

MAUI: Modeling, Analysis, and Ultrafast Imaging

LDRD Strategic Initiative 6-Month Report

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1. Background

Integrating ultrafast imaging with molecular dynamics modeling and data analysis and visualization can provide crucial insights for energy research. The temporal behavior of externally stimulated materials beyond equilibrium can lead to breakthroughs, for example, in heat dissipation of next-generation semiconductors, conversion of wasted heat into electricity in thermoelectric materials, and electrochemical processes across liquid-solid interfaces in water purification. These diverse applications all transport energy through phonons (sound waves that carry heat) in a time-evolving crystal lattice. We are researching an integrated approach to predict, image, and analyze phonon dynamics that can be applied to externally stimulated systems.

2. Proposed Work and Summary of Progress

The project consists of three main components: modeling, analysis, and imaging.

2.1 Modeling

Molecular dynamics (MD) simulations are used to model the phonon transport and lattice thermal conductivities for the proposed systems. By integrating modeling with experiment, we can improve phase retrieval accuracy and speed, improve the experimental design by predicting regions of interest for imaging, and use the simulation to improve the fidelity of the measured result and vice versa. We are exploring two approaches [Frenkel2002, Allen1987]: equilibrium MD and nonequilibrium MD.

2.1.1 Modeling Milestones:

Y1: Run equilibrium MD simulations; compute the heat correlation function and thermal conductivity. Y2: Impart a higher thermal energy at one point of the particle (nonequilibrium) and follow its dissipation as a function of time, calculating the ratio of

heat flux to temperature gradient. Y3: Address the relative strengths and limitations of each approach as we scale up both methods to represent experiments.

2.1.2 Modeling Progress to Date:

To complement the imaging experiments and gain further insights into the mechanistic sequence of steps that leads to the onset of strain in a gold-ascorbic acid system, we have started performing MD simulations using the ReaxFF force-field. These simulations allow for dynamic charge transfer and are suitable for modeling chemically reactive systems. The force-field parameters for the Au-hydrocarbon system were provided by an external collaborator (Adri Van Duin at Penn State) and are being used in the current simulations. The model test system comprised of Au (111) slab with 200 ascorbic acid molecules dispersed in 10,000 water molecules.

Our preliminary analysis indicated a total of ~90 “reactions” seen in the adsorption pathway in the short timeframe of ~20 ps. Many of these are fast reversible reactions associated with the rapid dissociation and recombination of ascorbic acid (top panel in Figure 1). The most prominent event comprised of ascorbic acid binding strongly at undercoordinated or defect sites. We further postprocessed the MD trajectories using MATLAB to estimate the temporal evolution of strain in the gold lattice. We found that regions adjacent to sites where ascorbic acid binds strongly (via Au-C bonding) are the ones that experience the highest strain (Figure 1 bottom panel). Our future plans include a more detailed post-processing of the simulation trajectories as well as understanding the correlation between size of the gold nanocrystal and the timescales for fluctuation of ascorbic acid induced strain in the gold lattice.

2.1.3 Modeling Next Steps:

We will continue to model the gold-ascorbic system using ReaxFF and post-process the MD trajectories to derive various structural and dynamical correlation functions (pair correlation functions, structure factors, etc.) to compare/complement the experiments. Identifying the atomistic mechanism by which strain is induced is one of the key objectives. To accomplish this, we are currently in the process of adapting and modifying the Molfract analysis tool in LAMMPS to develop automation strategies for obtaining chemical reaction pathways using gold-ascorbic acid as a representative test system. Since the ascorbic acid reduction is exothermic and might lead to localized heating, we also have plans to carry out non-equilibrium MD simulations to study phonon transport across solid-liquid interfaces such as in the gold-ascorbic acid system. We will subsequently extend the NEMD simulations to study phonon transport across solid interfaces such as in thermoelectric multi-layered materials to complement the imaging experiments (see section 2.3.3). The new postdoc (Kiran Sasikumar) has

submitted a rapid access proposal to CNM requesting computing time on carbon to carry out some of the proposed initial runs. We plan on submitting computing requests to other sources such as NERSC and ALCF as well to carry out some of the large-scale reactive MD simulations.

