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Equations incorporating adiabatic, isothermal, and isoenergetic constraints are developed and applied to simulations of gases, liquids, and solids. to We have obtained realistic fluid detonation-wave profiles. This work is summarized in Pages 2-18. We have studied the structure of uniaxially and hydrostatically-compressed solids and the transfer of energy among translational and internal molecular modes. are studied. This work is described in Pages 19-26. We have developed novel computational methods are dev for simulating nonequilibrium processes using Gauss' Principle of Least Constraint. Keywords: This work is described in Pages 27-38.

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"FUNDAMENTAL STUDY OF DENSE-FLUID DETONATION"

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Fundamental Study of Dense-Fluid Detonation

We have obtained realistic fluid detonation-wave profiles. This work is summarized in Pages 2-18.

We have studied the structure of uniaxially and hydrostatically-compressed solids and the transfer of energy among translational and internal molecular modes. This work is described in Pages 19-26.

We have developed novel computational methods for simulating nonequilibrium processes using Gauss' Principle of Least Constraint. This work is described in Pages 27-38.

SUMMARY

(1) TECHNICAL PROBLEM

We are investigating mathematical models of detonation in dense fluids and in solids. We wish to obtain a fundamental understanding of the interaction of pressure waves, or shockwaves, with high explosives.

(2) GENERAL METHODOLOGY

We are solving the steady-state dynamical equations of continuum mechanics, including viscosity, conductivity, and chemical reactions, to simulate detonation in fluids capable of undergoing fast exothermic reactions. We are solving the coupled ordinary differential equations of motion of molecular dynamics, for solids, to simulate the initiation process preceding detonation. We are examining simple models designed to describe the results of these macroscopic and microscopic approaches.

(3) TECHNICAL RESULTS

We have obtained detonation wave profiles, using a realistic dense-fluid equation of state. We have compared these profiles to the predictions of the simplified Zeldovich-Von Neumann-Doering model.

We have developed methods for simulating the rapid uniaxial compression of solids suited to molecular dynamics simulation.

We have formulated the interatomic distribution function in solids, for comparison with atomistic simulations and use in kinetic reaction models.

(4) IMPLICATION FOR FURTHER RESEARCH

The relatively long vibrational relaxation times occurring in shocked diatomic molecules with realistic values of viscosity and thermal conductivity suggest that the nonequilibrium distribution of energy is more important than the interaction of ordinary transport properties with chemical reactions. We therefore intend to concentrate, in the next two years, on reaction initiation and intramolecular energy transfers in reacting molecules in the solid phase.

I. INTRODUCTION

Shock and detonation waves involve atomic-scale processes which are imperfectly understood and hard to measure. For this reason we have embarked on a program, using modern computational methods, of studying the processes through which mechanical shockwave energy stimulates the release of chemical energy within a detonation wave.

Our work entails the correlation of two points of view: continuum mechanics and atomic mechanics. We seek to understand the limitations of the continuum approach in dealing with atomic-scale problems and to develop methods for describing these small-scale processes in a realistic way.

Considerable information on the equilibrium and transport properties of simple systems is now available(1,2). Computer simulations of dense fluids, coupled with thermodynamic perturbation theories(3) based on simple hard and soft sphere models, make it possible to describe the pressure-volume-temperature equation of state accurately, for sufficiently simple materials. For some "realistic" potentials, such as the Lennard-Jones 6-12 interatomic potential, comprehensive computer simulation studies have established the density and temperature dependence of the viscosities and the thermal conductivity as well(2). Much less is known about the contribution of intramolecular degrees of freedom to the transport properties and equation of state. Studies on molecules like methane and benzene indicate that the computer simulation approach is now feasible, even for molecules containing several atoms(4).

A numerical study, comparing the continuum and atomistic versions of a very strong dense-fluid shockwave made use of both the equilibrium and non-equilibrium constitutive properties of the 6-12 potential, and indicated that useful conclusions could be drawn by comparing the two approaches(5). A natural extension of that work is to consider the possibility of coupling chemical reactions with the dissipative processes of viscosity and thermal conductivity which appear in shockwaves. That coupled combination is a detonation wave.

The simplest prototype condensed-phase high explosive is probably nitric oxide, NO. This molecule forms molecular nitrogen and oxygen in an exothermic reaction generating approximately 100 kilobars pressure(6). We set out with the goal of simulating the detonation of liquid NO using both the continuum and atomistic approaches. The continuum calculations are complete. Using an equation of state which describes the Lennard-Jones potential throughout the fluid regions of the phase diagram, and transport coefficients from the Enskog theory, we have generated detonation profiles as functions of the energy release and activation energy of the dense-fluid detonation. These calculations, including viscosities and thermal conductivity, are compared to the Zeldovich-Von Neumann-Doering model in Section II.

Shortly after this work was begun, a research program was initiated at Los Alamos, designed to measure and to model the detonation of nitric oxide. This program includes experimental, quantum mechanical, and dynamical groups working toward a common goal. Related Los Alamos research, carried out by Brad Holian, Galen Straub, and their co-workers, has established that the equilibration time between vibrational and translational temperatures in dense diatomic fluids (nitrogen) is relatively long(7), just as in the gas phase. These long equilibration times, of order 100 vibration times, suggest that the complete combustion process is impractically long for an atomistic simulation. For this reason we have concentrated our more recent work on solid-phase initiation and mode equilibrium. We are developing solid-phase calculations in which chemically active molecules can be studied under uniaxial and homogeneous adiabatic compression. That work is described in Sections III and IV. We expect to devote the next two years' effort to enhancing our understanding of solid-phase detonation initiation from the atomistic mechanical point of view.

