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MOLECULAR DYNAMICS STUDIES OF ENERGY TRANSFER PROCESSES IN CRYSTAL SYSTEMS

(Annual Summary Report)

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Lawrence Livermore National Laboratory

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Annual Summary Report

MOLECULAR DYNAMICS STUDIES OF ENERGY TRANSFER PROCESSES IN CRYSTAL SYSTEMS

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A. INTRODUCTION

It is now well-established that computer molecular dynamics (CMD) can provide a unique insight into the behavior of shocked systems which, at present, is inaccessible to direct experimental investigation.[1-4] The basic reason is that CMD studies show that shock fronts are characterized by violent local structure at the atomic and molecular levels, which varies drastically over time durations of the order of femtoseconds to picoseconds.[5] Since present experimental studies typically examine a system over nanosecond or greater time intervals and in micrometer dimensions, it follows that such experiments will monitor spatial and temporal average behavior rather than the true local behavior. Although experiments have been done with considerably shorter scales of time or distance, none as yet have been done where both scales have been shortened simultaneously. However, recent studies on shocks in water[6] represent major advances toward this goal.

Shock-induced fast-decomposition processes brought about by shock passage through a condensed material represent the type of phenomena where the temporal and spatial scales involved lead us directly to considerations of a microscopic nature. Our present studies focus on an important specific facet of this problem, namely the energy transfer processes occurring in crystal and molecular lattices.[7,8] By studying the dynamics of intramolecular energy exchange we obtain information concerning the rate of energy concentration and partitioning in molecular bonds and, from this, the probability of a given amount of vibrational energy being found as a function of time in any given bond. By studying the relationship of intramolecular energy exchange to the initial energy distribution and distortion of different molecular entities after shock passage, we may be able to isolate conditions affecting the dynamics of vibrational energy transfer or leading to fragmentation or bond rearrangement (i.e., "chemistry"). Localization of bond energy coupled with specific athermal processes may well be important precursors to decomposition and reaction.

During the past year we have emphasized the development of techniques for post-processing the raw CMD data, with the principal aim of achieving some

optimum capability which will combine reasonable compactness with the retention of the maximum amount of information about the CMD history of each shock study.[9,10] It is important to avoid the wholesale destruction of information, obtained at considerable expense in computer time, that results from forming broad averages over many atoms and/or long time intervals. Our preliminary studies appear to clearly demonstrate the potential usefulness of Fourier transforming from the temporal to the frequency domain as a means of data reduction, thus providing a "fingerprint" identification of the various characteristic frequencies in any given atomic/molecular process. These transforms have, in addition, demonstrated again that shock loading can excite high-frequency intramolecular motions over picosecond time intervals in a strongly athermal manner.[9,10]

B. CODE DEVELOPMENT

During the preceding contract period, our molecular dynamics codes have been significantly extended to allow for a monitoring of local variables, such as energy, as a function of time for any selected region, or for the entire ensemble of interacting particles. In this way we can observe the manner in which energy flows into and out of any particular unit, and, in the case of a polyatomic unit, the energy flux between different degrees of freedom.[11,12] Further compacting of the flux data has been found desirable and is accomplished by computing the temporal Fourier transforms. This can be done for varying time intervals and the whole history reduced to a manageable number of figures. Thus, the frequency fingerprints for a given system can be presented before, during, and after shock front transit through the tagged system. For a one- or two-atom unit one can completely specify the state of the system by giving its center-of-mass energy, its rotational energy about the center of mass, and its vibrational energy. We have chosen to separate the total energy of any assembly into these constituents. This is a perfectly valid separation and no approximations are involved. However, the energy components are not constants of the motion, and even for a two-body system the vibrational and rotational motions are coupled by the Coriolis coupling which can be very strong.

