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13. ABSTRACT *(Maximum 200 words)*

Development of a coarse-grained chemical reaction model (CGCRM) for incorporation into molecular dynamics (MD) simulations in order to assess the effects of chemical reactions on the ablation process. This model has been successfully applied to the ablation of organic systems and is now being implemented for polymers and biological materials. Development of a combined molecular dynamics and direct simulations Monte Carlo (DSMC) methodology for combining the output from the MD simulations including the presence of clusters into the DSMC calculations that allow for long time and large space development of the plume. Developed a new protocol, substrate-assisted laser-initiated ejection, for mass spectrometry of biological molecules embedded in a water matrix, the simulations were aimed at modeling Charles Lin's (Harvard) drug delivery experiments but have inspired a new set of Mass Spectrometry experiments in Nick Winograd's group (Penn State). Sub-contract to UVa was used to support a graduate (MS.) student, Elodie Leveugle. During the reporting period, the focus of the research project of Ms. Leveugle was on the microscopic mechanisms of photomechanical spallation of molecular targets. It has been revealed in a series of large-scale MD simulations that the relaxation of laser-induced thennoelastic stresses is responsible for the nucleation, growth and coalescence of voids in a broad sub-surface region of the irradiated target. Two stages have been identified in the evolution of voids in laser spallation, the initial void nucleation and growth, with the number of voids of all sizes increasing, followed by void coarsening and coalescence, when the number of large void increases at the expense of quickly decreasing population of small voids.

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ANNUAL PROGRESS REPORT
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PRINCIPAL INVESTIGATOR: Dr. Barbara J. Garrison

CO-PRINCIPAL INVESTIGATOR: Dr. Leonid V. Zhigilei

INSTITUTION: Penn State University

GRANT TITLE: Modeling of Free Electron Laser Ablation II

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OBJECTIVE: To investigate microscopic mechanisms and dynamics of FEL initiated ablation with a focus on a fundamental understanding of the basic mechanisms of ablation and effects of selective targeting of the laser energy.

APPROACH: We are developing a multiscale computational technology that includes atomistic, mesoscopic/molecular, and continuum levels of description of fundamental processes involved in FEL laser ablation of biological materials.

ACCOMPLISHMENTS: The accomplishments support by this project include as follows:

- Development of a coarse-grained chemical reaction model (CGCRM) for incorporation into molecular dynamics (MD) simulations in order to assess the effects of chemical reactions on the ablation process. This model has been successfully applied to the ablation of organic systems and is now being implemented for polymers and biological materials.
- Development of a combined molecular dynamics and direct simulations Monte Carlo (DSMC) methodology for combining the output from the MD simulations including the presence of clusters into the DSMC calculations that allow for long time and large space development of the plume.
- Developed a new protocol, substrate-assisted laser-initiated ejection, for mass spectrometry of biological molecules embedded in a water matrix. The simulations were aimed at modeling Charles Lin's (Harvard) drug delivery experiments but have inspired a new set of Mass Spectrometry experiments in Nick Winograd's group (Penn State).
- Sub-contract to UVa was used to support a graduate (M.S.) student, Elodie Leveugle. During the reporting period, the focus of the research project of Ms. Leveugle was on the microscopic mechanisms of photomechanical spallation of molecular targets. It has been revealed in a series of large-scale MD simulations that the relaxation of laser-induced thermoelastic stresses is responsible for the nucleation, growth and coalescence of voids in a broad sub-surface region of the irradiated target. Two stages have been identified in the evolution of voids in laser spallation, the initial void nucleation and growth, with the number of voids of all sizes increasing, followed by void coarsening and coalescence, when the number of large void increases at the expense of quickly decreasing population of small voids. The void volume distributions are found to be relatively well described by power law $N(V) \sim V\text{-}\tau$, with exponent gradually increasing with time. A similar

volume distribution has been obtained in a series of simulations of uniaxial expansion of the same molecular system performed at a strain rate and temperature realized in the irradiated target. Spatial and time evolution of the laser-induced pressure predicted in the MD simulation has been related to the results of integration of a thermoelastic wave equation and the scope of applicability of the continuum calculations has been discussed.