II. DENSE-FLUID DETONATION WAVE STRUCTURE

The classical steady one-dimensional ZND (for Zeldovich, Von Neumann, and Doering) model of detonation-wave structure can be summarized with the help of Figure 1. It is assumed that the reactants can assume the equilibrium unreacted thermodynamic states shown on the lower Hugoniot curve as the result of shock compression. Each of these states satisfies the condition that its mass, momentum, and energy fluxes agree with those characterizing the initial state (state 0). This unreacted Hugoniot is hypothetical because chemical reactions will gradually transform the reactants, at least for strong enough shockwaves, to hot products.

The fully reacted products can also be described by a Hugoniot curve satisfying the conservation laws. This is the upper Hugoniot. Its position, relative to the lower Hugoniot, depends upon the heat of reaction Q. The Zeldovich-Von Neumann-Doering detonation wave model pictures the detonation process as two consecutive steps: first, the reactants are shock-compressed to the (Von Neumann spike) state S. Next, these hot reactants slowly undergo chemical reactions, proceeding to the final (Chapman-Jouguet) state CJ. During the reaction phase the state point follows the Rayleigh line, satisfying the constraints of constant mass and momentum flux necessary in a steady wave. Neither the transport coefficients nor the reaction rate enter into Figure 1. These state functions determine the space and time scales associated with the compression and reaction phases of the detonation wave.

The ZND model is an oversimplification. With the theory of liquids sufficiently advanced that quantitative calculations, including nonideal effects, can be made, there is no real need for an inaccurate treatment.

Molecular dynamics simulations have shown that strong dense-fluid shockwaves can be described fairly well by the Navier-Stokes equation(5). Figure 2 indicates the relatively good agreement between the Navier-Stokes continuum calculations and the atomistic simulations. The principle disagreements are these: The wave is about 30% broader than the continuum predictions and the velocity distribution is considerably more complex than is the equilibrium Maxwell-Boltzmann distribution. The alternative Mott-Smith approach(8), in which the velocity distribution is a weighted average of the reactant and product Maxwellian distributions, grossly overestimates the nonequilibrium character of the wave.

We initially planned to carry out a similar comparison for nitric oxide, a simple liquid which undergoes the reaction

$$2NO = N_2 + O_2. \qquad (1)$$

Exploratory calculations fitted to the kinetics of the reaction showed that the reaction zone extends for thousands of angstroms, far too long for molecular dynamics simulation. The liquid detonation wave profile that we display in Figure 3, together with the ZND approximation to that profile, was calculated(9) with an activation energy approximately half that of nitric oxide. This substantially reduced the spatial extent of the detonation wave. Under this artificial assumption there is a noticeable quantitative discrepancy between the simple two-step model and the solution of the coupled equations. There is no such dramatic difference for nitric oxide, at least for a one-dimensional wave.

The instability of one-dimensional low-density detonation waves is well-established experimentally(10). Because this effect is at least as important as that of the hydrodynamic transport coefficients we see that further study of the one-dimensional detonation wave for nitric oxide, is not feasible, using molecular dynamics.

Vibrational energy transfer is very slow in diatomic molecules because the single vibrational mode is well-separated from the "lattice modes." The situation is less clear cut for polyatomic molecules with many degrees of freedom. Can the solid-phase initiation problem be understood using equilibrium chemical kinetics and equilibrium energy surfaces? Are nonequilibrium velocity distributions and intramolecular energy transfer significant? The answers to these questions are unknown despite considerable interest and debate(11). We are concentrating our efforts on enhanced understanding of solid-phase initiation, using the methods outlined in the following sections.

III. COMPUTER SIMULATIONS AT HIGH RATES OF STRAIN

To explore the rapid deformation associated with shockwaves in condensed fluids and solids we have developed special methods for solving the equations of motion of atoms in a rapidly-deforming fluid or solid(12). These methods were originally developed and applied to the simulation of viscous flows(13) and were later applied to solid-phase plasticity(14). In either case the macroscopic flow is described by a given strain-rate tensor ∇u, where u is the hydrodynamic flow velocity. To incorporate the flow velocity into the equations of motion, a perturbation, the tensor product of ∇u and Doll's tensor (the dyadic composed the particles' summed coordinate-momentum product qp) is added to the Hamiltonian function. Equations of motion result which include contributions proportional to the strain rate:

$$\begin{aligned} \dot{q} &= (p/m) + q\cdot\nabla u \; ; \\ \dot{p} &= F - \nabla u\cdot p \; ; \\ \dot{E} &= - VP{:}\nabla u \; . \end{aligned} \tag{2}$$

Equations (2) describe adiabatic homogeneous deformation. This scheme has been used to make quantitative estimates of the shear and bulk viscosities for dense fluids.

Inhomogeneous compressions must be treated differently. The system is sheared or compressed by moving periodic images(5). Either method could be applied to chemically-reacting solids. We expect to explore the homogeneous uniaxial compression of two systems: The simple reaction model described in the next section and a "realistic" three-dimensional polyatomic model of a detonating solid. This latter application should allow us to map out the path followed by energy during the equilibration process.

IV. ATOMIC DISTRIBUTION FUNCTIONS IN SOLIDS

We are currently investigating a simple model for reacting atoms: Two atoms sufficiently close together react, releasing an energy Q. Equilibrium simulations (with $Q=0$) have been carried out to determine the density, strain, and temperature dependence of the "reaction rate." Figure 4 indicates the substantial dependence on strain biaxiality. Pastine's model(15), which contains an adjustable collision frequency ω, can be used to fit the uniaxial compression results.

