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William A. Goddard III, Michael Ortiz, Sergey Zybin

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14. ABSTRACT
We developed the ReaxFF first-principles based reactive molecular dynamics (RMD) modeling approach to determine the nanoscale phenomena underlying shock detonation processes of energetic materials (EM). Using the ReaxFF approach, we proposed Compressive Shear Reactive Dynamics (CS-RD) simulation methodology to predict sensitivity of explosive crystals under combined shock and shear load. We also developed empirical van der Waals correction to Density Functional Theory for calculating accurate equation of states (EOS) of EM. We

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high explosives (HE), reactive dynamics (RD), density functional theory (DFT), Compressive Shear Reactive Dynamics (CSRD)

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Report Title

The fundamental chemistry and physics of munitions under extreme conditions

ABSTRACT

We developed the ReaxFF first-principles based reactive molecular dynamics (RMD) modeling approach to determine the nanoscale phenomena underlying shock detonation processes of energetic materials (EM). Using the ReaxFF approach, we proposed Compressive Shear Reactive Dynamics (CS-RD) simulation methodology to predict sensitivity of explosive crystals under combined shock and shear load. We also developed empirical van der Waals correction to Density Functional Theory for calculating accurate equation of states (EOS) of EM. We
implemented ReaxFF in parallel multiprocessor software to carry out large-scale simulations of initiation chemistry in homogeneous and heterogeneous HE under mechanical shock and shear on supercomputers. We discovered that sensitivity is dominated by a combination of shear and compression, with the rate of decomposition and temperature increase correlating with the
experimental differences in sensitivity. The second major focus was on the development of multiscale modeling of HE detonation using novel finite elements method with explicit generation of slip lines in the subgrain microstructure and inclusion of thermochemical constitutive parameters obtained from RD modeling to predict the hot spot formation and reaction initiation at the subgrain scale in polycrystalline explosives. The methodologies were successfully tested and validated by computational prediction of anisotropic sensitivity of PETN, as well as the formation of hot spots and chemical initiation in polycrystalline PETN.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

1. Liu, Y; Goddard, WA; First-Principles-Based Dispersion Augmented Density Functional Theory: From Molecules to Crystals; J. Phys. Chem. Lett., 1 (17): 2550-2555, (2010).
2. J. J. Rimoli, E. Gurses, and M. Ortiz, “Shock-induced subgrain microstructures as possible homogenous sources of hot spots and initiation sites in energetic polycrystals”, Phys. Rev. B., 81, 014112, (2010).
3. Rimoli J.J. and Ortiz M., “A three-dimensional multiscale model of intergrandular hydrogen-assisted cracking”, Philosophical Magazine 90: 2939-2963, (2010).
4. S.V. Zybin, W.A. Goddard III, P. Xu, A.C.T. van Duin, and A.P. Thompson, “Physical mechanism of anisotropic sensitivity in pentaerythritol tetranitrate from compressive-shear reaction dynamics simulations”, Appl. Phys. Lett., 96, 081918, (2010).
5. L. Zhang, S.V. Zybin, A.C.T. van Duin, and W.A. Goddard III, “Modeling High Rate Impact Sensitivity of Perfect RDX and HMX Crystals by ReaxFF Reactive Dynamics”, J. Energetic Materials, 28(1), 92-127, (2010).
6. L. Zhang, S.V. Zybin, A.C.T. van Duin, S. Dasgupta, W.A. Goddard III, and E.M. Kober, “Carbon Cluster Formation during Thermal Decomposition of Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine and 1,3,5-Triamino-2,4,6-trinitrobenzene High Explosives from ReaxFF Reactive Molecular Dynamics Simulations”, J. Phys. Chem. B, 113 (40), 10619-10640,(2009).
7. W.-G. Liu, S.V. Zybin, S. Dasgupta, T.M. Klapotke, and W.A. Goddard III, “Explanation of the Colossal Detonation Sensitivity of Silicon Pentaerythritol Tetranitrate (Si-PETN) Explosive”, J. Am. Chem. Soc. v.131(22), 7490, (2009).
8. Budzien J., Thompson A.P., Zybin S.V., “Reactive Molecular Dynamics Simulations of Shock Through a Single Crystal of Pentaerythritol Tetranitrate”, J. Phys. Chem. B, 113 (40), 13142-13151, (2009).
9. Zhang, L. Z., van Duin, A. C. T., Zybin, S. V., and Goddard, W. A., “Thermal Decomposition of Hydrazines from Reactive Dynamics Using the ReaxFF Reactive Force Field”, J. Phys. Chem. B, 113, 10770-10778.
10. M. W. Conroy, I. I. Oleynik, S. V. Zybin, and C. T. White, “Density Functional Theory Calculations of Solid Nitromethane under Hydrostatic and Uniaxial Compressions with Empirical van der Waals Correction”, J. Phys. Chem. A, 113 (15), 3610-3614, (2009).
11. Chenoweth, K; van Duin, A.C.T.; Dasgupta, S.; Goddard, W. A., Initiation Mechanisms and Kinetics of Pyrolysis and Combustion of JP-10 Hydrocarbon Jet Fuel. J. Phys. Chem. A, 113(9). 1740-1746, (2009).
12. Abou-Rachid H., Song Y., Hu, A., Dudiy, S., Zybin, S. V., Goddard III, W.A., “Predicting Solid-State Heats of Formation of Newly Synthesized Polynitrogen Materials by Using Quantum Mechanical Calculations”, J. Phys. Chem. A, 112 (46), 11914-11920, (2008).
13. Chenoweth, K; van Duin, A.C.T.; Goddard, W. A., ReaxFF reactive force field for molecular dynamics simulations of hydrocarbon oxidation. J. Phys. Chem. A, 112(5), 1040-1053, (2008).
14. M. W. Conroy, I. I. Oleynik, S. V. Zybin, and C. T. White, “Density functional theory calculations of anisotropic constitutive relationships in alpha-cyclotrimethylenetrinitramine”,
J. Appl. Phys., 104 (11), 113501, (2008).
15. M. W. Conroy, I. I. Oleynik, S. V. Zybin, and C. T. White, “First-principles anisotropic constitutive relationships in beta-cyclotetramethylene tetranitramine (beta-HMX)”, J. Appl.
Phys., 104 (5), 053506, (2008).
16. M. W. Conroy, I. I. Oleynik, S. V. Zybin, and C. T. White, “First-principles investigation of anisotropic constitutive relationships in pentaerythritol tetranitrate”, Phys. Rev. B, 77 (9),
094107, (2008).
17. A. Nakano, R. K. Kalia, K. Nomura, A. Sharma, P. Vashishta, F. Shimojo, A. C. T. van Duin, W. A. Goddard, III, R. Biswas, D. Srivastava, and L. H. Yang, “”. Int. J. High Perform. Comput. Applic. 22(1), 113-128, (2008).
18. Nakano, A.; Kalia, R. K.; Nomura, K.; Sharma, A.; Vashishta, P.; Shimojo, F.; van Duin, A. C. T.; Goddard, W. A.; Biswas, R.; Srivastava, D., A divide-and-conquer/cellulardecomposition
framework for million-to-billion atom simulations of chemical reactions. Comput. Mater. Sci., 38(4): p. 642-652, (2007).
19. Nomura, K.; Kalia, R. K.; Nakano, A.; Vashishta, P.; van Duin, A. C. T.; Goddard, W. A., Dynamic transition in the structure of an energetic crystal during chemical reactions at shock front prior to detonation. Phys. Rev. Lett., 99(14): 148303, (2007).
20. Buehler, M.J., A.C.T. van Duin, and W.A. Goddard, “Multiparadigm modeling of dynamical crack propagation in silicon using a reactive force field”, Phys. Rev. Lett, 96(9), 095505,(2006).
21. A. Strachan, E. Kober; A.C.T. van Duin, J. Oxgaard and W.A. Goddard III, “Thermal decomposition of RDX from reactive molecular dynamics”, J. Chem. Phys. 122, 054502,(2005).
22. Chenoweth, K., Cheung, S., van Duin, A.C.T., Goddard, W.A.; Kober, E.M., “Simulations on the thermal decompositions of a poly(dimethylsiloxane) polymer using the ReaxFF reactive force field”, J.Amer. Chem. Soc. 127, 7192-7202. (2005).
23. van Duin, A.C.T., Goddard, W.A; Israel: Zeiri,Y., Dubnikova, F., Kosloff, R., “Atomistic scale simulations of the initial chemical events in the thermal initiation of triacetonetriperoxide”, J.Amer. Chem. Soc. 127, 11053-11062, (2005).

