be reused.

The next steps are to optimize the force constants in a NAMD simulation using Dakota and a Kepler workflow on our test system. With NAMD, each simulation will run in parallel using the cores of Chadwick. Then we will test using a grid certificate for communication between the machines and apply for a community grid certificate for SNS users. We also plan to use ActiveMQ for communication between the Kepler workflow and Dakota optimization instead of checking for file existence. When the test system is working well, we will move the simulations to Titan, the Oak Ridge National Laboratory Cray XK7 high performance computer that is first on the Top 500 Supercomputer list.
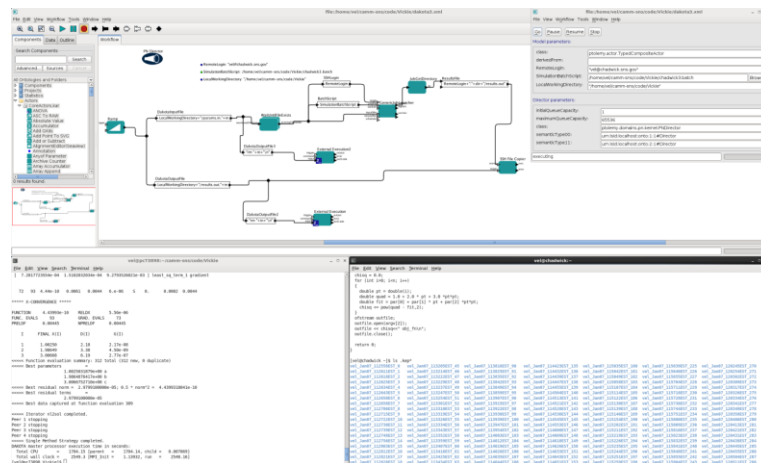
Figure 1: Top window shows the Kepler workflow running on the workstations with its GUI in the upper right. Lower left window shows Dakota at the end of the optimization on the workstation. Lower right window shows the function being optimized on Chadwick and all the working directories created for the simulation batch jobs.

The system we have chosen to carry out our first tests is that of aqueous lithium chloride. For comparison with the simulation results there is experimental data taken on the BASIS beam line at the SNS facility. This case is sufficiently simple that we are able to do the optimization 'by hand', without Dakota and Kepler. The optimization parameter in this test case are the partial atomic charges (PAC) for the three-point model of the water molecule in the presence of a concentrated solution of lithium chloride ions. To this effect, we have carried out MD simulations for a wide range of PAC-values and compared the resulting simulated dynamics structure factors S(Q,E) to the experimental results.

Bulk aqueous solutions of concentrated lithium chloride do not freeze in the 220K -230K temperature range where a dynamic crossover between non-Arrhenius and Arrhenius behavior was experimentally observed for pure water in confined geometries. Thus, the bulk system allows the study of the dynamic crossover temperature with no contamination of results from the confining material which are significant at low Q-values. From the point of view of our optimization test, polarization of the water molecules may be relevant due to the high ion concentration. Polarization would express itself as a significant deviation of PAC values with respect to those of pure bulk water. We seek to obtain new PAC values for the water molecule consistent with the experimentally observed dynamic structure factor.

A 30Å x 30Å x 30Å box containing 1128 water molecules along with 154 Cl$^-$ and 154 Li$^+$ ions matching the experiment concentration was prepared (see Figure 2). Systems were equilibrated in the NPT ensemble at 1atm and temperatures in the 10K-290K range. Subsequent production runs were executed in the NVE ensemble to prevent atomic de-correlations due to an external heat bath. Each simulation was set for particular values of the water PAC. The charge of the hydrogen atom, *Hq*, was varied in the 0.3e to 0.5e range. As a comparison, the standard values for the TIP3 and SPC/E water models are 0.417e and 0.4238e, respectively.

The open-source MC simulation package NAMD was selected for this test study. The open-source package Sassena was selected for the calculation of the intermediate scattering quantities. Sassena is developed and maintained at the Center for Molecular Biophysics in ORNL. The open-source framework Mantid, housed in our group, was selected for fast Fourier transform, implementation of the fitting model, and inner optimization of the parameters associated with the experiment.

Figure 2. Simulated system: Lithium atoms shown as blue spheres, chloride atoms as green spheres, and water molecules as white and red sticks.

A proper comparison between simulated and experimental dynamic structure factors require taking into account the specifics of the experimental set up. We considered: (*i*) an elastic line modeled as the experimental structure factor at low (6K) temperature, S_{lowT}; (*ii*) a flat background, A_0; and (*iii*) a resolution function Res derived from the experimental structure factor at the same low temperature. When applied to the simulated dynamic structure factor, S_{MD}, we obtain a simulated structure factor S_{MD}' that takes into account the specifics of the experiment:

$$S_{MD}'(\omega) = h_1 \cdot S_{lowT}(\omega) + A_0 + h_2 \cdot \text{Res}(\omega) \otimes S_{MD}$$

There are three parameters, h_1, A_0, and h_2 wich conform the parameter set pertaining to the experiment.