A more fundamental approach incorporates the distribution of neighboring atoms. In the quasiharmonic case this can be done exactly. We have developed a numerical method for the partial integration of the Boltzmann factor, $\exp(-\Phi/kT)$, over all but two particle coordinates, leading to an atom-atom distribution function. This function is a product of Gaussians.

Because the calculation is somewhat intricate it is important to have a check available. The close-packed lattice, with nearest-neighbor interactions, is ideal for this purpose. Because the potential energy of a nearest-neighbor pair in a D-dimensional close-packed crystal is $kT/(D+1)$, the mean-squared deviation in the nearest-neighbor spacing should be $2kT/(D+1)\kappa$, where κ is the nearest-neighbor force constant. We have verified that this result is reproduced exactly by our numerical approach, and find that the convergence of higher-order and transverse correlations is relatively rapid and smooth as the number of particles in the periodic cell is increased. In the two-dimensional case, for example, the ratios of the nearest-neighbor mean-squared longitudinal to transverse fluctuations for 9, 16, 25, and 36-atom crystals are 0.667, 0.688, 0.695, and 0.696(16).

We expect to apply this same technique to the atom-atom distribution function for polyatomic crystals undergoing uniaxial compression. This analog of Pastine's model should prove useful in estimating the dependence of reaction rate on the macroscopic strain rate.

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FIGURES:

1. Diatomic reactant and product Hugoniots calculated with the Lennard-Jones equation of state. The well depth and collision diameter are ε and σ, respectively. The initial volume is $0.8442N\sigma^3$. The initial temperature is $0.722\varepsilon/k$.
2. Shockwave profile for a strong fluid shock carrying the triple-point argon to a final temperature of about one electron volt. The smooth curves are the Navier-Stokes solution. The points correspond to data from nonequilibrium molecular dynamics.
3. Detonation profile calculated using (a) the hydrodynamic equations, including viscosity and heat conduction, and (b) using the ZND model. The activatation energy is artifically reduced to enhance the difference between the two approaches. The heat of reaction is 100ε and the activation energy is 70ε.
4. Reaction rate as a function of density for a simple binary-collision model. Both uniaxial and hydrostatic compressions are shown at a temperature about half the melting temperature. Pastine's model for the rate is shown as the full curve.