Specifically, in computer program development during the contract period we have:

- revised and extended the codes that have been developed for general heterogeneous systems. A more intelligent neighbor search algorithm has been implemented. Mirror boundary conditions have been added to supplement the standard periodic boundary conditions. Any combination of periodic, mirror, and free boundary conditions can now be selected for any one-dimensional, two-dimensional, or three-dimensional system. Codes that formerly were maintained separately for 1D, 2D, or 3D systems have now been combined into a single, more compact routine in which the dimensionality is pre-selected. A more general multi-grid, or multi-cluster, setup has supplanted the earlier version of the code where only a single plate and one lattice could be completely specified. Now each lattice, or grid, is given equal consideration and is specified by an appropriate set of initial conditions (temperature, center-of-mass motion, composition, etc.) that describe it. Any number of such lattices can be constructed for a given calculation.

- continued to develop the post-processing subroutines for Fourier analysis of the response of some pre-selected subset of the system to shock loading. Any number of regions can now have tagged particles, e.g., a "region" may be a specified polyatomic molecule or a number of similar or different molecules within the total assembly. The tagged particles can then be chosen to identify a particular bond, e.g., C-H or N-O, within these molecules. We monitor as a function of time the total energy of the tagged system, the total internal energy, the energies associated with rotational or librational motion (about the center of mass), and the vibrational energy imparted by the passage of the shock front, as well as the influence of the surrounding lattice cage.

- begun to incorporate the one-particle and two-particle statistical mechanical subroutines into the general molecular dynamics code. These subroutines enable us to calculate for a shock-loaded system such averaged quantities as the mass density, the longitudinal component of the momentum density, the longitudinal and transverse components of the kinetic contributions to the stress, the potential energy density, the longitudinal and transverse components of the potential contributions to the stress, and various contributions to the heat flux.

- continued to add graphics capabilities to aid in interpreting results. Specifically, the fast Fourier transform graphics have been considerably improved and made more user-interactive.

- begun to devise and implement procedures for following bond breaking and recombination using an approach that treats bonds on the basis of molecular units rather than on an atomic basis. This will be tested initially on a problem involving surface dissociation and recombination, a less complex dynamics problem, but where three-body interactions play an important role.

C. STUDIES OF ENERGY TRANSFER PROCESSES

Shock studies were carried out during the past year on ordered diatomic systems and on disordered systems.[9] Diatomic systems are important in their own right as the first step to the truly polyatomic systems represented by organic explosives and binders. Diatomic systems also lead naturally to the simplest type of disorder that can be implemented in a controlled fashion. For example, mass disorder can be introduced by beginning with a regular diatomic array and randomly replacing atoms of one sublattice by atoms of the other sublattice. Our results have shown the almost complete suppression of the atomically sharp shock front found in ordered systems.[9] This is shown by the disappearance of spall and by the general tendency for the coherent shock energy to degrade into quasi-random atomic motion leading to "quasi-melting," i.e., the semi-random emission of fragments. Examination of energy propagation through the light and heavy sublattices shows that propagation occurs primarily through the heavy sublattice.[9] This is consistent with the partition of energy between the center-of-mass and internal motion of each diatomic unit. The internal (within the center-of-mass system) motion, by definition, has no net momentum, thus momentum propagation is confined entirely to the overall center-of-mass motion and, for widely disparate masses, is primarily carried by the heavier atom.

This simplified picture would seem to imply that energy never reaches the internal motion, at least not beyond the first pair of columns. On closer examination, however, we can see that the impact of a neighboring pair of shocked columns on their unshocked forward neighbors is a more complex process. The pairs do not strike one another as hard rods; rather, the heavy members of the moving pair push directly only against the light column of the unshocked pair. Thus, initially they effectively push the light column before them without resistance. However, as this process compresses the initially unshocked columns, the bonds between them become more and more rigid, until the heavy column has assumed the bulk of the center-of-mass motion of the impacting pair of columns. At this point the shock front has effectively jumped one pair of columns and the transfer of energy is complete, <u>including</u>

the transfer of energy to the internal motion (light atom beating against heavy atom) within the center-of-mass system. This is an important point, possibly crucial, because it implies that the internal motion will be drastically athermal due both to the coherent and rapid nature of the energy transfer during a time $\sim$10-100 femtoseconds. From such a mechanism arise the bond ruptures at surfaces and other imperfections that we observe in our simulations.[5]