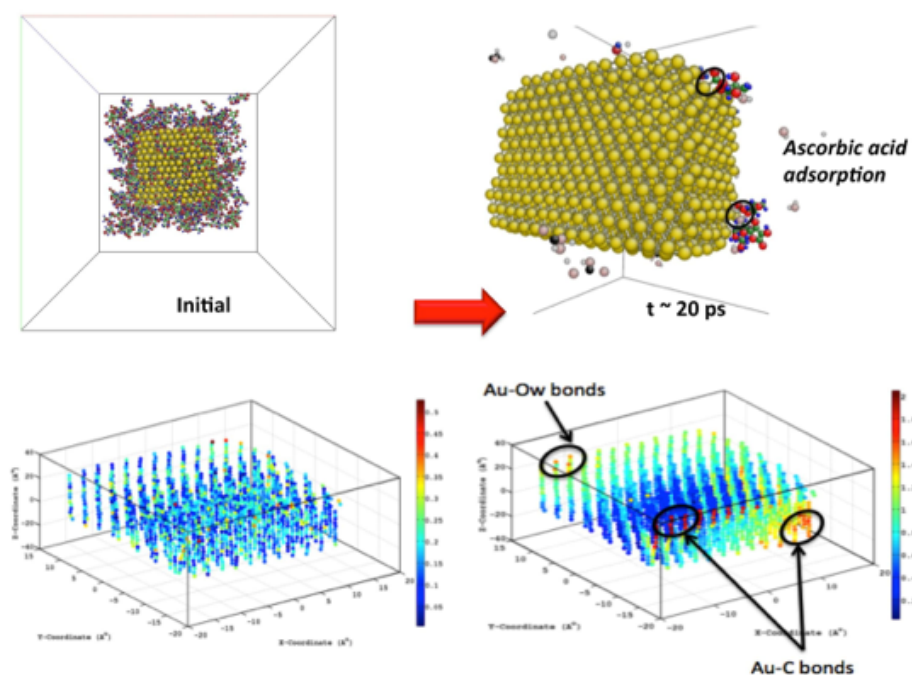


Figure1: Reactive simulations of ascorbic acid interaction with Au surfaces. Top panel shows snapshots from the molecular dynamics simulation at time $t=0$ (left) and $t \sim 20$ ps (right). Ascorbic acid adsorption on undercoordinated corner sites is clearly visible at $t \sim 20$ ps. The corresponding strain generated in the Au slab is shown in the bottom panel. The regions corresponding to strong ascorbic acid adsorption experience the highest strain (bottom left). Yellow spheres are gold, red are oxygen, green are carbon and blue are hydrogen. Light pink, black and gray depict neighboring or non-relevant oxygen, carbon and hydrogen atoms, respectively.

2.2 Analysis

In order to combine the reverse (imaging) with the forward (simulation) models, data transformations between model spaces are being investigated. We are analyzing data in the spatial, temporal, and feature domains, for example, to compute trajectories from phonons. Once we have such trajectories, temporal and spatial correlation functions map out the strain fields to identify structural deformations, slip planes, and twinning events. Such data analyses are the “glue” between forward modeling and reverse image reconstruction.

2.2.1 Analysis Milestones:

Y1: Develop data transformations between model spaces. Y2: Reduce raw spatiotemporal data into a space of features. Y3: Classify, compare, track, and correlate predicted and measured features.

2.2.2 Analysis Progress to Date:

Simulation code: At MCS, we have installed and compiled LAMMPS locally on small-scale workstation platforms so that we can generate test data locally. The instructions for building, configuring, and running LAMMPS are included in our project wiki so that all team members can reproduce the installation. We also successfully compiled LAMMPS as a library and executed it within a related project that couples simulations with analysis operations in a unified, generic framework called Decaf [Peterka2015].