Number of Papers published in peer-reviewed journals: 23.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations

1. [invited], "Fast multiscale models of polycrystalline plasticity", M. Ortiz, E. Gurses, J. Rimoli, ARL, Aberdeen Proving Ground, MD, March 26-27, 2009.
2. [invited], “Multiscale modeling of HE detonation initiation”, M. Ortiz, E. Gurses, J. Rimoli, Weapons and Materials Research Directorate, ARL, Aberdeen Proving Ground, MD, 2009.
3. [invited], “Atomistic View of Material Dynamics under High-Rate Mechanical or Thermal Loading”, International Symposium Plasticity’09, S.V. Zybin, Peng Xu, W. A. Goddard III, St Thomas, Virgin Islands, USA, January 2009.
4. “Initiation of PETN decomposition under shock compression: Reactive molecular dynamics simulation”, Peng Xu, S.V. Zybin, J. Budzien, A. P. Thompson, William A. Goddard III, at:
16th APS Conference on Shock Compression of Condensed Matter, Nashville, TN, June 2009.
5. “Compressive shear reactive dynamics to evaluate the anisotropic sensitivity of single-crystal energetic materials”, Zybin S. V, Peng Xu, Yi Liu, William A. Goddard III, at: 16th APS Conference on Shock Compression of Condensed Matter, Nashville, TN, June 2009.
6. “Explanation of the Colossal Sensitivity of Silicon Pentaerythritol Tetranitrate (Si-PETN)“, Wei-Guang Liu, S. V. Zybin, S. Dasgupta, William A. Goddard III, at: 16th APS Conference
on Shock Compression of Condensed Matter, Nashville, TN, June 2009.
7. “Reactive Molecular Dynamics of Initiation Chemistry in Energetic Materials under Shock and Shear Impacts”, Sergey V. Zybin, Joanne Budzien, Aidan P. Thompson, and William, A. Goddard III, at:. 2009 DoD HPCMP Users Group Conference, San Diego, CA, June 2009.
8. [invited], “Reactive Dynamics of Initiation Chemistry in Materials under High-Rate Mechanical or Thermal Loading”, S. V. Zybin, A.C.T. van Duin, W. A. Goddard III, at: DoD HPTi Workshop on Molecular Dynamics with Reactive Potentials, August 2009, Memphis, TN.
9. [invited], “Molecular Dynamics Studies of Reactive Processes in Energetic Materials”, Goddard W.A. et al, Gordon Research Conference on Energetic Materials, Tilton, NH, June, 2006.
10. [invited], "Applications of first principles theory to understanding shock induced chemistry, detonation, and combustion in energetic materials", Goddard W.A. et al, Naval Air Warfare Center at China Lake, February, 2006.
11. [invited], “Atomistic Modeling of Shock and Detonation Phenomena in Condensed Matter”, Zybin S.V. et al, Lawrence Livermore National Laboratory, September, 2006.
12. “Shock Induced Decomposition And Sensitivity Of Energetic Materials By ReaxFF Molecular Dynamics”, S.V. Zybin et al, 14th APS Conference on Shock Compression in Condensed Matter, Baltimore, USA, August 2005.
13. “Reactive Force Fields Based On Quantum Mechanics For Applications To Materials At Extreme Conditions”, W.A. Goddard et al, 14th APS Conference on Shock Compression in Condensed Matter, Baltimore, USA, August 2005.

Number of Presentations: 13.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

1. S.V. Zybin, P. Xu, W.A. Goddard III, J. Budzien and A.P. Thompson “Reactive Molecular Dynamics of Shock- and Shear Induced Chemistry in Energetic Materials for Future Force Insensitive Munitions”, DoD HPCMP Users Group Conference 2008, IEEE Computer Society.
2. S.V. Zybin, P. Xu, Q. An, and W.A. Goddard III, “ReaxFF Reactive Molecular Dynamics: Coupling Mechanical Impact to Chemical Initiation in Energetic Materials”, DoD HPCMP Users
Group Conference 2009, IEEE Computer Society.

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 2

Peer-Reviewed Conference Proceeding publications (other than abstracts):

1. S.V. Zybin, L. Zhang, H. Kim, A.C.T. van Duin, and W.A. Goddard III, “Analysis of Shock Decomposition and Sensitivity of Energetic Materials with ReaxFF Molecular Dynamics, Proc. of 13th Int. Detonation Symposium, Norfolk, VA, 2006, pp. 848-856.
2. L. Zhang, S.V. Zybin, A.C.T. van Duin, W.A. Goddard III, and E.M. Kober “Analysis of Carbon Cluster Formation During High Temperature Decomposition of HMX and TATB with ReaxFF Reactive Molecular Dynamics” Proc. of 13th Int. Detonation Symposium, Norfolk, VA, 2006, pp. 786-794.
3. A.C.T. van Duin, S.V. Zybin, K. Chenoweth, L. Zhang, S.-P. Han, A. Strachan, and W.A. Goddard III, “Reactive Force Fields Based on Quantum Mechanics for Applications to Materials at Extreme Conditions”, AIP Conf. Proc. 845 (2006), pp. 581–584.
4. L. Zhang, S.V. Zybin, A.C.T. van Duin, S. Dasgupta, and W.A. Goddard III, “Shock Induced Decomposition and Sensitivity of Energetic Materials by ReaxFF Molecular Dynamics”, AIP Conf. Proc. 845 (2006), pp. 585–588.
5. L. Zhang, S.V. Zybin, A.C.T. van Duin, S. Dasgupta, and W.A. Goddard III, “Thermal Decomposition of Energetic Materials by ReaxFF Reactive Molecular Dynamics”, AIP Conf. Proc. 845 (2006), pp. 589–592.
6. I.I.Oleynik, M.Conroy, S.V.Zybin, L.Zhang, A.C. van Duin, W.A.Goddard, and C.T.White, “Energetic Materials at High Compression: First-Principles Density Functional Theory and Reactive Force Field Studies”, AIP Conf. Proc. 845 (2006), pp. 437–441.
7. W Huang, JE. Patterson, A Lagutchev and DD Dlott, “Shock compression spectroscopy with high time and space resolution”, AIP Confer. Proc. 845, pp. 1265-1270 (2006).

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts): 7

(d) Manuscripts

Number of Manuscripts: 0.00

Patents Submitted

Patents Awarded

Awards

1. Goddard awarded ACS 2008 National Award in Theoretical Chemistry.
2. Goddard elected Fellow of the Royal Society Chemistry (2008)
3. Goddard awarded NASA Space Sciences Award for Space Shuttle Sensor (2009)
4. Goddard elected Fellow of American Academy of Arts and Sciences (2010)
5. Ortiz awarded 2008 IUTAM Rodney Hill Prize
6. Ortiz awarded 2010 Hans Fischer Senior Fellowship, Institute for Advanced Study, Technical University of Munich

Graduate Students

NAME	PERCENT_SUPPORTED
Mujeng Cheng	0.06
Daniel Fisher	0.06
Frank Ducheneaux	0.28
Peng Xu	0.45
Qi An	0.03
Julian Rimoli	1.00
FTE Equivalent:	**1.88**
Total Number:	**6**

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Kimberly Chenoweth	0.40
Jason Gonzales	0.81
Jun Tan	0.52
Ercan Gurses	1.00
FTE Equivalent:	**2.73**
Total Number:	**4**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
William A. Goddard III	0.02	Yes
Michael Ortiz		No
FTE Equivalent:	**0.02**	
Total Number:	**2**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	0.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:.....	0.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:.....	0.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):	0.00
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The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:	0.00

Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME
Hyungjun Kim
Daniel Fisher
Si-ping Han
Julian Rimoli
Total Number: **4**

Names of other research staff

NAME	PERCENT_SUPPORTED	
Siddharth Dasgupta	0.05	No
Adri van Duin	0.13	No
Soo-Kyung Kim	0.10	No
Yi Liu	0.10	No
Sergey Zybin	0.34	No
Darryl Willick	0.05	No
Bo Li		No
FTE Equivalent:	**0.77**	
Total Number:	**7**	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment

Technology Transfer

Final Report - Grant # W911NF-05-1-0345
(Reporting Period: July 1, 2005 – September 20, 2010)

The fundamental chemistry and physics of munitions under extreme conditions

PI: William A. Goddard III
Division of Chemistry and Chemical Engineering
California Institute of Technology, Pasadena, California, 91125

Co-PI: Michael A. Ortiz
Division of Engineering and Applied Science
California Institute of Technology, Pasadena, California, 91125

Objective

Develop modeling and simulation technologies validated by experiment and sufficient to predict the chemical and physical phenomena involved in the energy initiation and release processes of high explosives (HE) under extreme conditions of mechanical and thermal energy deposition. Our goal is to develop methodologies for large-scale reactive dynamics (RD) simulations to determine the atomistic mechanisms relevant to detonation and sensitivity. Elucidating the interplay between the reaction chemistry and the shock dynamics is important for understanding the shock-to-detonation transition when reaction products may affect the mechanical strains and stresses in reacting material and resulting shear / heat flows, and vice versa. One of the critical issues is how the strength properties and failure mechanisms (shear banding, slipping, fracture, etc) of the material influence the dissipation of the mechanical energy of impact. This requires a detailed microscopic description of the anisotropic nonlinear response of the material under large deformations to determine preferred slip planes and shear flows in HE micrograins under stresses generated by the interference of shock waves and the material microstructure

Approach

While the propagation of the steady detonation front is accurately predicted by continuum mechanics models, how this detonation front forms due to an initial mechanical or thermal excitation is not. This is because the initiation process depends strongly on sub-continuum properties, such as slip and shear bands formation, grain orientation, intergranular interfaces, voids, inclusions, and crystal morphology. In attempt to elaborate the mechanisms of energy transfer, excitation and decomposition of energetic molecules we suggest to use first-principles based atomistic simulations capable to capture basic physical and chemical processes dominating initiation of HE and determine critical properties affecting their sensitivity.