During the past year we have begun an examination of the importance of the interactions of shocks with lattice irregularities or surfaces, processes which seem to provide the most efficient means of conversion of shock-energy into single atom/radical energy. Initial calculations in which a line defect is simulated by heavy substitutional atoms, a zero-order approximation to a dislocation or twin boundary, indicate that high-frequency components are suppressed in the atomic and molecular motions in the "sheltered" region behind the line defect.[10] With respect to surfaces, it is of interest to observe the amount of energy delivered to one of the diatomic units whose history is being studied, and to compare this with the bond rupture energy, in order to determine whether bond rupture would be possible at some local surface. Bond rupture in the bulk of the lattice is precluded by the caging effect of the neighboring atoms. In all of our studies it appears that surface bond breaking is indeed the case for moderate to strong shock loading even though the actual lattice "temperature" is quite low. The principal reason for this apparent paradox is that bond rupture at a surface is an irreversible process which is likely to occur whenever the instantaneous bond energy exceeds the bond rupture energy. Thus, while in the bulk, energy flows coherently into and out of bonds as the shock transits the lattice and, after the passage of the front, the average bond energy reverts essentially to its value prior to the shock incidence, at the surface/void the instantaneous bond extension can exceed the bond energy and readily produced rupture, or monomolecular decomposition. Hence, by this means are formed atomic (ionic/-radical) fragments of high reactivity which, when produced in sufficiently large concentrations, can initiate a propagating chemical reaction.

Finally, we have completed a series of two-dimensional model studies of the nitroso-methyl radical incorporated into a matrix of atoms three or four times heavier than the heaviest of the molecular atoms. The entire array is shocked by bringing in with uniform velocity a small "plate" of the same atoms as those of the host matrix. The energy content of the molecule as a whole has been monitored as a function of time, as well as the energy flux into and out of specific bonds. This has been done for two cases, one in which the radical is embedded well within the lattice and a second where the radical is ejected from the lattice along with a sizeable amount of spalled material. The second case simulates a typical molecule spalled from the surface of a shocked medium and allows us to examine to what extent the energy distribution among the various bonds is athermal and to monitor the subsequent history including possible bond rupture. The results of this study of the evolution of a shocked molecule in a host matrix are being analyzed and will be shortly submitted for publication.[13]

Thus, as we have discussed in the previous Annual Report,[14] our present CRAY computer codes provide us with unique resources for investigating on a microscopic scale all aspects of energy transfer from a shock front to the molecular substructure of a condensed system, as well as intermodal energy transfer between or within molecular units, or between the unit and its surrounding lattice cage.

We are planning to continue studies of the underlying mechanisms of intermolecular-intramolecular energy transfer and the dynamics of intramolecular energy exchange. These, we believe, are central issues for an understanding of shock-induced initiation. In addition, we are planning more studies involving features such as defects, voids, and grain boundaries in order that the influence of such heterogeneities on energy transfer can be evaluated. We will continue to exploit the following features of our molecular dynamics codes:

- the ability to handle totally heterogeneous dynamical systems with arbitrarily complex subensembles. This feature, which has been made even more general during the past year, allows us to include explicitly in the

molecular dynamics those portions of the total potential energy surface relevant to bond formation and configurational restructuring.

- the ability to look explicitly at complex molecular structures embedded in host lattices and molecular matrices. This enables us to consider in detail the pathways by which energy can be transferred from the shock front region to specific bonds or molecular units, and to delineate the dynamics of energy concentration and partitioning among the molecular bonds. The ability to treat systems of arbitrary complexity also permits an examination of energy transfer from a propagating shock front to such structural irregularities as dislocations and grain boundaries, with the possibility of generating high-frequency modes that may excite molecular modes of the lattice.

- the developing ability to treat bonds based on molecular units rather than atoms. This enables us to treat the restructuring of bonds and, therefore, the associated chemistry and will enable us to examine exothermic systems under varying initial conditions of shock pressure, temperature, and the presence or absence of defects and structural features. The specific design of our computer codes permits early implementation of this "chemically smart" molecular dynamics. Much of our program development during the next year will be focussed in this direction.

In summary, we are continuing to implement novel features in our codes, codes that represent many years of development and a resource enabling us to treat the problems that we have described in a successful and timely fashion.

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