Data model and model space transformations: We have identified the following native and derived data products: atomic positions, atomic velocities, 3D phonon density, 2D and 3D heat current maps, 3D heat vector field, temperature profile, and 3D atomic density. We are able to extract the native products from simulation and imaging experiments; furthermore, we are able to input those data models into analysis tasks, and we are able to extract the derived data models from those tasks.

Development of analysis workflow: We have identified the following analysis tasks: FFT of correlation of atomic velocity, derivation of heat currents, density estimation, density thresholding, insertion and orientation of an atomic lattice within the density of the 3D image, Voronoi and Delaunay tessellation, particle advection, and various visualization operations. These tasks are illustrated in the workflow of Figure 2.

Analysis of imaging data: We are processing the volumetric density data from the recent imaging experiment of the gold and ascorbic acid system. The raw density data are uploaded to our project repository, and we are applying different density thresholds to the data in order to extract the gold region. We will be removing the interior, keeping only the outer surface. These atom positions will then be used as the input to a LAMMPS MD model of the same system.

2.2.3 Analysis Next Steps:

On the data analysis side, we will continue to incorporate individual analysis tasks listed above in a combined workflow. On the experimental side, we will work to apply research from a related project, ROMPR [Wild2015], to reconstruct actual data, and in particular to 3D crystals by extending optimized reconstruction algorithms to 3D, evaluating with 3d stacks of 32-bit tiff images from a recent experiment, and applying to highly strained objects using phase and sharpness constraints.

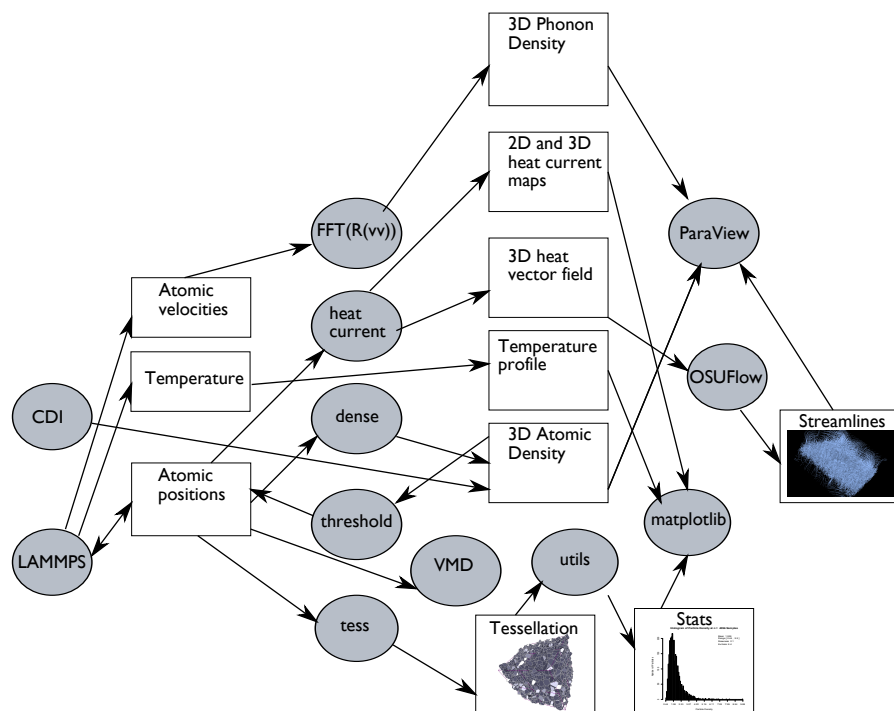


Figure 2: Workflow diagram

2.3 Ultrafast Imaging

We are conducting laser pump-probe imaging experiments to study the structure dynamics originating from electron-phonon interactions. By integrating the time dimension in reconstruction, we are investigating differential CDI based on phase retrieval from earlier time steps and other constraints to improve convergence of phase retrieval algorithms.