The hot spots formation in heterogeneous materials usually occurs due to the interaction of shocks with material heterogeneities such as grain boundaries, defects, voids and cracks. In case of detonation in homogeneous materials, the initiation mechanisms may be related to the heterogeneity of crystal plasticity at the subgrain scale with high localization of strain, stress, and temperature extremes. Conventional mean-field models convey no information about these local extremes and, therefore, are insufficient for present purposes.

In this work, we have developed a multiscale model that explicitly accounts for three scales: (i) the polycrystalline structure at the macroscale, (ii) single crystal plasticity (including subgrain

microstructure formation) at the mesoscale and (iii) chemical kinetics at the molecular scale. The centerpiece of the model is an explicit construction that: i) gives the effective or macroscopic behavior of plastically deforming crystals with microstructure, and ii) enables the reconstruction of optimal microstructures from the computed macroscopic averages. An intrinsic feature of the optimal deformation microstructures is the presence of highly localized regions of plastic deformation, or slip lines (see Fig. 2.1). Temperatures, strain-rates and pressures in these slip lines rise well in excess of the average or macroscopic values. Slip lines thus provide a plentiful supply of likely initiation sites, or hot-spots, in defect-free crystals.

We develop and use:

1. The reactive force field ReaxFF framework for describing the complex chemical and energy releasing phenomena in play during the initial steps of the interactions between the threat and the HE for both shock impact and thermal impact over the full range of pressures and temperatures.

2. Empirical vdW-correction of the density functional theory (DFT) for accurate calculations of constitutive properties and equation of state (EOS) of HE over a wide interval of strains to achieve accurate description of their response under shock / thermal loading.

3. Compressive Shear Reactive Dynamics (CSRD) to predict the anisotropy of shock sensitivity on HE single crystals.

4. Large-scale parallel codes for RD modeling of initiation chemistry in homogeneous and heterogeneous HE under thermal and mechanical shocks and shear.

5. Multiscale model that explicitly accounts for three scales: (i) the polycrystalline structure at the macroscale, (ii) single crystal plasticity (including subgrain microstructure formation) at the mesoscale and (iii) chemical kinetics at the molecular scale. The centerpiece of the model is an explicit construction that: i) gives the effective or macroscopic behavior of plastically deforming crystals with microstructure, and ii) enables the reconstruction of optimal microstructures from the computed macroscopic averages. An intrinsic feature of the optimal deformation microstructures is the presence of highly localized regions of plastic deformation, or slip lines (see Fig. 2.1). Temperatures, strain-rates and pressures in these slip lines rise well in excess of the average or macroscopic values. Slip lines thus provide a plentiful supply of likely initiation sites, or hot-spots, in defect-free crystals.

Relevance to Army

This project is part of an integrated research program to address various fundamental issues critical to the development of insensitive munitions for Future Force Insensitive Munitions (FFIM). The developed methodologies should provide critical data on atomistic mechanisms of initiation and detonation in condensed-phase HE and support the development of advanced energetic compositions. Use of predictive simulation technique should decrease the time and cost of development for enhancing performance and safety of new HE and formulations for FFIM. The proposed methodology may be also helpful in prediction of the properties and responses of HE in improvised explosive devices (IED), and currently is being used by Israeli collaborator at the Hebrew University of Jerusalem (Prof. Ronnie Kosloff). Besides of the military applications, developed methodology of reactive simulation and nanoscale experimental techniques are already being used to study reactive processes in combustion, catalysis, fuel cells, and other civilian applications of the reaction modeling in nanostructures.

Our multiscale simulations of hot spots formation in homogeneous HE due to the stress localization and temperature increase at the slip lines in subrain microstructures allows to

develop a predictive model of initiation and sensitivity of realistic HE compositions which is impossible to construct on a basis of conventional mean-field approaches currently used for detonation simulations at the macroscale level. The developed codes will help DoD researchers in the the development of new and improved materials and structures with enhanced energy density and reduced sensitivity for a wide range of DoD applications.

Accomplishments

1. Large-scale ReaxFF simulations of the shock wave propagation in a single crystal of PETN to model the effect of initiation of chemical reactions and shock-to-detonation transition in homogeneous HE (Figs. 1, 2, 4). By looking at particular chemical species concentrations as a function of time and space (Figs. 5–7), we have been able to correlate the observed changes in shock-front velocity with the storage and release of chemical energy.

2. Predictive modeling of anisotropy of shock sensitivity of HE single crystals. Compressive Shear Reactive Dynamics (CSRD) protocol was developed to study the effect of crystal structure and slip directions on chemical initiation and sensitivity of HE single crystal (Figure 8). We show that shocks with simultaneous shear and compression leads to enhanced chemical initiation and that in some materials (PETN) this depends dramatically on the slip system. Our protocol was validated by comparison with experimental results of J. J. Dick on single crystal of PETN (Fig. 10 and Table 1). Now the protocol is being used to simulate other single-crystal HE as RDX (figures 11-15) as well as more complex HE composites with grains and polymer binders.

3. Empirical vdW-correction of the density functional theory (DFT) to include accurate London Dispersion for calculations of wide-range EOS for HE crystals with accurate description of both equilibrium and high-pressure properties. It has been successfully validated on hydrocarbon crystals commonly used for testing purposes (Figs. 1.1–1.3). We now use it to determine EOS of HE crystals (PETN, RDX, HMX, TNT) and provide accurate training data for a development of new generation of the reactive force fields.

4. Fast multiscale models of shock-induced plasticity and hot spot formation in energetic polycrystals. We have assessed the feasibility of the slip-line initiation mechanism by simulating a PETN plate impact experiment and comparing the resulting predictions with experimental pop-plot data. The computed characteristic exponents are in the ballpark of experimental observation, which furnishes a modicum of validation of the model and illustrates the ability of the multiscale model to make contact with full-scale experimental data and applications.

We have specifically assessed the ability of the model to predict experimentally observed pop-plot characteristic exponents for PETN. We exercise the multiscale model described in the foregoing in a simple plate impact configuration, Fig. 2.3, where a target plate of polycrystalline PETN that is impacted on its rear surface by a rigid striker plate. The finite element mesh used in the simulations to resolve the polycrystalline structure of the material, is shown in Fig. 2.3b. The dimensions of the sample are 800 x 400 x 400 μm, and the maximum grain size is 100 μm. Fig. 2.5 shows the evolution of the macroscopic temperature for the impact velocity of 700 m/s. At material points where deformation microstructures form, the macroscopic temperature follows as the volume-average of the microscopic temperature field, which varies sharply on the scale of the microstructure. A typical temporal evolution of the temperature and reacted molar fraction within a slip line is shown in Fig. 2.7.

The comparison with experimental data is predicated on the assumption that initiation in a pop-plot test requires the formation of a critical number N_c of hot-spots. Fig. 9 shows the pop-plot predicted in the manner just described, with hot spots identified with slip lines that attain a

temperature greater than 700 K, a reacted fraction greater than 1% and a pressure greater than 6 GPa. As may be seen from the Fig. 2.9, the pop-plot predicted by the model is consistent with power-law scaling, in agreement with experiments. The characteristic exponent predicted by the model is 2.9, which slightly overestimates the experimental range of 2.01 – 2.58 for single crystal PETN.

Collaborations and Technology Transfer

1. The Caltech team has established close collaboration with personnel from the Army Research Laboratory (ARL) and the Naval Research Laboratory (NRL). Since the beginning of the MURI, there has been an expanded effort to exchange research data and codes between Caltech team and research groups at ARL and NRL. Caltech's simulation codes and ReaxFF force fields for reactive atomistic modeling have been transferred to ARL, NRL, Air Force Institute of Technology at Wright Patterson Air Force Base (WPAFB), Los Alamos National Laboratory (LANL), Sandia National Laboratories (SNL), NASA Ames Research Center, and other national research institutions. A close working relationship has been developed with the High Performance Technologies Inc. (HPTi) at WPAFB on customization, distribution, and training for ReaxFF codes and force fields for the users at ARL, NRL, and other DoD high-performance centers (HPC). The ReaxFF codes and force fields for HE are being transferred to DoD labs in collaboration with ARL and HPTi researchers (Betsy Rice, Anthony Yau, James Lill, James Larentzos). Currently, there is an ongoing HPTi/WPAFB – Caltech effort (PETTT project# PP-CCM-KY02-008) on the support and further modernization of ReaxFF with novel optimization algorithms developed at the ARL and HPTi.