Figure 1

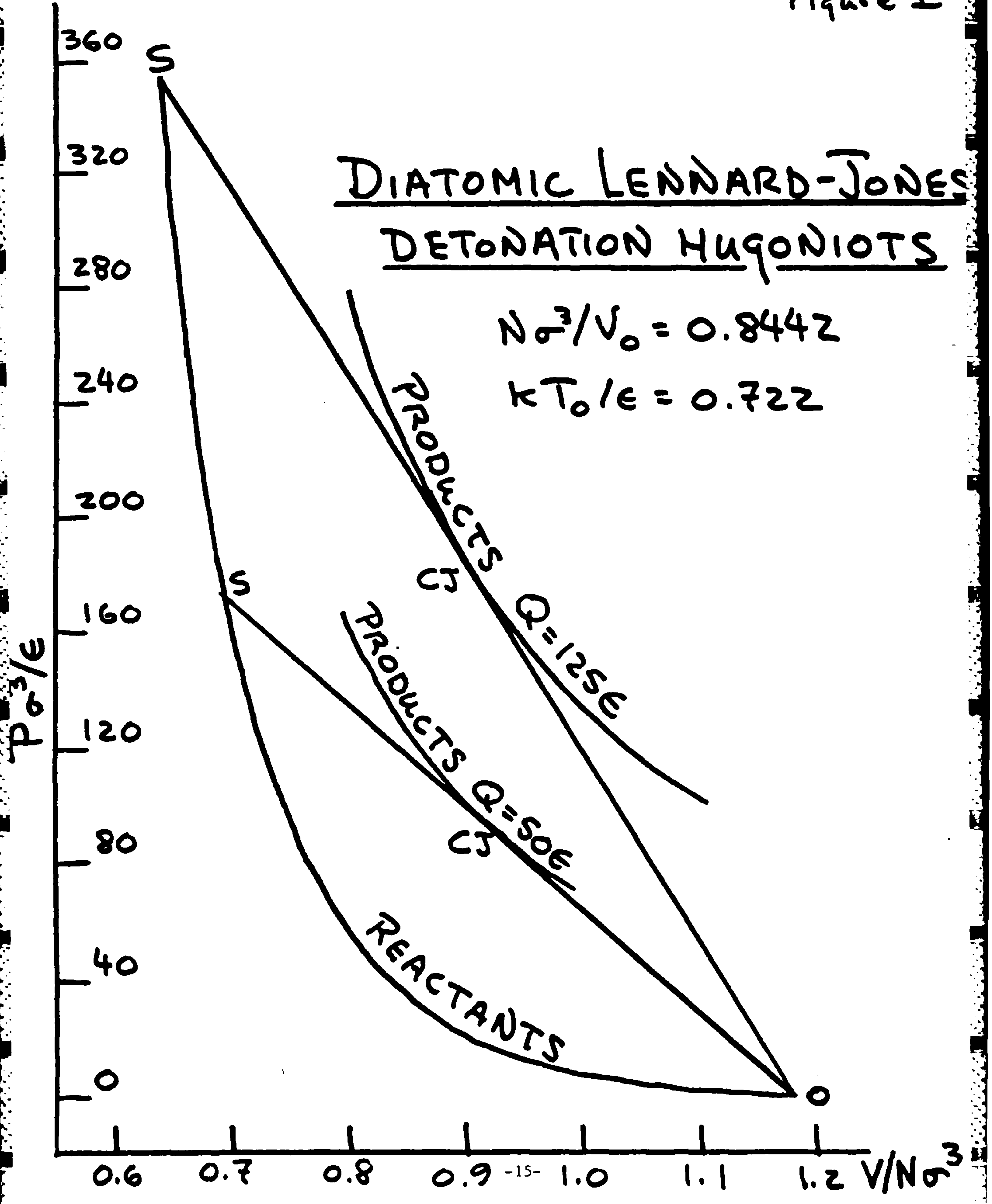

DIATOMIC LENNARD-JONES
DETONATION HUGONIOTS
$N\sigma^3/V_0 = 0.8442$
$kT_0/\epsilon = 0.722$
S
S
PRODUCTS
Q=125ε
CJ
PRODUCTS Q=50ε
CJ
REACTANTS
O
$P\sigma^3/\epsilon$
360