In this test study, we ran a set of ten simulations in parallel, each with a different value of the water-hydrogen PAC. Then parameters, h_1, A_0, and h_2 were optimized for each simulation to obtain the best fit between S_{MD}' and the experimental dynamics structure factor.

A cost function was calculated for each simulation (see Figure 3 for visual representations of the best fits), and a cubic interpolation of the points (see Figure 4) suggests a value of the water-hydrogen PAC of Hq^*=0.43 yields the best comparison between simulations and experiments. This Hq^* value is higher than those of the standard TIP3 and SCP/E water models, indicating that the presence of LiCl has increased the dipole moment of the water molecule.
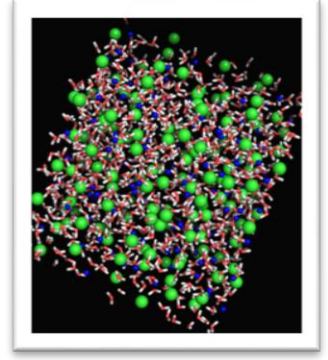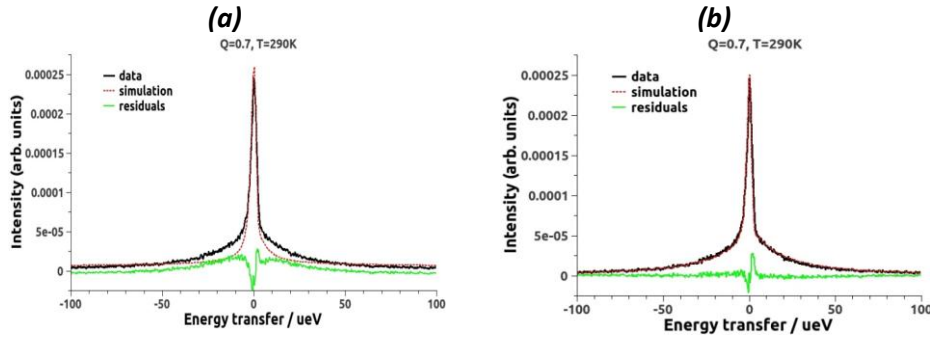

Figure 3. Comparision between two fits. (a) Fit between experiment (black) and simulated (red) dynamics structure factors for water-hydrogen PAC Hq=0.38. The difference between experiment and simulation is shown in green. (b) Same as (a), but now Hq=0.42
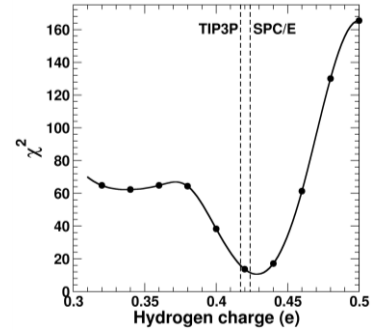
Figure 4. The cost function for the fits as a function of the dipole moment value.

Science project on Polyethylene Oxide-Acrylic Acid

Our research is directed toward developing fundamental understanding of the effects of conformational characteristics of polymers on ionic agglomeration and transport. We believe that such understanding can set the stage for directly impacting the worldwide efforts to understand correlation and collective effects in neutral and especially charged polymer systems.

Our research on modeling ionic and charged polymeric materials is focused on understanding the intrinsic correlation and collective effects of this class of materials by direct integration of simulation with neutron and x-ray scattering experimental data in a feedback loop to allow interpretation of experiments and refinement of the computational models. A validated model will then be used for predictive simulation/design for identifying materials that have transport properties appropriate for energy storage applications.

Details and To-Date Results:
The fundamental structure of ionomer electrolytes and its effect on ion mobility in polymer electrolyte batteries are of major importance due to the wide applications in consumer electronics, nanotechnology and biomaterials. Numerous experimental studies have been carried out in this field to understand the structure property relationships but there is still not a complete understanding of the fundamental physics underlying the observations. A fundamental understanding of structure-property-transport relations for this class of polymers is of paramount importance for realization of an efficient materials design. To develop such an understanding requires extensive study of the counterion dynamics of ionomer aggregates for rigorously equilibrated systems [3-6]. Here we have used large-scale molecular dynamics (MD) simulations to explicitly examine the morphology and dynamics of ionomers containing various charge states and chain lengths. Our preliminary simulations are performed for systems [7] composed of a ionomer chains with length of N = 70 and 6 charges, +q, on each chain at every 13th backbone monomer, exactly mimicking the system that has been experimentally studied. The charges interact via Coulomb forces with equal number of counterions randomly dispersed in the system.
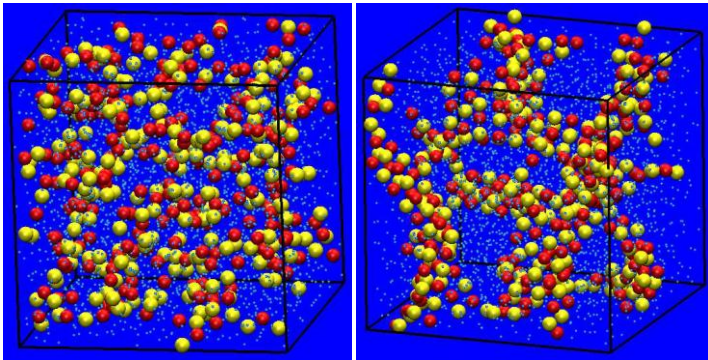