2. There have been a series of visits to ARL, NRL, HPTi, LANL, SNL, other universities, and continuing technical interactions on the multiscale reactive modeling in energetic materials with:

- Betsy Rice (ARL), Jan Andzelm (ARL), Anthony Yau (HPTi), James Lill (HPTi), James Larentzos (HPTi): optimization and training of the ReaxFF force fields for energetic materials and applications;
- Peter Chung (ARL), Jaroslaw Knap (ARL), Betsy Rice (ARL): coupling continuum (Prof. Ortiz) and atomistic (Prof. Goddard) simulations of polycrystalline plasticity, hot spots formation and initiation of detonation in heterogeneous polycrystalline energetic materials;
- Carter White (NRL), Ivan Oleynik (USF): anisotropic nonlinear elasticity and equations of states of crystalline EM (PETN, RDX, HMX, TATB, nitromethane);
- James Lill (HPTi), Betsy Rice (ARL), and Dr. Aidan Thompson (SNL): large-scale simulations of shock-induced chemistry in HE single crystals (RDX, HMX. PETN), polycrystalline HE and HE/binder composites (RDX/HTPB, PETN/HTPB) using DoD HPCMP high-performance computers (CAP project);
- Ed Kober (LANL) and Tomas Sewell (Univ. of Missouri): ReaxFF reactive modeling of chemical kinetics of thermal decomposition and formation of hot spots in HMX, TATB, and nitromethane;
- Aidan Thompson (SNL): shock-to-detonation transition in PETN and CL-20;
- Ronnie Kosloff (Hebrew University of Jerusalem): ReaxFF modeling of the HE response to the terahertz (THz) spectroscopy probing; simulation of initiation and decomposition kinetics in nitromethane, TNT, TATP, and DATP.

3. Prof. William Goddard gave multiple invited talks at national and international workshops and symposiums on reactive force fields and RMD modeling of energetic materials and sensitivity:

- Gordon Research Conference on Energetic Materials, Tilton, NH, June, 2006.
- 7th International Conferences "New Models and Hydrocodes for Shock Wave Processes in Condensed Matter" 2008 (Lisbon, Portugal)
- Goddard all day visit and seminar LANL, April 19, 2010
- Goddard all day visit and seminar SNL, April 20, 2010
- International Conference and Advanced School Turbulent MIxing and Beyond TMB-2009, Trieste Italy, June 2009, Goddard gave invited talk
- Prof. Michael Ortiz visited ARL multiple times (2009, 2010) to give a presentation on multiscale modeling of HE detonation initiation with the finite elements code developed at Caltech. The code is being developed with a goal to transfer it to ARL for simulations of impact sensitivity and initiation in polycrystalline and polymer-bonded explosives.
- Dr. Sergey Zybin and Dr. Adri van Duin visited ARL (2005, 2007) and SNL (2006, 2008) to discuss development, maintenance, and use of the ReaxFF force fields in EM applications as well as parallel implementation of ReaxFF in multiprocessor software Grasp and Lammps.

Resulting Journal Publications

1. Liu, Y; Goddard, WA; First-Principles-Based Dispersion Augmented Density Functional Theory: From Molecules to Crystals; J. Phys. Chem. Lett., 1 (17): 2550-2555, (2010).
2. J. J. Rimoli, E. Gurses, and M. Ortiz, "Shock-induced subgrain microstructures as possible homogenous sources of hot spots and initiation sites in energetic polycrystals", Phys. Rev. B., 81, 014112, (2010).
3. Rimoli J.J. and Ortiz M., "A three-dimensional multiscale model of intergrandular hydrogen-assisted cracking", Philosophical Magazine 90: 2939-2963, (2010).
4. S.V. Zybin, W.A. Goddard III, P. Xu, A.C.T. van Duin, and A.P. Thompson, "Physical mechanism of anisotropic sensitivity in pentaerythritol tetranitrate from compressive-shear reaction dynamics simulations", Appl. Phys. Lett., 96, 081918, (2010).
5. L. Zhang, S.V. Zybin, A.C.T. van Duin, and W.A. Goddard III, "Modeling High Rate Impact Sensitivity of Perfect RDX and HMX Crystals by ReaxFF Reactive Dynamics", J. Energetic Materials, 28(1), 92-127, (2010).
6. L. Zhang, S.V. Zybin, A.C.T. van Duin, S. Dasgupta, W.A. Goddard III, and E.M. Kober, "Carbon Cluster Formation during Thermal Decomposition of Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine and 1,3,5-Triamino-2,4,6-trinitrobenzene High Explosives from ReaxFF Reactive Molecular Dynamics Simulations", J. Phys. Chem. B, 113 (40), 10619-10640, (2009).
7. W.-G. Liu, S.V. Zybin, S. Dasgupta, T.M. Klapotke, and W.A. Goddard III, "Explanation of the Colossal Detonation Sensitivity of Silicon Pentaerythritol Tetranitrate (Si-PETN) Explosive", J. Am. Chem. Soc. v.131(22), 7490, (2009).
8. Budzien J., Thompson A.P., Zybin S.V., "Reactive Molecular Dynamics Simulations of Shock Through a Single Crystal of Pentaerythritol Tetranitrate", J. Phys. Chem. B, 113 (40), 13142-13151, (2009).
9. Zhang, L. Z., van Duin, A. C. T., Zybin, S. V., and Goddard, W. A., "Thermal Decomposition of Hydrazines from Reactive Dynamics Using the ReaxFF Reactive Force Field", J. Phys. Chem. B, 113, 10770-10778.

10. M. W. Conroy, I. I. Oleynik, S. V. Zybin, and C. T. White, “Density Functional Theory Calculations of Solid Nitromethane under Hydrostatic and Uniaxial Compressions with Empirical van der Waals Correction”, J. Phys. Chem. A, 113 (15), 3610-3614, (2009).
11. Chenoweth, K; van Duin, A.C.T.; Dasgupta, S.; Goddard, W. A., Initiation Mechanisms and Kinetics of Pyrolysis and Combustion of JP-10 Hydrocarbon Jet Fuel. J. Phys. Chem. A, 113(9). 1740-1746, (2009).
12. Abou-Rachid H., Song Y., Hu, A., Dudiy, S., Zybin, S. V., Goddard III, W.A., “Predicting Solid-State Heats of Formation of Newly Synthesized Polynitrogen Materials by Using Quantum Mechanical Calculations”, J. Phys. Chem. A, 112 (46), 11914-11920, (2008).
13. Chenoweth, K; van Duin, A.C.T.; Goddard, W. A., ReaxFF reactive force field for molecular dynamics simulations of hydrocarbon oxidation. J. Phys. Chem. A, 112(5), 1040-1053, (2008).
14. M. W. Conroy, I. I. Oleynik, S. V. Zybin, and C. T. White, “Density functional theory calculations of anisotropic constitutive relationships in alpha-cyclotrimethylenetrinitramine”, J. Appl. Phys., 104 (11), 113501, (2008).
15. M. W. Conroy, I. I. Oleynik, S. V. Zybin, and C. T. White, “First-principles anisotropic constitutive relationships in beta-cyclotetramethylene tetranitramine (beta-HMX)”, J. Appl. Phys., 104 (5), 053506, (2008).
16. M. W. Conroy, I. I. Oleynik, S. V. Zybin, and C. T. White, “First-principles investigation of anisotropic constitutive relationships in pentaerythritol tetranitrate”, Phys. Rev. B, 77 (9), 094107, (2008).
17. A. Nakano, R. K. Kalia, K. Nomura, A. Sharma, P. Vashishta, F. Shimojo, A. C. T. van Duin, W. A. Goddard, III, R. Biswas, D. Srivastava, and L. H. Yang, “”. Int. J. High Perform. Comput. Applic. 22(1), 113-128, (2008).
18. Nakano, A.; Kalia, R. K.; Nomura, K.; Sharma, A.; Vashishta, P.; Shimojo, F.; van Duin, A. C. T.; Goddard, W. A.; Biswas, R.; Srivastava, D., A divide-and-conquer/cellular-decomposition framework for million-to-billion atom simulations of chemical reactions. Comput. Mater. Sci., 38(4): p. 642-652, (2007).
19. Nomura, K.; Kalia, R. K.; Nakano, A.; Vashishta, P.; van Duin, A. C. T.; Goddard, W. A., Dynamic transition in the structure of an energetic crystal during chemical reactions at shock front prior to detonation. Phys. Rev. Lett., 99(14): 148303, (2007).
20. Buehler, M.J., A.C.T. van Duin, and W.A. Goddard, “Multiparadigm modeling of dynamical crack propagation in silicon using a reactive force field”, Phys. Rev. Lett, 96(9), 095505, (2006).
21. A. Strachan, E. Kober; A.C.T. van Duin, J. Oxgaard and W.A. Goddard III, “Thermal decomposition of RDX from reactive molecular dynamics”, J. Chem. Phys. 122, 054502, (2005).
22. Chenoweth, K., Cheung, S., van Duin, A.C.T., Goddard, W.A.; Kober, E.M., “Simulations on the thermal decompositions of a poly(dimethylsiloxane) polymer using the ReaxFF reactive force field”, J.Amer. Chem. Soc. 127, 7192-7202. (2005).
23. van Duin, A.C.T., Goddard, W.A; Israel: Zeiri,Y., Dubnikova, F., Kosloff, R., “Atomistic scale simulations of the initial chemical events in the thermal initiation of triacetonetriperoxide”, J.Amer. Chem. Soc. 127, 11053-11062, (2005).