320
280
240
200
160
120
80
40
0
0.6
0.7
0.8
0.9
1.0
1.1
1.2
$V/N\sigma^3$

Figure 2

MONATOMIC LENNARD-JONES SHOCKWAVE PROFILES (SEE REF. 5)

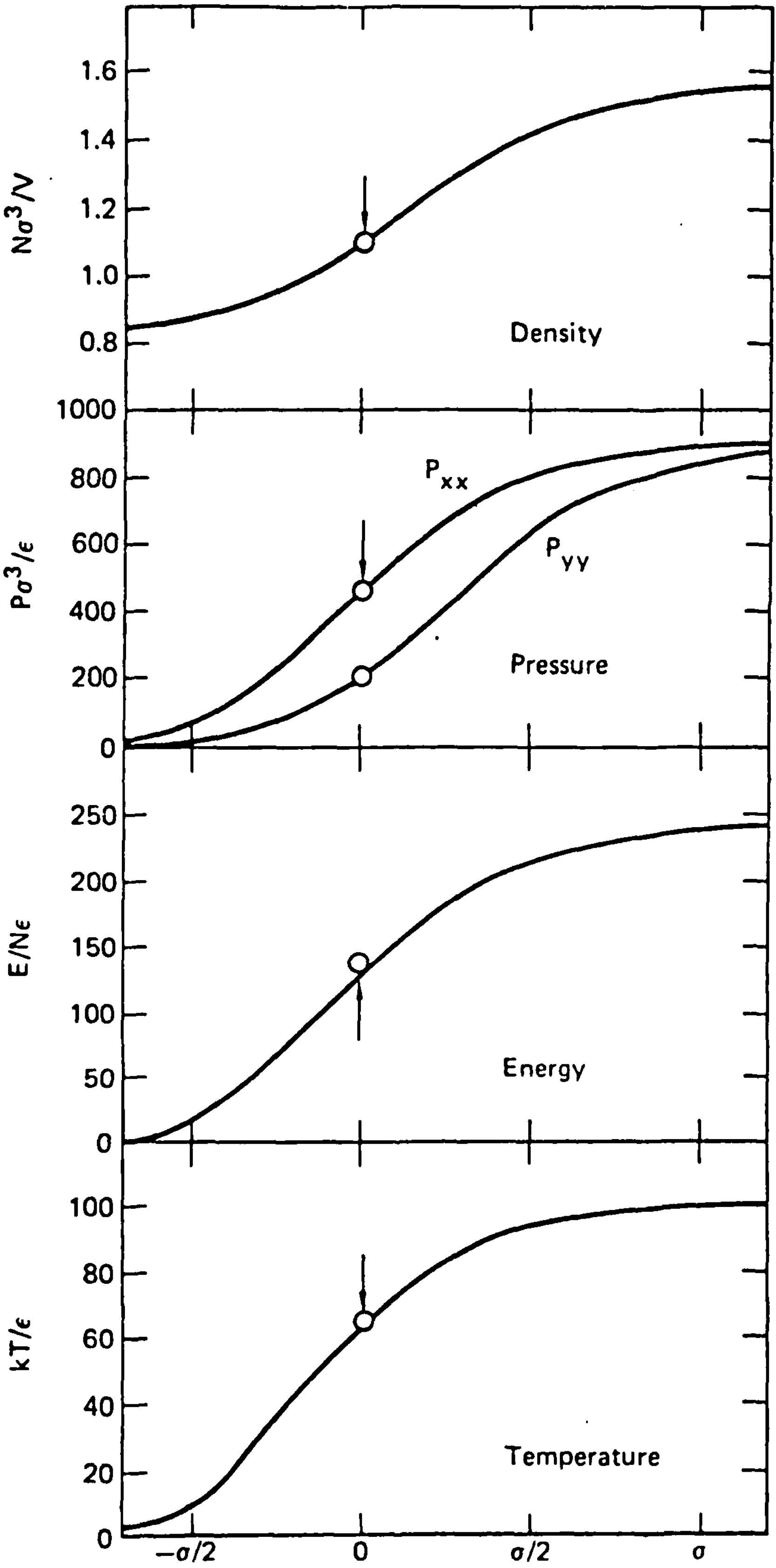
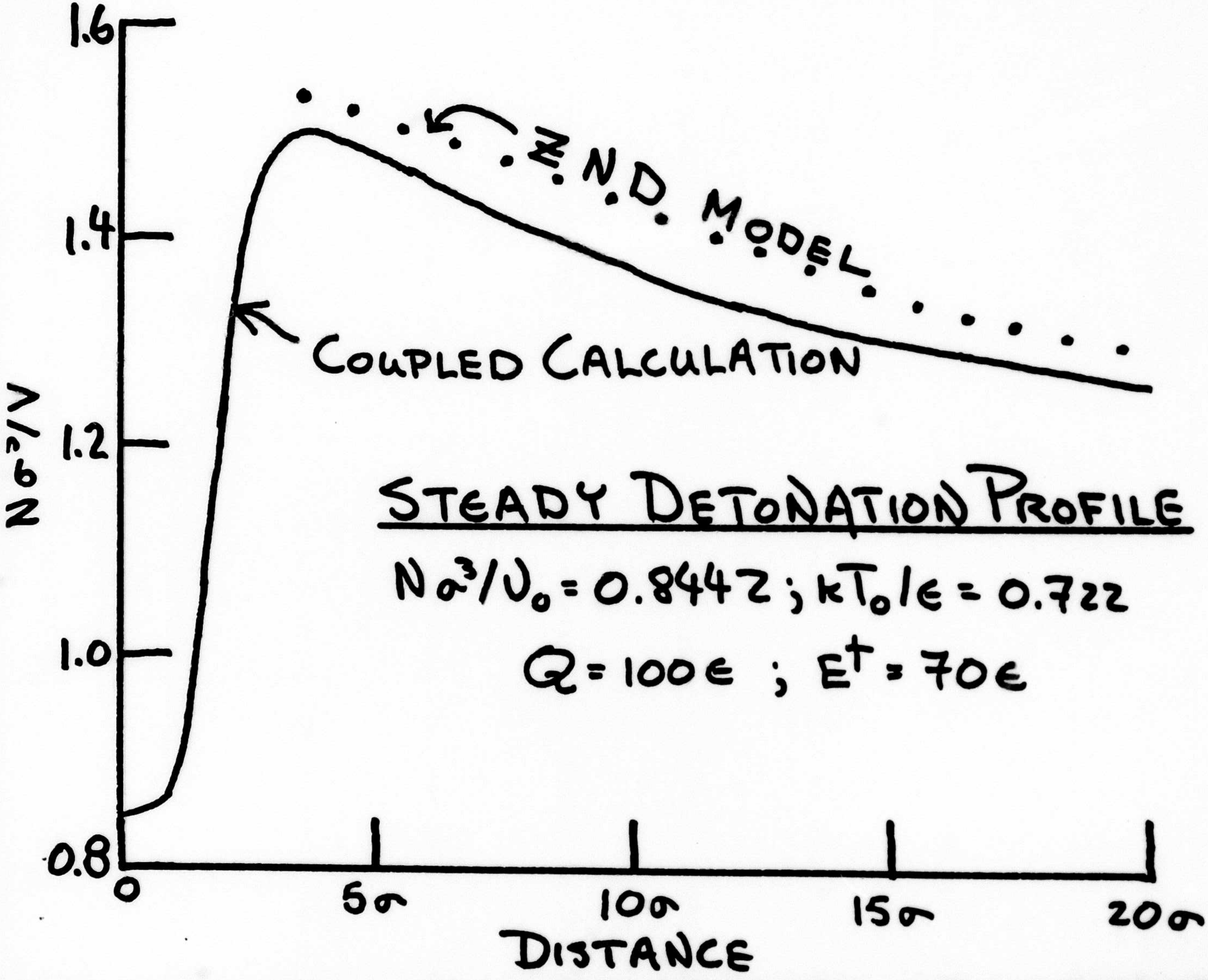


