AD-A148 017 APPLICATIONS OF MOLECULAR DYNAMICS TO THE STUDY OF SHOCK-INDUCED CHEMISTRY(U) NAVAL RESEARCH LAB WASHINGTON DC E S ORAN OCT 84 1/1

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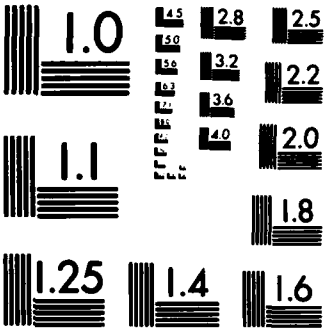

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) APPLICATIONS OF MOLECULAR DYNAMICS TO THE STUDY OF SHOCK-INDUCED CHEMISTRY		5. TYPE OF REPORT & PERIOD COVERED ~~1984~~ Annual Report 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Elaine S. Oran		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Laboratory for Computational Physics Naval Research Laboratory, Code 4040 Washington, D.C. 20375		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 61153N, RR011-03-0D NR 602-013 44-1950-0-4
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Arlington, Virginia 22217		12. REPORT DATE October 1984 13. NUMBER OF PAGES 7
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Molecular dynamics
Shock-induced chemistry
Energetic materials

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The goal of the program on Applications of Molecular Dynamics to the Study of Shock-Induced Chemistry is to develop and apply molecular dynamics techniques to problems in shock-induced chemistry in reactive and non-reactive materials. The three major thrusts of the work proposed are: (1)

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S/N 0102-LF-014-6601

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To develop phenomenological submodels of molecular interactions that can be used in full molecular dynamics calculations. In particular, to develop models which include known quantum mechanical properties of atoms and molecules, (2) to develop a model for doing many particle interactions on a vector computer, and (3) to apply the resulting numerical models to problems of shocks in condensed phase materials.

The first part of this research has been done in close collaboration with Dr. Hersch Rabitz at Princeton University and Dr. Robert Wyatt at the University of Texas in Austin. Recently, Dr. Boyd Waite from the U.S. Naval Academy has also been participating. The work has been coordinated with the Special Focus Programs in Energetic Materials at NRL and ONR. The work at NRL is partially supported by a 6.1 NRL research program in Computational Physics.

To date, we have concentrated on the first two aspects of the research. We have worked with Drs. Wyatt and Rabitz in deciding how to set up a test problem that could be used to test the way in which quantum mechanical effects can be phenomenologically modelled in a classical representation. Also, we have begun development and testing of a new vectorized algorithm for performing molecular dynamics simulations that will take advantage of the abilities of a CRAY. The progress on these areas is summarized in this report.

1984 ANNUAL REPORT FOR THE PROJECT

APPLICATIONS OF MOLECULAR DYNAMICS TO THE STUDY OF SHOCK-INDUCED CHEMISTRY

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Ms. Liz Gold (summer student, freshman at Princeton University)

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1. To develop phenomenological submodels of molecular interactions that can be used in full molecular dynamics calculations. In particular, to develop models which include known quantum mechanical properties of atoms and molecules.

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CURRENT STATUS OF RESEARCH

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Development of Submodels for Molecular Dynamics

Our goal is to create models of molecular interactions that represent some of the known quantum mechanical effects that do not appear in a purely classical representation. Such models could then be used in molecular dynamics calculations and would be one way of bridging the gap between classical and quantum calculations. Selected test problems are being solved classically, semi-classically, and quantum mechanically in order to develop these models.

After extensive discussions we decided on a test problem in which there are two collinear quantum harmonic oscillators, i.e., four particles, for which we nominally chose the masses and force constants to correspond to the oxygen and nitrogen molecules. The closest oxygen and nitrogen atom interact through a Lennard-Jones potential. This problem was solved three ways: classically (NRL), semi-classically (NRL), and quantum mechanically (Texas). The total energy of the system was to be large enough so that energy could go into the harmonic oscillator states and there would still be enough energy left for an unbound Lennard-Jones collision. Below we describe the current status of each of these calculations.

(a) Quantum Mechanical Calculations

A code to do the test problem quantum mechanically was set up at the University of Texas by Dr. Wyatt and his student, Mr. Don Miller. From this code we have extracted those portions required for the semi-classical calculation, i.e. the potential energy matrix. They have run the code for the test problem.

As the code is now written, direct comparisons can be made of the final state of the two molecules, given an initial state. However, we are interested in comparing the results along the course of a collision in order to develop models to update the states of many particles at fixed short intervals in the molecular dynamics simulations. We have not yet found a way to do this with their current formulation without a great deal of effort on their part. Thus for now, we can only compare their final answers to the semi-classical and classical calculations.

(b) Semi-Classical Calculations

There are three aspects of the work on the semi-classical formulation that we describe here: (1) finding the best way to solve the ordinary differential equations, (2) how to make the solutions conserve energy, i.e., how to handle the quantum-classical feedback problem; and (3) the recent interest of Dr. Boyd Waite from Annapolis in solving the test problem by the methods pioneered by Dr. William Miller from the University of California, Berkeley.