Awards, Honors and Appointments

1. Goddard awarded ACS 2008 National Award in Theoretical Chemistry.
2. Goddard elected Fellow of the Royal Society Chemistry (2008)
3. Goddard awarded NASA Space Sciences Award for Space Shuttle Sensor (2009)
4. Goddard Elected Fellow of American Academy of Arts and Sciences (2010)
5. Ortiz awarded 2008 IUTAM Rodney Hill Prize
6. Ortiz awarded 2010 Hans Fischer Senior Fellowship, Institute for Advanced Study, Technical University of Munich

Graduate Students Involved

Goddard's group:

Qi An (Ph.D, current)

Mu-Jeng Cheng current

Frank Ducheneaux graduated MS chem. 2009

Peng Xu (Ph.D, graduated MS Mat sci 2009)

Si-Ping Han (Ph.D, Mat Sci graduated, 2009)

Hyungjun Kim (Ph.D, Chem graduated, 2009)

Daniel Fisher (Ph.D, Chem graduated, 2010)

Ortiz's group:

Julian Rimoli (Ph.D, graduated, 2010)

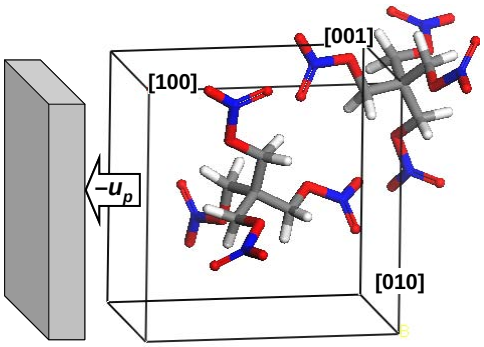


Figure 1. Tetragonal PETN unit cell with a schematic of shock generation by impact against a stationary wall at particle (i.e. piston) velocity $-u_p$

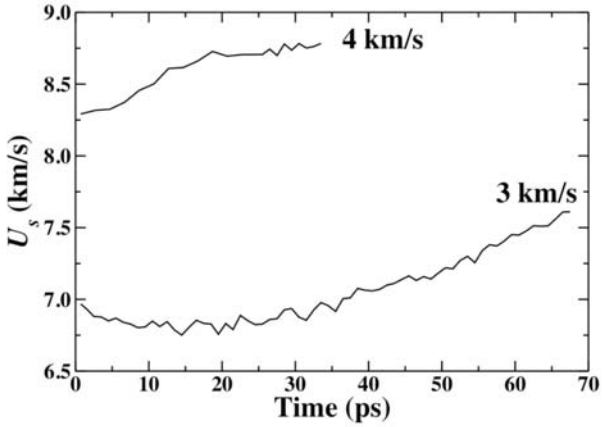


Figure 4. Plot of instantaneous shock-front velocity as a function of time for a weak shock (3 km/s) and a strong shock (4 km/s) along [100] direction in PETN crystal with density ~1.5 g/cm^3. The observed acceleration of the shock-wave (shock to detonation transition) is due to the net energy release that occurs when final reaction products are formed. In the case of the weak shock, the initial deceleration is due to energy storage (endothermicity) in intermediate reaction products.

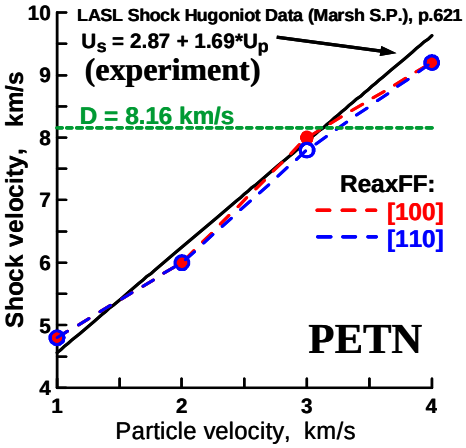


Figure 2. Hugoniot adiabat from ReaxFF-MD simulations of unidirectional shocks in PETN single crystals with density ~1.7 g/cm^3 show good agreement with experiment [**Error!**

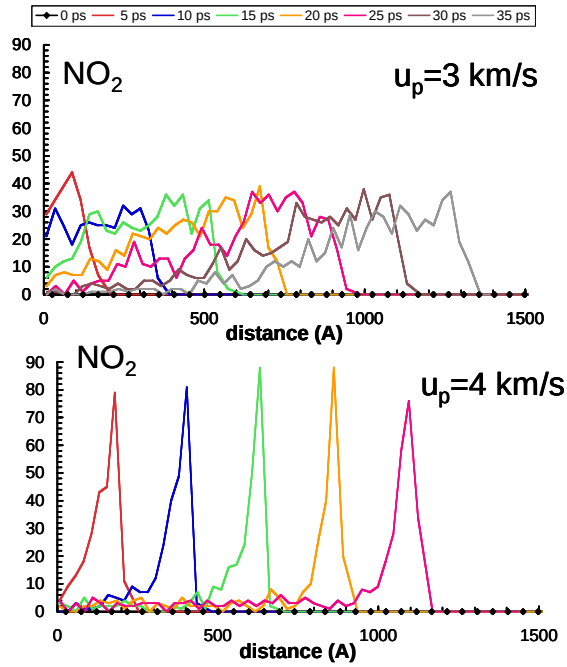


Figure 5. Distribution of primary reaction products (dissociated NO_2 per PETN molecule) along [100] shock direction.

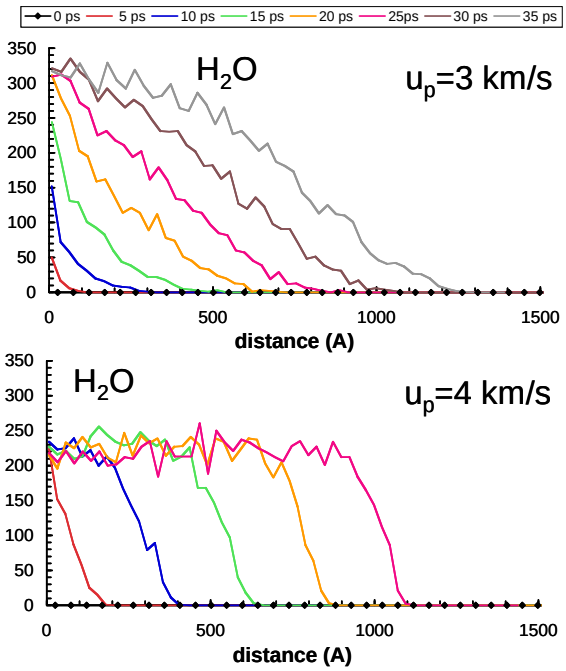


Figure 6. Distribution of secondary reaction products (H_2O per PETN molecule) along the [100] shock direction.

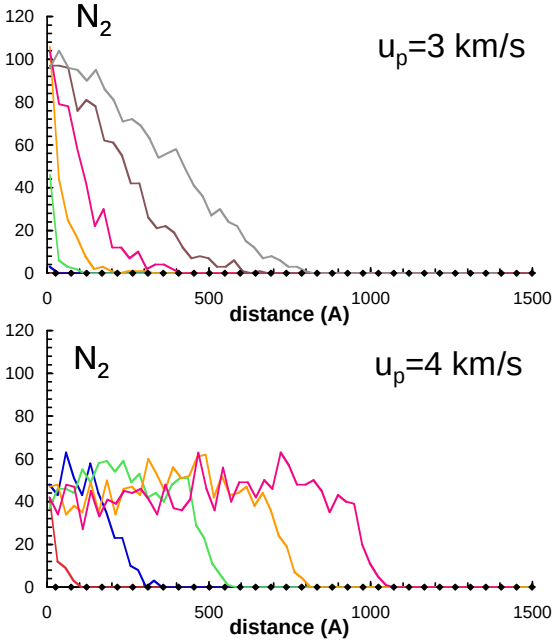


Figure 7. Distribution of secondary reaction products (N_2 per PETN molecule) along the [100] shock direction.

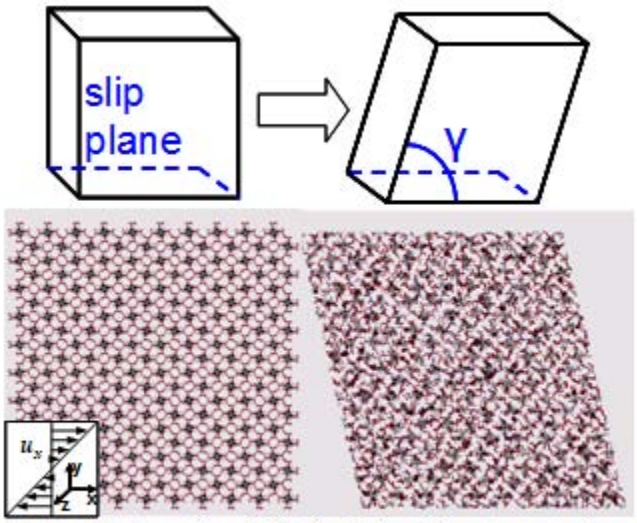


Figure 8. Schematics of MD simulation of constant-rate shear along one of the slip plane in PETN single crystal to evaluate the effect of shear deformation on chemical initiation.