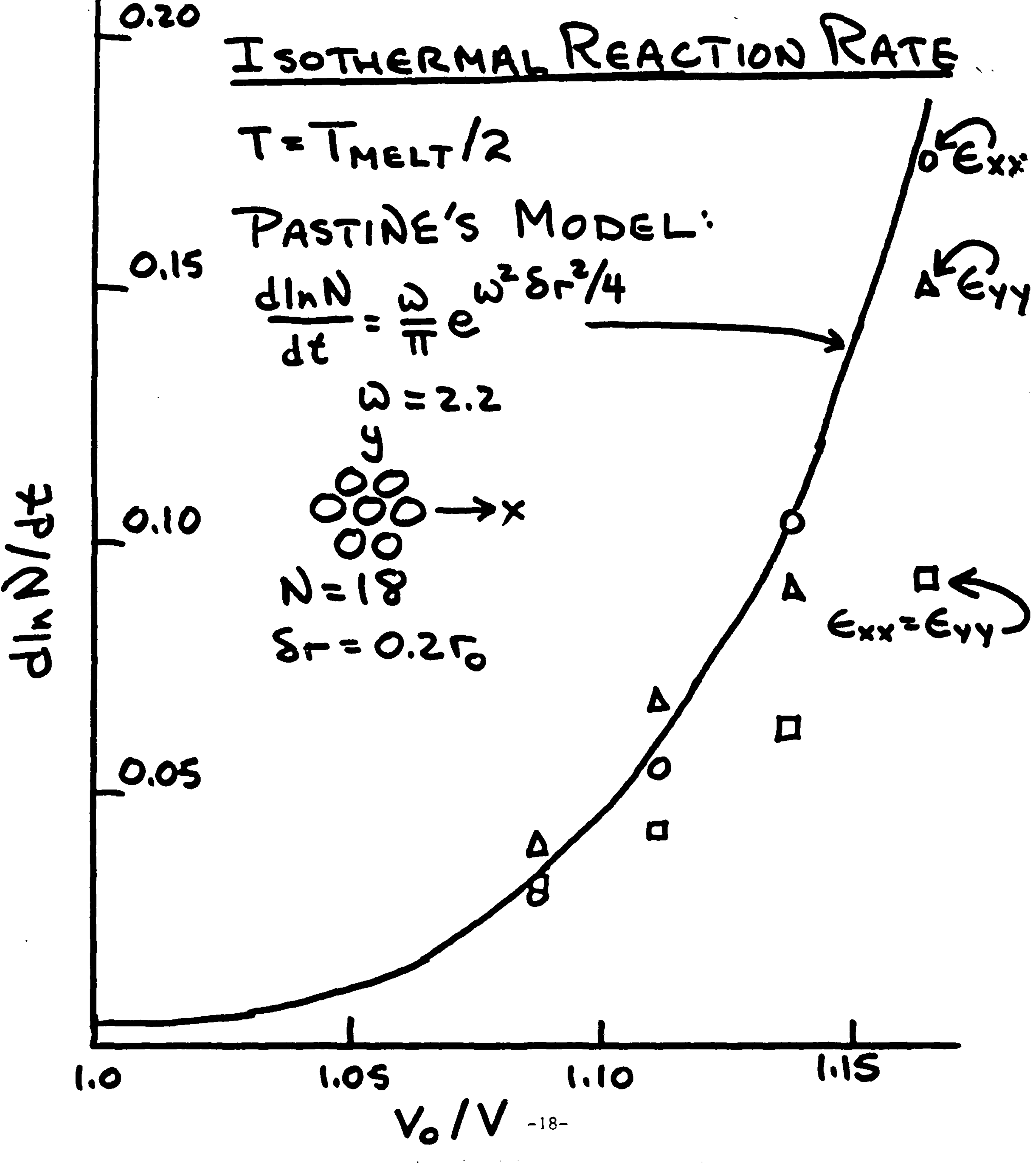
Figure 3



STEADY DETONATION PROFILE
$N\sigma^3/V_0 = 0.8442$; $kT_0/\epsilon = 0.722$
$Q = 100\epsilon$; $E^{\dagger} = 70\epsilon$
Z.N.D. MODEL
COUPLED CALCULATION
$N\sigma^3/V$
1.6
1.4
1.2
1.0
0.8
0
5σ
10σ
15σ
20σ
DISTANCE

Figure 4

Triangular Lattice



SUMMARY

(1) TECHNICAL PROBLEM

We are investigating atomistic mathematical models of energy transferred in condensed media. We wish to obtain a fundamental understanding of the interaction of compressive waves with intermolecular and intramolecular energies, leading to the initiation of detonation.

(2) GENERAL METHODOLOGY

We analyze quasistatic compression by comparing equilibrium statistical-mechanical calculations with the results of equilibrium Newtonian molecular dynamics simulations. We are developing and solving nonequilibrium, equations of motion to describe the rapid compression of microscopic polyatomic systems. We emphasize the flow of energy among the molecular degrees of freedom excited by the compression process.

(3) TECHNICAL RESULTS

We have determined the atomistic pair distribution function for planar crystals undergoing both uniaxial and hydrostatic compression. We have compared these distributions to the predictions of the Pastine-Kamlet-Jacobs model.

We have simulated bimolecular collisions of triatomic and hexatomic planar molecules (with hexanitrobenzene in mind). We analyze the normal-mode vibrations before and after collision and observe the transfer of energy among the translational, rotational, and vibrational modes.

(4) FURTHER RESEARCH IMPLICATIONS

The simulations of rapid deformation will be extended to larger molecules, in three dimensions, and will be made consistent with macroscopic thermodynamics. These extensions require equations of motion incorporating a nonequilibrium inhomogeneous deformation satisfying the adiabatic first law $\dot{E} \equiv -VP:\nabla u$.

I. INTRODUCTION

Shock and detonation waves involve atomic-scale processes which are imperfectly understood and hard to measure. The systems contain too many atoms for an accurate quantum-mechanical treatment. Classical calculations can deal with systems of hundreds or thousands of interacting atoms, over hundreds or thousands of vibrational periods.

To evaluate the utility of the microscopic approach we have embarked on a program to develop and apply modern computational methods to the nonequilibrium dynamical processes responsible for explosive initiation. A detailed microscopic view is necessitated by the violent nonequilibrium nature of shock compression. Simulations show that the intrinsic width of a shock front is only a few atomic diameters.[1] Thus the usual concept of equilibrium temperature, with Arrhenius kinetics, is unlikely to provide an understanding of the initiation of chemical reactions.[2] To achieve understanding of initiation detailed studies of rapid nonequilibrium intermolecular and intramolecular energy transfer must be carried out and analyzed.

Over the past several years there has been considerable progress in treating the deformation of simple monatomic fluids and solids. The techniques developed have been tested by intercomparison with experimental data and with less-efficient older simulation techniques.[3] The irreversible heating associated with rapid viscons and plastic deformation has been avoided by developing isothermal equations of motion.[4] These equations constrain the second moment of the velocity distribution, $\langle(v-\langle v\rangle^2\rangle$, to a fixed value. Analogous developments for treating diffusion and conduction stem from this same foundation.[5]

These new methods have not been applied to flexible polyatomic molecules. In order to carry out this generalization we have analyzed both quasistatic and rapid deformations of monatomic crystals (Section II), the rotational and collisional transfer of polyatomic molecular energies (Section III), and the thermodynamic consistency of rapid polyatomic deformation (Section IV). During the remainder of this contract we will combine the energy transfer and deformation techniques to study a model of solid hexanitrobenzene.

II. DEFORMATION OF MONATOMIC SOLIDS

In a series of studies we have characterized the compression of simple fluids and solids. We recently carried out a detailed study of equilibrium pair distribution functions in deformed two-dimensional crystals.[6] Both Hooke's-Law and Lennard-Jones forces were used. The pair distributions, obtained by integrating the quasiharmonic canonical probability density, differ from approximate theoretical treatments in two ways. First, contributions from all normal-mode vibrations are included. Second, reaction-rate contributions from all diatomic orientations are included. For these reasons the reaction rates follow neither the simple Gruneisen density dependence nor Arrhenius kinetics. Even under quasistatic conditions, uniaxial compression generally yields significantly higher collision (or reaction) rates than does the corresponding hydrostatic compression.