2.3.1 Imaging Milestones:

Y1: Investigate differential CDI based on phase retrieval from earlier time steps and the combination of multiple image modalities such as single-shot and ptychography [Spangenberg2014] to improve convergence of phase-retrieval algorithms using techniques from stochastic optimization. Y2: Explore difference density maps [Stewart1993] to identify what has changed from one time step to the next. Y3: Explore the use of the forward MD model in the phase-retrieval inverse problem to improve the reconstruction capabilities of our optimization algorithms.

2.3.2 Imaging Progress to Date:

A user group of 34-ID-C conducted experiments involving an important industrial chemical reaction, the reduction of ascorbic acid on a nanocrystalline gold catalyst. The

coherent imaging was performed on gold nanocrystals (~200nm) before, during and after exposure to 1M ascorbic acid. The crystals were observed to exhibit distortions of their lattice near edges of the top and bottom (111) oriented facets and as a function of time in the acid solution. Literature suggested that the lifetime of this reaction would be about 50 minutes and this was also observed in the lattice of the gold crystal imaged with CDI [Novo2008].

The MAUI project was just getting off the ground when Dr. Deshmukh was brought on board for a short time. It seemed like a perfect opportunity to tap MD simulation to attempt to understand the response of the gold nanocrystal to ascorbic acid, and also shed light on the mechanism by which the reaction is observed to cease. Early MD results are encouraging and an effort is underway to better understand the imaging results based on them.

To begin to reconcile the MD with CDI of ascorbic acid on gold, the CDI images are being meshed and fitted with a gold lattice. The lattice will be strained in a manner consistent with that observed with CDI, as a function of time, for comparison to MD atomistic simulation. Further MD based on this model may be needed.

2.3.3 Imaging Next Steps:

A proposal for APS beamtime has been submitted to the most recent call (March 6). The proposal focused on coherent imaging of phonon modes excited in a multilayer structure via ultrafast laser pumping. Multilayer structures are particularly promising for thermoelectric (TE) materials as the interfaces between different lattices in the layers act as scattering centers for phonons incident on them leading to phononic band gaps in the materials. This is highly desired in TE materials as the goal is to transfer maximal energy into the electrons and not into the lattice in the form of phonons. The experiments are proposed for Sector 7 of the APS, as this beamline is equipped with necessary laser and x-ray diffraction instrumentation. Pending award of beamtime, simulations and sample preparation will commence.

3. Staffing

The staffing for the project is also on track.

3.1 PIs:

In the early stages of the project, the PIs are devoting significant effort to the project. During this time, the PIs developed position descriptions, advertised those positions,

evaluated applicants, and interviewed candidates. The PIs are also working extensively to develop the research agenda during the first year.

3.2 Postdocs:

We immediately began the search for two postdocs: one in imaging and one in modeling. For the imaging postdoc, there were approximately 15 applicants, and 3 were interviewed remotely using BlueJeans. Two candidates were brought in for in-person interviews, and a formal offer is being extended to Mathew Cherukara. Informal communication with the candidate indicates that he is interested in accepting the position.

For the modeling postdoc, there were approximately 80 candidates, and 5 were interviewed remotely using BlueJeans. An offer was extended to Kiran Sasikumar, who accepted. Kiran officially joined ANL on February 23, 2015, and is now actively working on the project.

While searching for Matthew and Kiran, we reallocated the effort of one existing postdoc, Sanket Deshmukh, in the Theory and Modeling group for 3 months. During the November 2014 - January 2015 timeframe, Sanket worked to set up ReaxxFF runs of LAMPPS for the gold-ascorbic acid system and to identify the needed analysis programs. Although Sanket has now officially left ANL, he and Kiran are working together to transfer information.