Shear simulations on 10%-compressed PETN (after 6ps)

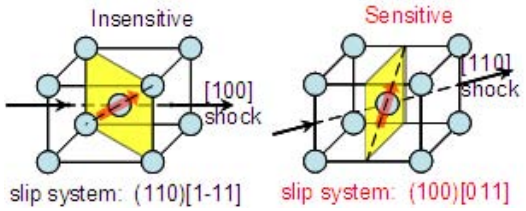
Table 1

Shock plane [a]	Sensi-tivity [b]	Slip system	NO_2 per PETN (%)	$\tau_m - \tau_c$ GPa [c]	$\tau_m - \tau_0$ GPa [c]	T(K) at 6 ps
(110)	**S**	**{100}⟨011⟩**	**1.5**	**1.19**	**1.66**	**960**
(001)		{101}101⟩	1.5	1.38	2.28	910
(001)	**S**	**{101}111⟩**	**0.8**	**1.03**	**1.93**	**826**
(111)	**M**	**{110}⟨001⟩**	**1.0**	**0.76**	**1.02**	**830**
(101)		{100}⟨001⟩	2.6	1.60	1.77	1000
(101)		{110}⟨001⟩	0.75	1.08	1.76	820
(101)	**I, M**	**{110}⟨1-11⟩**	**0.2**	**0.45**	**1.04**	**690**
(100)	**I**	**{110}⟨1-11⟩**	**0.2**	**0.49**	**0.69**	**725**

[a] Shock plane normal is parallel to the shock direction.

[b] S – sensitive, I – insensitive, M – intermediate and velocity-dependent.

[c] τ_0 is the initial, τ_m is the maximum, and τ_c is the steady state shear stress



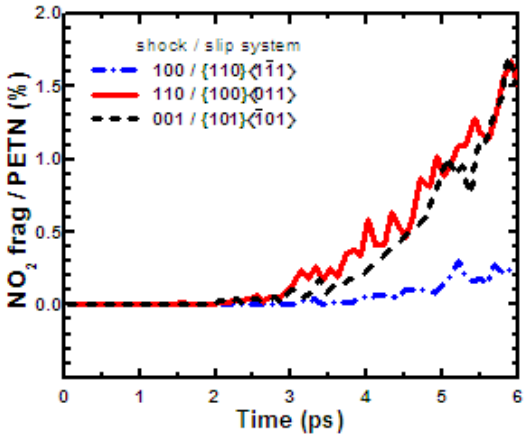


Figure 10. ReaxFF MD simulation of constant -rate shear predicts much faster chemical initiation (dissociation of NO_2) in PETN single crystal for experimentally more sensitive [110] and [001] directions of shock compression.

Least Hindered Shear System (B) in RDX

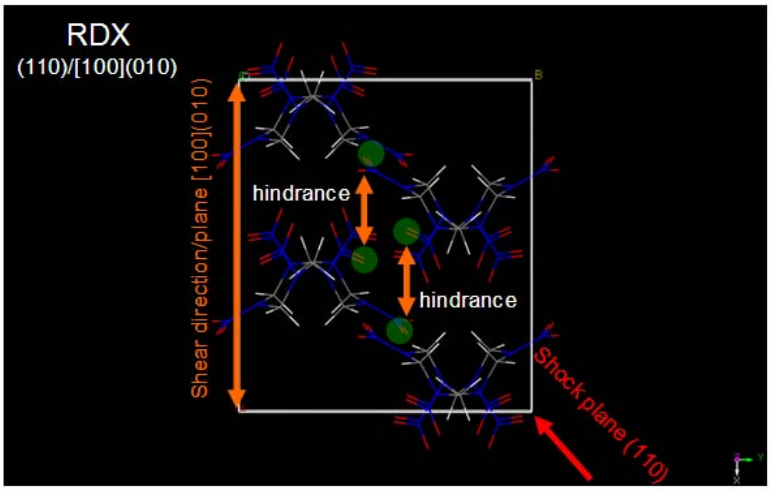


Fig.11 Steric hindrance index: 0.09

Least Hindered Shear System (B) in RDX

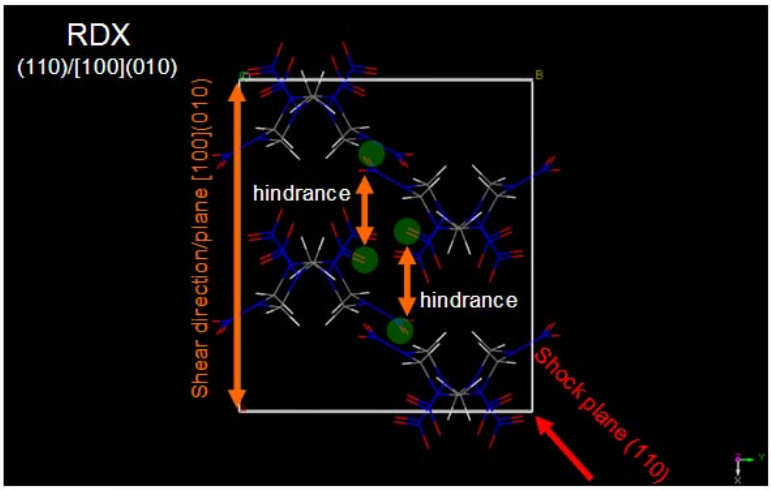


Fig.12 Steric hindrance index: 0.09

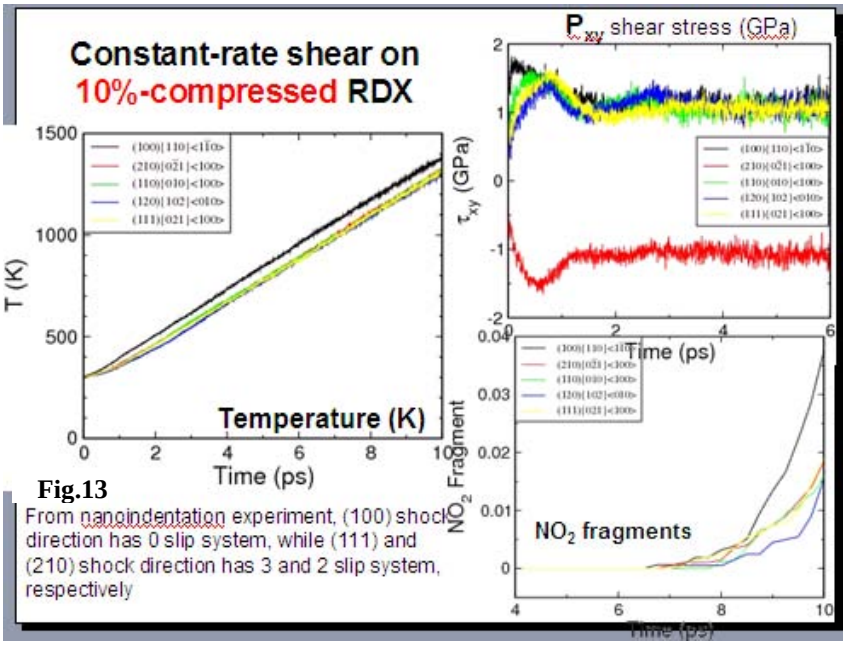


Fig.13

From nanoindentation experiment, (100) shock direction has 0 slip system, while (111) and (210) shock direction has 3 and 2 slip system, respectively

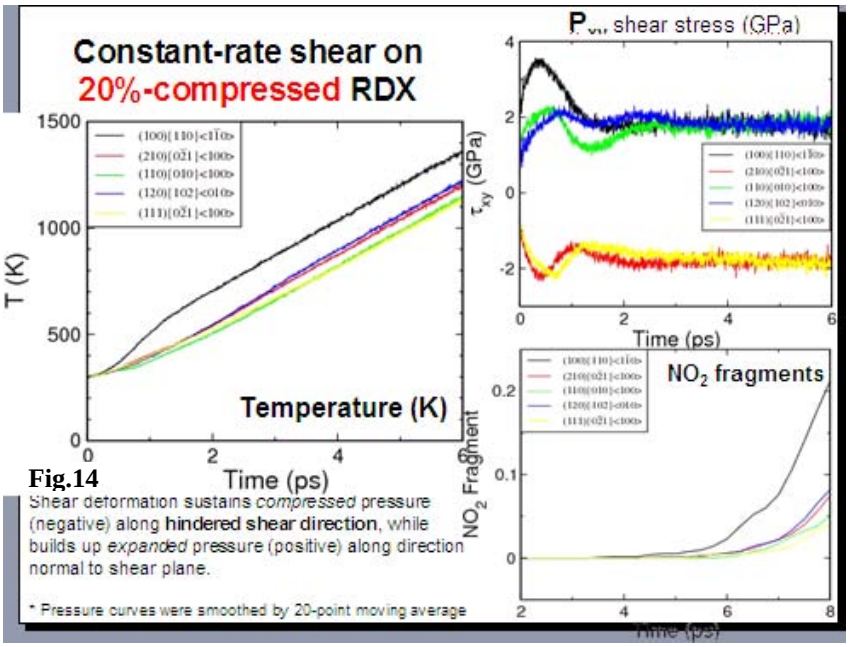


Fig.14

Shear deformation sustains *compressed* pressure (negative) along **hindered shear direction**, while builds up *expanded* pressure (positive) along direction normal to shear plane.