Earlier deformation studies, under both shockwave and homogeneous conditions, have demonstrated the utility of incorporating the macroscopic velocity gradient ∇u directly into microscopic equations of motions. The shockwave studies emphasized the nonequilibrium velocity distribution in the shock-front. Shockwave structure, bulk and shear viscosities, and solid-phase high-strain-rate yield stengths[7] have all been determined in this way. Adiabatic deformation can be modeled by adding an extra contribution to the atomic velocities, $\dot{q} = q \cdot \nabla u$, and a corresponding force $\dot{p} = -\nabla u \cdot p$. The two modifications lead to the thermodynamic identity

$$\dot{E} = -VP:\nabla u,$$

where E is internal energy and P is the pressure tensor. This adiabatic deformation can be made isothermal instead by including an additional collective force $-\zeta p$, with ζ chosen to keep $\langle p^2/m \rangle$ constant.

III. ENERGY TRANSFER IN POLYATOMIC MOLECULES

The simplest polyatomic molecule exhibiting energy transfer is a planar triatomic molecule, with three vibrational degrees of freedom. In this case the two degenerate vibrational modes are coupled by Coriolis forces. Thus rotation of the molecule, even very slowly, leads to a geometric coupling of two vibrational amplitudes.

Regular hexatomic planar molecules have nine vibrational degrees of freedom, with four pairs of degenerate modes in addition to the symmetric breathing mode. At reasonable rotational velocities the coupling among the four pairs is negligible. Even at vanishing velocities Cordiolis coupling again causes the cycling back and forth between degenerate mode amplitudes.

We have simulated bimolecular collisions of both triangular and hexagonal planar molecules, have analyzed their normal-mode vibrations throughout the collision process, and have observed energy transfer among all the translational, rotational, and vibrational degrees of freedom. Presently we are characterizing the energy distribution during a homogeneous compression.

IV. THERMODYNAMICS OF RAPID DEFORMATION

The virial theorem relates the pressure tensor to interatomic forces. In the familiar monatomic form[8] each Newton's equation of motion is multiplied by the corresponding particle coordinate, summed and averaged, to give

$$\sum\sum r_i F_{ij} - VP = \sum \frac{d}{dt}(m r \dot{r})_i - (m \dot{r} \dot{r})_i .$$

which is equivalent to

$$PV = NkTI + \sum r_{ij} F_{ij}$$

where N is the number of atoms in the volume pairs. For polyatomic molecules it is convenient to multiply each atom's equation of motion by the center of mass coordinate for its molecule. The force terms in each molecule cancel, with the result:

$$PV = NkTI + \sum R_{ij} F_{ij}$$

where N is now the number of <u>molecules</u> and F_{ij} is the vector sum of forces of all atoms in molecule I due to atoms in molecule J.

Now consider two kinds of adiabatic deformation. In "atomic" deformation each atom undergoes a displacement proportional to its location

$$\dot{r} = r \cdot \nabla u$$

and a corresponding force

$$\dot{p} = -p \cdot \nabla u .$$

The adiabatic first-law identity, $\dot{E} = -VP:\nabla u$, follows. In "molecular" deformation each atom undergoes a displacment proportional to the center-of-mass coordinate R:

$$\dot{r} = R \cdot \nabla u$$

as well as a corresponding force

$$\dot{p} = -P\left(\frac{m}{M}\right) \cdot \nabla u .$$

The identify $\dot{E} = -PV:\nabla u$ again follows, provided that P is the "molecular" pressure.

It is presently unknown which of these formulations best describes adiabatic polyatomic deformation. We will apply both methods to rapid deformation of hexagonal molecules in our energy transfer simulations in the coming year.

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SUMMARY

(1) TECHNICAL PROBLEM

We consider atomistic descriptions of matter, far from equilibrium, in order to understand the mechanisms underlying detonation in high explosives. We focus on solid hexanitrobenzene.

(2) GENERAL METHODOLOGY

We develop equations of motion incorporating both thermal and mechanical constraints. Adiabatic, isothermal, and isoenergetic processes can be simulated by solving these equations numerically. We study many special cases involving gases, liquids, and solids.

(3) TECHNICAL RESULTS

We have established the usefulness and the limits of "Gauss' Principle of Least Constraint" in classical many-body simulations. We have applied three different types of feedback control to atomistic systems in studying fluid and solid heat flow. We have considered the size-dependence of constitutive properties. We have developed a simple stress-free model for crystalline hexanitrobenzene.

(4) IMPLICATION FOR FURTHER RESEARCH

The tools developed facilitate simulations far from equilibrium. The result is enhanced correlative and predictive capabilities for systems undergoing nanosecond to picosecond thermal and mechanical processes. This is a rapidly-changing field fundamental to the understanding of complex material behavior.

I. INTRODUCTION

Systems far from equilibrium can only be simulated with dynamic equations of motion incorporating nonequilibrium temperature, velocity, and stress distributions. During the past decade a variety of nonequilibrium simulation techniques have been developed. During the past three years a consolidation and simplification has taken place: it has been realized that simple feedback analysis can be applied to hydrodynamic and solid mechanics problems in a way consistent with macroscopic constitutive analyses. This field has been reviewed recently[1,2,3]. The highlights are as follows:

(1) There is an old mechanical principle, due to Gauss, "Gauss' Principle of Least Constraint", which is more general than Newtonian or Lagrangian mechanics. Gauss' Principle makes it possible to develop equations of motion with nonholonomic constraints. Such constraints include, for instance, the restrictions that a particular process be carried out with a given time and space variation of temperature or energy or stress. Gauss' Principle has been widely tested, during the past three years, and found to be useful in studying steady flow far from equilibrium.