3.3 Spending to Date and Projected Spending for the Remainder of the Fiscal Year

Table 1 summarizes the project spending as of February 22, 2015. These reports are issued at the end of the month; hence, this is the latest report currently available. It does not yet show the effort of Kiran Sasikumar, who started on February 23. This is one reason why our spending is below the target rate. The other reason is because the effort of Haidan Wen and Ross Harder was not charged to this cost code. This oversight has now been corrected, which will be reflected in next month's statement.

Table 2 shows our projections for the remainder of the fiscal year. The upper half of the table, rows 1-25, shows the projected spending at the current rate. These numbers include postdoc Kiran Sasikumar charging 100% of his effort to the project as of March and prospective postdoc Mathew Cherukara to begin charging 100% in May. To offset the fact that we underspent our projections for the first 5 months of the project, we are proposing increasing the effort of the PIs uniformly by 5% for the remainder of the fiscal year. These projections are shown in the lower half of the Table 2, rows 27-39. With

these adjustments, we will end the fiscal year within approximately \$3000 of the total budget. Given the significant effort required by the PIs in the early stages of the project and early successes achieved so far, we argue that the increase is justified. The adjustment will be removed after the fiscal year because the postdocs will be charging 12 months effort in the following year, and the PIs' involvement will be reduced.

MCS PI Report		PETERKA, TOM	FYTD costs thru 2/22/2015										
ACCOUNT	BR	TITLE	FY14 C/O	FY15 New Funding	Total Funding Balance	FYTD Cost	Current Mo. Cost	Avail. Balance	Net Enc.	Net Avail. Balance	Rec'd Funding End Date*	Burn Rate**	Project End Date
9328		Integrated Imaging, Modeling, and Analysis of Ultrafast Energy Transport in Nanomaterials	0.00	380.00	380.00	74.21	13.80	305.79	0.00	305.79	9/30/2015	47%	09/30/2015

Group/Description	Name/Vendor	Account	Cur Per Hours	Cur Per Months	Cur Per Cost	FYTD Hours	FYTD Months	FYTD Cost	Encumbrance
37	Sankaranarayanan, Subramanian	09328	40.00	0.25	4,532.00	157.00	0.94	17,783.00	
38	McNulty, Ian	09328	7.00	0.04	1,141.00	28.00	0.16	4,562.00	
39	Deshmukh, Sanket Avinash	09328	0.00	0.00	0.00	312.00	1.75	14,600.00	
AM	Munson, Todd S.	09328	7.60	0.05	1,150.00	28.20	0.17	4,270.00	
DA	Peterka, Thomas	09328	14.00	0.09	1,636.00	50.40	0.30	5,890.00	
EC	Ferrier, Nicola J.	09328	8.50	0.05	1,287.00	35.00	0.21	5,299.00	
Common Support - Common Support		09328			3,080.73			16,564.95	0.00
Common Support - IGPP		09328			424.95			2,284.86	0.00
General & Administrative Indirect Exp		09328			549.65			2,955.54	0.00
		09328 Total	77.10	0.48	13,801.33	610.60	3.53	74,209.35	0.00