* Pressure curves were smoothed by 20-point moving average

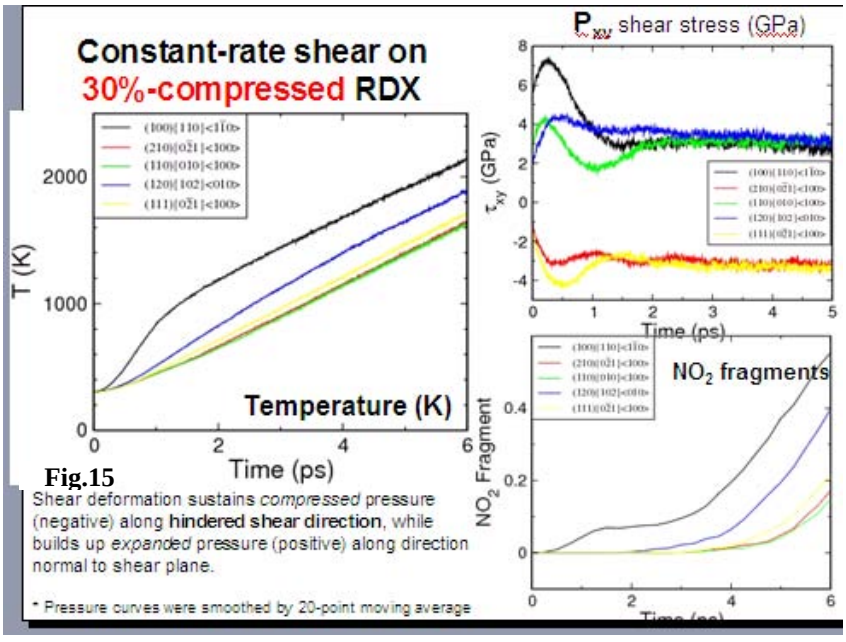


Fig.15

Shear deformation sustains *compressed* pressure (negative) along **hindered shear direction**, while builds up *expanded* pressure (positive) along direction normal to shear plane.

* Pressure curves were smoothed by 20-point moving average

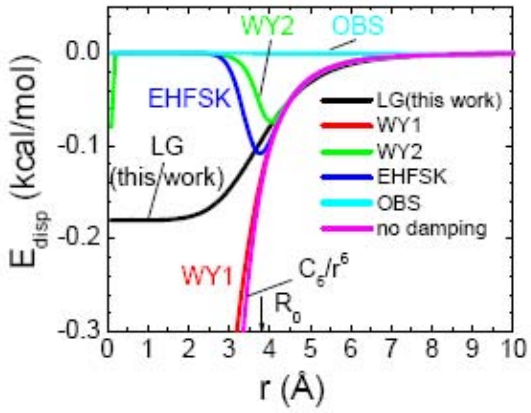


Fig.1.1 Dispersion correction (E_{disp}) for a pair of carbon atoms developed in this work (denoted as LG) compared with those in literatures including WY1[26], WY2[26], EHFSK[28], and OBS[29]. The same C-C equilibrium bond distance R_0 = 3.851 Å and C_6 = 586.8 kcal/mol Å^6 are used for the sake of comparison. E_{disp}= C_6/r^6 without damping is also plotted as a reference.

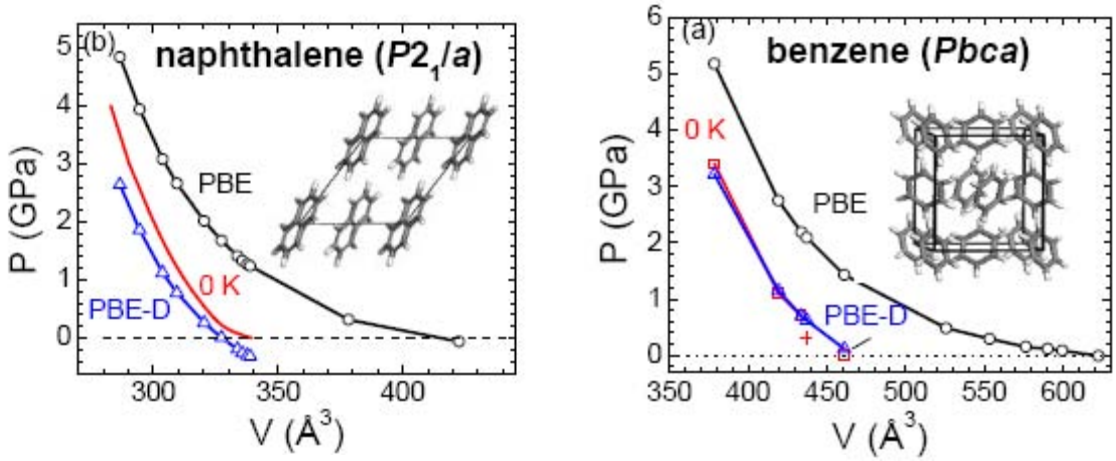


Fig.1.3 (a) EOS of benzene crystal (orthorhombic phase I) and (b) naphthalene crystal calculated using PBE and PBE-D together with the extrapolated 0 K EOS. The inserts show the unit cells of the crystals.

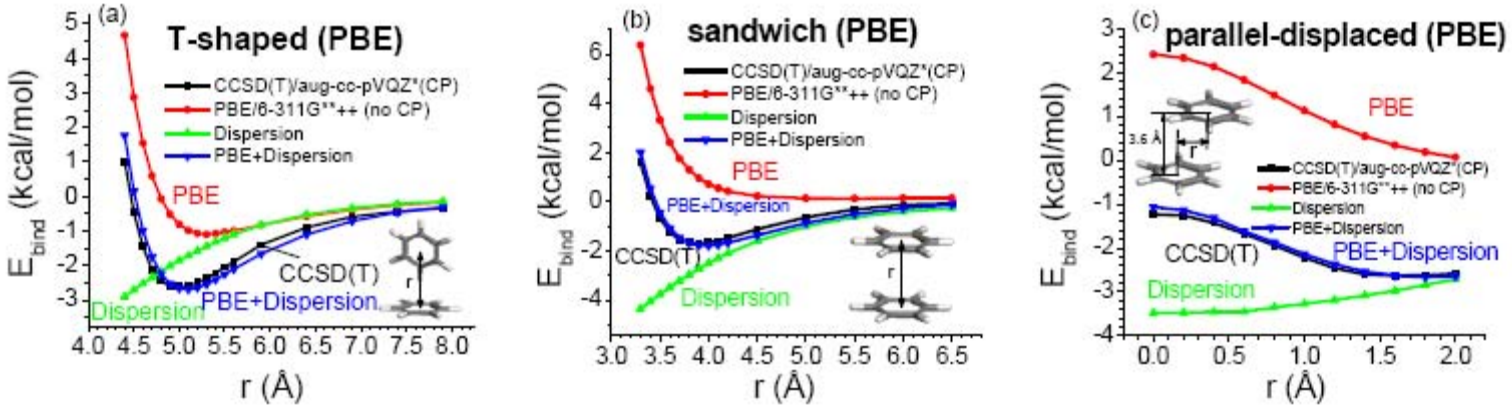


Fig.1.2 Binding energy of benzene dimers as a function of distance calculated using pure PBE and its dispersion corrections (PBE-D) for (a) T-shaped, (b) sandwich, (c) parallel-displaced configurations.

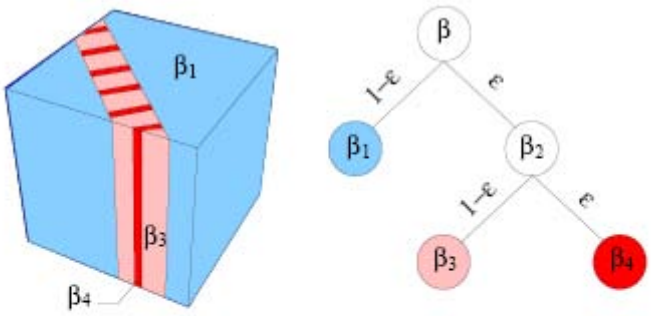


FIG. 1: Simplest possible microstructure. Macroscopic deformation β has two active slip systems, and decomposes into first order laminates β_1 and β_2 with single and double slip, respectively. Similarly, β_2 decomposes into second order laminates β_3 and β_4 with single and double slip, respectively. Highly localized plastic deformations occur in β_4 which is considered as a potential hot spot.