Figure 5: Snapshots of the central simulation box for different ζ_B. left figure: D = 1/2 and right figure: D = 1/10 The yellow spheres are free counterions and the red spheres are the charged monomeric units. For clarity, the neutral monomer units are represented in tiny cyan spheres. Lower dielectric constant (right figure) show highly percolated charge states.
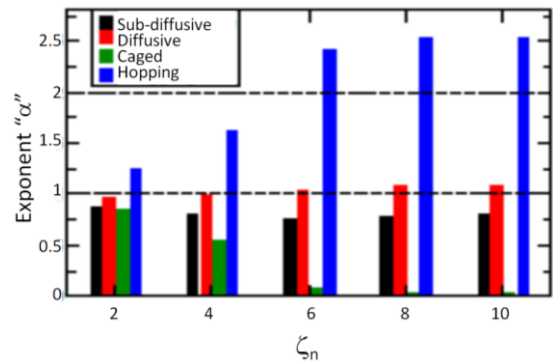
Figure 6: Histogram of slopes at different time segments. Black, red, green and blue bars are for the lowest, lower middle, upper middle and the highest time steps. The slopes show anomalous diffusion (black), Fickian diffusion (red), Slow counterion motion (green) and superdiffusive ballistic motion (blue).

The initial configuration of the model system is randomly generated at melt density. The ionomer chains were modeled following the Kremer-Grest bead spring polymer model [7] in which bonded beads are connected by finitely extensible nonlinear elastic (FENE) springs. The energetic interaction between any pair of beads is

modeled by a truncated and shifted Lennard-Jones potential and each monomer of the system interacts via a short-range repulsive potential. The long-range interactions between the charges and the counterions are modeled by a Coulomb potential, calculated using the Ewald summation technique. As our focus is to study the dynamics and the self-assembly of the charges for different entropic conditions, we varied the temperature of the system. The dielectric constant, D, is varied to understand the consequence of D to the overall dynamics of the system.

In Figure 5, the structures of the charges are shown. Higher agglomeration can be observed as dielectric constant decreases which can easily be understood by the following: As D decreases, electrostatic interaction strength increases giving rise to enhanced attraction between the oppositely charged species. This causes larger agglomeration through percolated charge-counterion pairing. The slopes of the counterion MSD are shown in histogram of Figure 6, and indicate a unique behavior. At the early and intermediate times, anomalous diffusion followed by normal Fickian diffusion is observed. At longer times, the slopes show two values one near to zero and the other at ~ 2: The counterions are immobile for certain times and then the counterion becomes super-diffusive. This can be explained as follows: The counterions, once passed the diffusive regime (equilibrium), stay on the percolated cluster thereby making them immobile for a certain time frame. While the counterions are at their lowest entropy states with almost zero mobility, they slowly gain energy through collisions that induces thermal activation. These thermally activated counterions 'hop' from one site to another. The presence of the superionic channels that are present in the percolated structures (seen in Figure 1) enable charge hopping in these systems thereby giving rise to a jump of half of the chain radius of gyration, Rg. This jump is a friction free ballistic type of motion, therefore causing a significant increase in conduction that can is observed. The tunneling step hopping has been observed in charge migration through DNA which is quite different than the thermal hopping in conjugated polymers [8]. We propose the presence of both tunneling and thermal activation that leads to a higher rate of hopping in ionomer electrolytes [7].

Current on-going work:
The results obtained from these coarse-grain calculations provide us with important insight for polymer electrolyte battery materials. However, this preliminary study does not capture every aspect of the material, in particular the length and time scales are too small to reliably predict ionomer materials properties. Therefore, a detailed study is required in order to compare with experiments in order to better design these materials. To this end, we have started calculations on NERSC that are large enough to enable achieving this goal. These simulations are performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) at melt and solution densities in order to fully account for charge agglomeration and its' effect on the ion dynamics. To understand the morphology, the static and dynamic structure factors for all the charges will be computed and can be compared with data obtained from neutron scattering experiments. The simulations and experimental data will thus be used to calibrate the underlying model for the molecular dynamics simulations. From a validated simulation/model, predictive simulations can be made to explore the temperature and dielectric strength dependence of the structure and the effects on the ion dynamics.

At the same time, for the diblock copolymer melts containing monovalent salt ions, we are working toward extending the theory [9] of neutral copolymers to develop a fundamental understanding of ion solvation in polymeric media. Starting with our recently developed [10] self-consistent field theoretical (SCFT) framework for the computation of local dielectric function to the non-polar-b-polar diblock copolymer system we can compute the effects of added salt concentration on the disorder-order transition boundary, density profiles of the ions, structure factor and domain spacing of the ordered morphologies. As with the large-scale molecular dynamics simulations, the results will be compared with neutron and x-ray scattering experiments in a feedback fashion (to refine model potentials/fields against neutron scattering data).

References:

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