(1) A number of integration methods for the ordinary differential equations were tried. It was quickly determined the even a sophisticated fourth order Runge-Kutta was not good enough at the turn-around point of a collision. We were able to solve this problem by using a trick which we had already used very successfully in the classical calculations described

below: use a leap-frog method, which is second order, for the classical variables. The difference here was that we still used the Runge-Kutta for the quantum mechanical variables. This gives excellent results, due to the reversible property of a leap-frog method. It also allows us to take larger timesteps and do the calculation much more quickly. The variable timestep Runge-Kutta required an inordinate amount of time, especially at the turn-around points and lack of microscopic reversibility led to a nonphysical drift in the total energy of the system.

(2) In the first semi-classical calculations we performed, no feedback was allowed to the classical trajectory from anything happening to the quantum mechanical variables. The molecules approached each other, and the kinetic energy of the collision was converted into internal energy of the molecules through the Lennard-Jones potential. However, no mechanism existed in the formulation to slow down the collision as a result of energy being extracted. When the molecules separated, no mechanism existed to take energy from the internal states of the molecules and put it into kinetic energy of the system. Thus the result showed non-conservation of energy. Our solution was to devise a feedback mechanism which introduced this vibration-translation energy transfer in such a way that the energy conservation constraint remained satisfied. The idea is to monitor the expectation value of the unperturbed harmonic oscillator Hamiltonians and adjust the classical trajectory accordingly. This procedure gives a classical path which is a weighted average of the individual state-to-state trajectories at each point. These calculations are complete now, and must be compared with the the quantum mechanical and classical solutions.

(3) Dr. Boyd Waite from the Chemistry Department at Annapolis has done semi-classical calculations using the methods developed by Dr. William Miller

from the University of California, Berkeley. Dr. Waite is now applying his methods to the test problem we are doing.

(c) Classical Calculations

A rather general classical code was written that will treat an arbitrary number of particles, each pair of which will interact with an arbitrarily specified potential. This is not meant to be a full molecular dynamics model, but something which can be used as a test-bed for various potentials and models to be developed for the large scale molecular dynamics model described below. This model was configured for the four-particle test problem and a number of preliminary tests have been run.

The first tests involved integration method tests. Here we thoroughly tested the leap-frog method and found that it was extremely accurate and did an excellent job at conserving energy. The method was best when we kept the timestep constant, which is required to maintain the reversibility property. We have also devised an algorithm which keeps the distance between two atoms in a molecule fixed and still retains the necessary microscopic reversibility in the integration.

Calculations were then done to test the validity of the expansion of the Lennard-Jones potential developed at the University of Texas by comparing a range of classical calculations using it and the full potential. The expansion is excellent and for the worst cases tested, differences appeared only in the third or fourth decimal place.

We then performed the classical calculations of the test problem to compare with the semi-classical and quantum mechanical results. This involves many thousands of collision calculations with this code, each with varying initial energies and phases. There are a number of different ways to perform the statistics on these calculations. The

different ways involve different procedures for choosing initial energies and phases and binning the results. Dr. Waite consulted with us on how to formulate the statistics on the classical problem. We have also tested our classical calculation code against his as a benchmark, and currently his programs are also being used to solve the problem classically.

Molecular Dynamics Calculations

We are currently developing a three-dimensional vectorized molecular dynamics model that will host the submodels described above. Performing accurate enough calculations with enough particles to get reasonable statistics is the heart of the molecular dynamics problem. One of the key problems here is computing the interaction of each particle with all of the particles around it. Among N particles, there are N-squared interactions to be considered. The computer costs to perform all of these calculations is exhorbitant without a suitable trick.

This problem has led us to devise a three-dimensional nearest neighbor algorithm whose cost scales as the number N of independant objects, not the square of N as with previous algorithms. The algorithm is based on a dynamic monotonic logical grid which is constructed so that nearby data in the logical grid is automatically guaranteed to correspond to points which are nearby in real space. It executes in small array processors and also partitions directly to take advantage of multitasking asynchronous parallelism in distributed processing systems. We have shown that the present test model executes extremely fast on a problem involving 512 particles, and we believe that this is an order of magnitude faster than any other current existing method. The relative gains will be even greater for larger systems because of the favorable scaling.

PROPOSED RESEARCH

In FY'85 we will

1. Complete the comparisons of the solution of the test problem which was solved classically, semi-classically, and quantum mechanically.

2. Begin development of phenomenological models for including quantum mechanical effects in classical molecular dynamics calculations.

3. Set up the molecular dynamics calculation with the new monotonic logical grid algorithm. Test it on a standard condensation problem after a number of suitable tests of the new gridding algorithms. Include a framework for inserting phenomenological quantum models.

PUBLICATIONS and PRESENTATIONS

A Comparison of Quantal, Classical, and Semiclassical Descriptions of a Model Collinear Inelastic Diatomic Collision, currently being completed, M.Page, D. Miller, R. Wyatt, H. Rabitz, E. Oran, and B. Waite.

A Vectorized "Nearest-Neighbor" Algorithm of Order N Using a Monotonic Logical Grid, currently being completed, J. Boris.

A Vectorized "Nearest-Neighbor" Algorithm of Order N Using a Monotonic Logical Grid, J. Boris, Meeting of the American Physical Society, Boston, October, 1984.

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