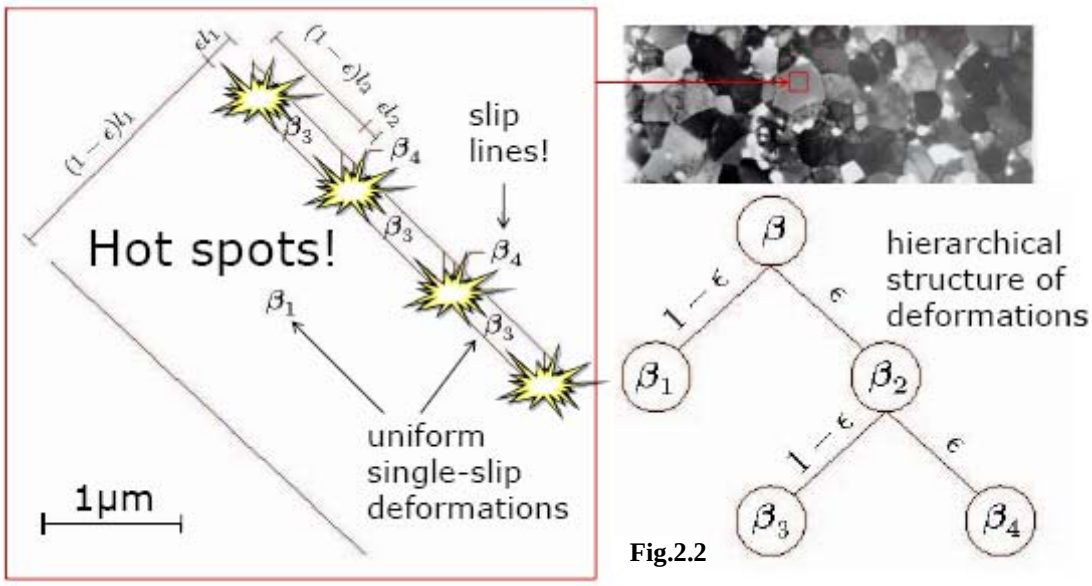
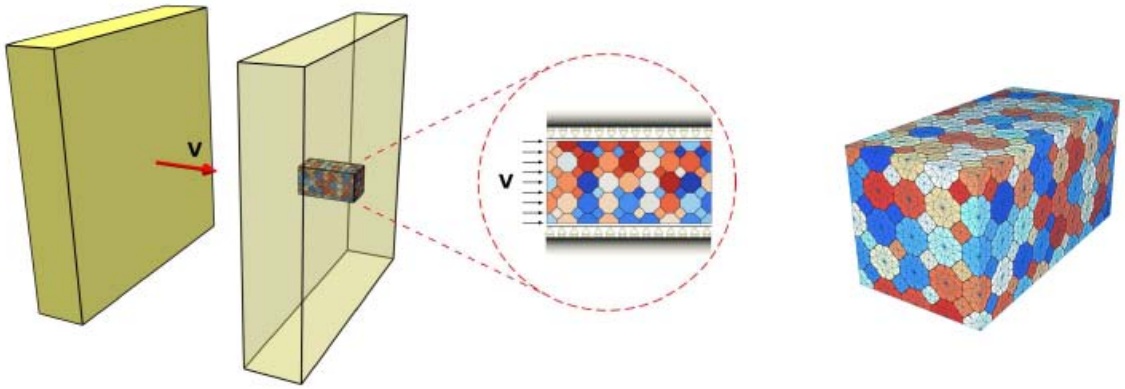


Fig.2.2



(a) (b)

FIG. 3: Plate impact test simulation. a) Definition of computational domain and boundary conditions. b) Finite-element mesh resolving the polycrystalline structure of the sample.

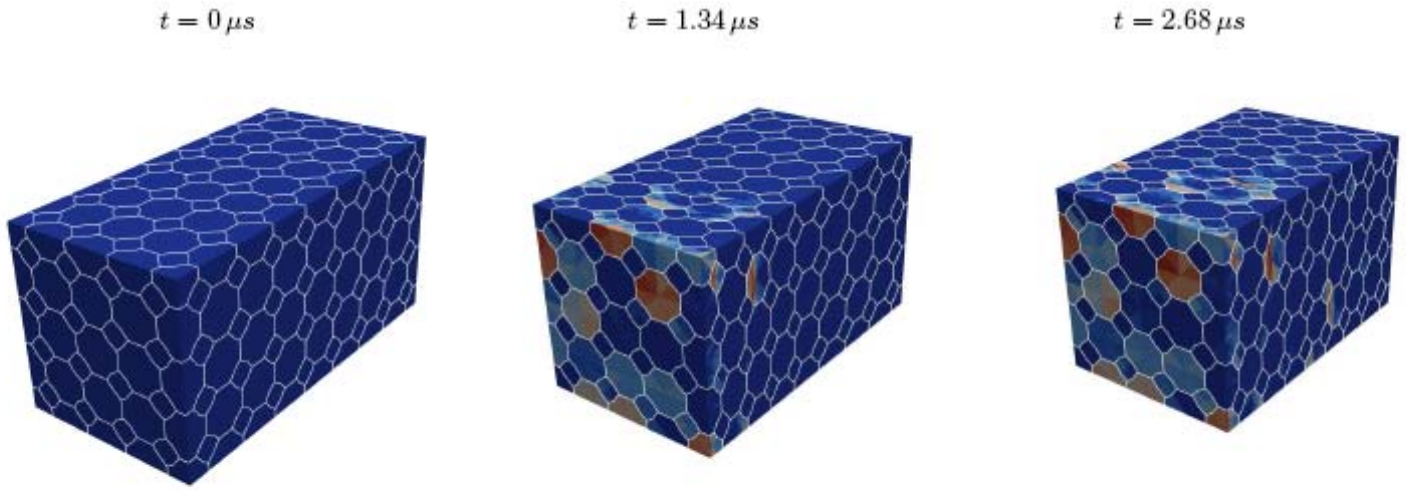


Fig.2.5 Macroscopic evolution of temperature for an impact velocity of 700m/s. Red and blue colors in the figure correspond to temperatures of θ=400 K and θ=273 K, respectively.

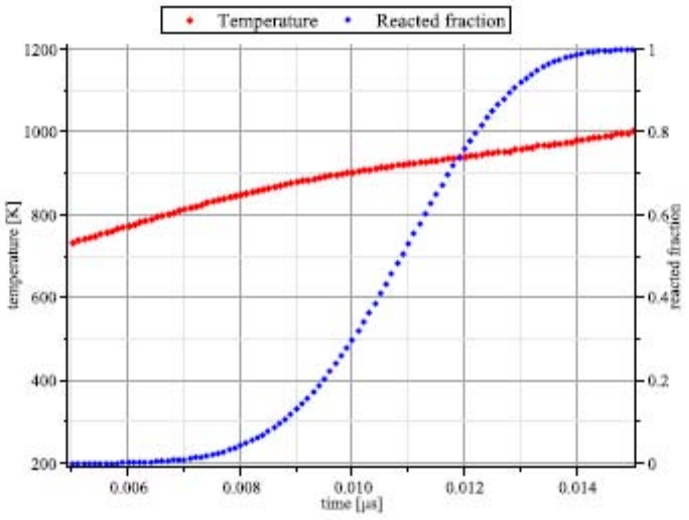


Fig.2.7: Temperature and reacted fraction evolution in a typical hot spot. Red diamonds and blue circles correspond to the temperature and the reacted fraction, respectively.

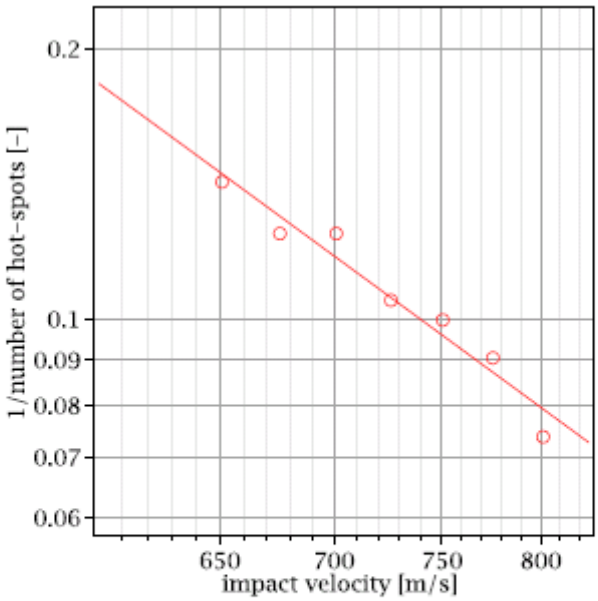


Fig.2.9: PETN plate impact simulation. Power-law scaling relation between the inverse of number of hot spots and the impact velocity. The circles are the simulation results for different impact velocities. The least square fit to the data shown by the solid line has the slope of 2.91.