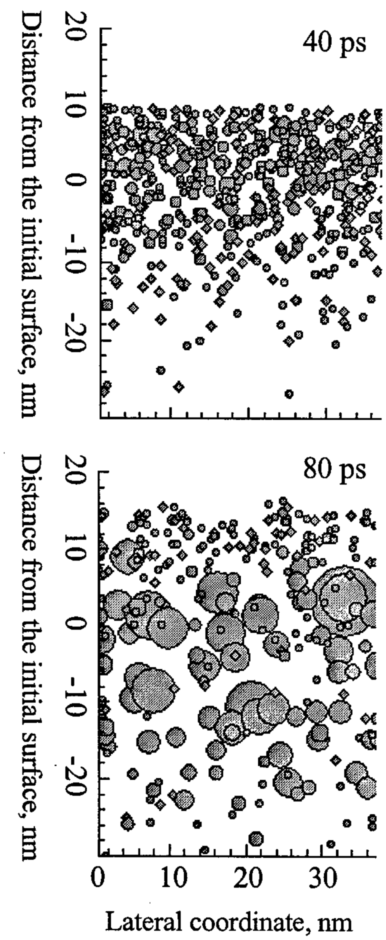

Figure 1. Nucleation and grow of sub-surface voids in a MD simulation of laser spallation. Voids are represented by spheres of the same volume as the actual voids

SIGNIFICANCE: Our simulations give a unique opportunity to study the laser ablation phenomena at molecular level and compose an important part of the effort to better understand the mechanisms of laser damage/desorption/ablation at a microscopic level. The insight provided into these physical processes can help in developing medical applications of FEL.

WORK PLAN: A steady progress in the development of advanced and unique computational methodology and understanding the basic mechanisms of laser interaction with organic materials make a solid foundation for extending the research work to more complex organic systems and addressing complex processes in the expanding ablation plume. Below are some of the directions to be pursued.

- The developed methodology for molecular dynamics modeling of bond breaking/making chemical reactions, such as photofragmentation of excited molecule and the subsequent various chemical reactions, opens up new possibilities in the investigation of photochemical processes. We are developing this methodology for polymer ablation.
- We will continue our analysis of the microscopic mechanisms of laser spallation of organic materials. In the case of spallation, the material disintegration proceeds in the form of void nucleation and growth and is localized within the spallation region at a certain depth under the irradiated surface. Analysis of the laser ablation in this case leads to a more general question on the microscopic mechanisms of the dynamic fracture under conditions of ultra-high strain rate and elevated temperature.

PERSONNEL SUPPORTED:

Professor Barbara J. Garrison, Principal Investigator, Penn State University
Professor Leonid V. Zhigilei, Co-Principal Investigator, University of Virginia
Dr. Yaroslava G. Yingling, Graduate Student & Post Doctoral Reseacher, Penn State University
Dr. Michael Zeifman, Post Doctoral Reseacher, Penn State University
Dr. Uchkun Kutliev, Post Doctoral Reseacher, Penn State University
Elodie Leveugle, Graduate (M.S.) Student, University of Virginia

PUBLICATIONS:

[1] L. V. Zhigilei, Dynamics of the plume formation and parameters of the ejected clusters in short-pulse laser ablation, Appl. Phys. A 76, 339-350, 2003.

[2] L. V. Zhigilei, Y. G. Yingling, T. E. Itina, T. A. Schoolcraft, and B. J. Garrison, Molecular Dynamics Simulations of Matrix Assisted Laser Desorption - Connections to Experiment, Int. J. Mass Spectrom. 226, 85-106, 2003.

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HONORS AND AWARDS:

Barbara J. Garrison, Shapiro Professor of Chemistry, 2002-present

Leonid V. Zhigilei, American Society for Mass Spectrometry, 2002 Research Award Recipient

Yaroslava Yingling, Best Ph.D. Award from the Materials Research Institute at the Pennsylvania State, April 2003

Yaroslava Yingling, Braucher Scholarship Award for Graduate Student Research from the Chemistry Department at the Pennsylvania State University, Fall 2002

Yaroslava Yingling, Gordon Research Conference Travel Award, July 2002

Elodie Leveugle, "Outstanding Poster Presentation," at the 7th International Conference on Laser Ablation, Crete, Greece, October 2003

Elodie Leveugle, Travel Grants for Young Researchers through the European Union "Marie Curie Programme, October 2003

Elodie Leveugle, M.S. Thesis defense, University of Virginia, December 2003