Table 1. Spending Summary and Detail as of February 22, 2015

	A	B	C	D	E	F
1	Integrated Imaging Budget					
2	FY15					
3						
4	Total Budget			\$ 380,000		
5	FYTD15 spend			\$ 74,210		
6	subtotal			\$ 305,790		
7						
8	Current Effort	Cost Center %		FTE \$	FTE Cost \$	Mar-Sep
9	Tom Peterka	145	8.61%	\$ 299,014	\$ 25,745	\$ 15,018
10	T. Munson	145	6.50%	\$ 387,100	\$ 25,162	\$ 14,678
11	Nicola Ferrier	145	11.50%	\$ 387,100	\$ 44,517	\$ 25,968
12	S. Sankaranarayanan	153	8.27%	\$ 289,653	\$ 23,954	\$ 13,973
13	I. McNulty	153	5.72%	\$ 417,101	\$ 23,858	\$ 13,917
14	S. Deshmukh	153	0.00%	\$ 125,898	\$ -	\$ -
15	Kiran Sasikumar	153	100.00%	\$ 125,898	\$ 125,898	\$ 73,441
16	W. Haiden	132	11.86%	\$ 199,368	\$ 23,645	\$ 11,823
17	R. Harder	132	10.58%	\$ 223,462	\$ 23,642	\$ 11,821
18	TBD Postdoc (Matthew Cherukara)	132	100.00%	\$ 125,898	\$ 125,898	\$ 52,458
19	Subtotal of Projected effort (Mar - Sept)					\$ 233,096
20						
21	FYTD costs less projected			\$ 72,694		
22						
23	Estimated M&S			\$ 5,000		
24						
25	Rem bal			\$ 67,694		
26						
27	Additional increased effort Plan (Mar - S Cost Center		5.00%			
28	T. Peterka	145	\$ 8,721			
29	T. Munson	145	\$ 11,290			
30	N. Ferrier	145	\$ 11,290			
31	S. Sankaranarayanan	153	\$ 8,448			
32	I. McNulty	153	\$ 12,165			
33	W. Haiden	132	\$ 5,815			
34	R. Harder	132	\$ 6,518			
35						
36						
37	Subtotal		\$ 64,248			
38						
39	Est. rem balance at 9/30/15		\$ 3,446			

Table 2. Projected Spending or Remainder of FY 2015

4. Publications, Presentations, and Project Materials

Publications:

- Deng, J., Vine, D., Nashed, Y., Chen, S., Phillips, N., Peterka, T., Ross, R., Vogt, S. Jacobsen, C.: Fly-Scan Ptychography. *Optics Express Journal*, 2015.
- Yuelin Li, Zhang Jiang, Xiao-Min Lin, Haidan Wen, Donald A. Walko, Sanket A. Deshmukh, Ram Subbaraman, Subramanian K. R. S. Sankaranarayanan, *et al.* Femtosecond Laser Pulse Driven Melting in Gold Nanorod Aqueous Colloidal Suspension: Identification of a Transition from Stretched to Exponential Kinetics. *Nature Scientific Reports*, 5, Article number: 8146 doi:10.1038/srep08146 9 (2015)

Presentations:

- 9/30/14, First Imaging Initiative Workshop: Tomography and Ptychography, Argonne IL: Imaging Meets HPC Through Scalable Data Analysis.
- 2/10/15 Microscopy Group Coffee talk: MAUI: Modeling, Analysis, and Ultrafast Imaging

Project repository and wiki (access available upon request):

- Source code and data: <https://bitbucket.org/tpeterka1/maui>
- Wiki containing project meeting (every two weeks) notes and all project documents: <https://bitbucket.org/tpeterka1/maui/wiki>

5. References

[Spangenberg2014] Spangenberg et al. Ptychochronography: Ultrafast lens-less imaging in the time domain, 2014.

[Stewart1993] Stewart et al., Difference imaging of adenovirus: bridging the resolution gap between X-ray crystallography and electron microscopy, EMBO, 1993.

[Frenkel2002] D. Frenkel and B. Smit: Understanding Molecular Simulation, From Algorithms to Applications (2nd ed.), Academic Press, 2002.

[Allen1987] M. P. Allen and D. J. Tildesley: Computer simulation of liquids, Oxford University Press, 1987.

[Novo2008] Novo, C., Funston, A. M., & Mulvaney, P. (2008). Direct observation of chemical reactions on single gold nanocrystals using surface plasmon spectroscopy. *Nature Nanotechnology*, 3(10), 598–602. doi:10.1038/nnano.2008.246

[Peterka2015] <https://bitbucket.org/tpeterka1/decaf>

[Wild2015] <http://www.mcs.anl.gov/project/rompr-robust-optimization-and-modeling-phase-retrieval>