(2) There is a new idea, due to Shuichi Nosè(Yokahama), which makes it possible to simulate, with molecular dynamics, systems described with independent variables such as temperature and stress, as opposed to energy and volume.[4,5,6] Nosè's ideas are extremely interesting for theoretical mechanics and suggest new practical techniques, different to Gauss', for treating systems far from equilibrium.

(3) Both Gauss' and Nosè's ideas can be viewed as special cases of Control Theory[7]. This realization has increased the multiplicity of algorithms available, but with the advantage of a systematic description. The

consequences of this development are now only beginning to be explored. This is a most exciting development in mechanics, with implications for quantum as well as classical systems.

During the past three years we have contributed to the development of these ideas while carrying out an investigation of solid hexanitrobenzene. The complexities associated with modelling this material precluded a complete study of its response to shockwave initiation and detonation, but the groundwork and the tools necessary to this simulation are now in place.

The following sections describe the new techniques available for atomistic simulations, a simple model for crystalline hexanitrobenzene, and recommendations for further work.

II. NEW TECHNIQUES IN SIMULATIONS FAR FROM EQUILIBRIUM

In 1972 Ashurst simulated the flow of momentum p and the flow of heat between atomistic reservoirs. He performed a momentum rescaling

$$p' = (1 + e_2)\, p + e_1$$

in which the small numbers e_1 and e_2 were chosen to restore the first and second moments of the velocity distribution to desired values. His were the first systematic studies of nonequilibrium systems using nonequilibrium molecular dynamics[8].

In 1982 Evans and Hoover noted that the rescaling of momenta could be carried out in a continuous way by adding a constraint force to the equation of motion for each particle:

$$F_c = - zp + F_o \quad .$$

Hoover pointed out that this same constraint force can be derived from Gauss Principle of Least Constraint. By 1985 it became clear that many forms of nonequilibrium constraint forces are possible. These were applied to a variety of systems far from equilibrium[3].

The theoretical bases of these constraint forces advanced too. It was possible to show that exact linear transport coefficients could be generated in steady nonequilibrium simulations. Even nonlinear effects, such as the decrease of viscosity with strain rate and the increase or decrease of conductivity with heat flux, depended only weakly on the particular constraint force used. In the present section we summarize the two successful approaches which emerged from this work and point out their usefulness in studying systems far from equilibrium.

A. Gauss' Principle

Gauss stated that any conceivable constraint on a dynamical system should be implemented by minimizing the mean squared value of the constraint force divided by the corresponding mass:

$$\Sigma F^2/m \text{ minimized. (Gauss' Principle)}$$

This principle provides a unique prescription for carrying out simulations of nonequilibrium flows. Several consequences of this principle have been explored. Constant-energy and constant-temperature (with temperature $T = p^2/3mk$, where k is Boltzmann's constant) shear flows yield nearly identical viscosity coefficients, even far from equilibrium.[9] Self-diffusion, shear and bulk viscosity, and heat conduction can be studied in very small systems (two particles for the first three transport coefficients, and three for heat flow).[10-12] When periodic boundaries are used, to eliminate surface effects, the resulting two-particle transport coefficients lie within a factor of two of the many-body thermodynamic limit. Thus it appears that nonequilibrium results have an intrinsic number-dependence no greater than the equilibrium dependence, 1/N, where N is the number of particles.[13]

Gauss' principle can lead to erroneous results. If a simulation is carried out with fixed heat-flux vector and fixed temperature the corresponding thermal conductivity can be in error, in a dense fluid, by several percent.[14]

Nevertheless, a variety of simulations led to accurate values for the transport coefficients of simple fluids and solids. These new data suggested useful corresponding states relations between the transport coefficients and equilibrium data[15].

These same calculations also suggest that the nonequilibrium conditions prevailing in a strong shockwave be simulated by dynamical adiabatic compressions, with the time of the compression chosen to correspond to the picosecond timescale of rising stress in a real shockwave. In such a rapid compression it can be anticipated that coupling of the vibrational and translational modes is incomplete and that highly nonequilibrium energy distributions resulting from the lack of coupling produce chemical reactions at far different rates than would be predicted from Arhenius kinetics. The relaxation process is just beginning to be studied in a serious way by using nonequilibrium molecular dynamics.[16] These results indicate that Nosé's Dynamics is best suited to simulations far from equilibrium.

B. Nosé's Dynamics

Nosé pointed out that if the friction coefficient z in the generalized equation of motion

$$m\ddot{r} = F(r) - zp \quad ,$$

relaxes according to a first-order differential equation

$$\dot{z} = a(p^2 - 3mkT) \quad ,$$

where a is fixed, the equilibrium distribution is identical to Gibbs' canonical distribution for the temperature T.

This approach has been generalized to nonequilibrium systems and appears to be very successful. Just as is the case with Gauss' principle it is possible to analyze systems close to equilibrium and to show that Nosé's dynamics provides exact linear transport coefficients. By making temperature depend upon space and time, and by introducing also stress as an independent (tensor) variable it is straightforward to generalize Nosé's approach to the treatment of nonequilibrium problems such as the adiabatic compression of hexanitrobenzene. These simulations have not yet been carried out, because they are relatively complex, but the tools for doing this are now available. The model for crystalline hexanitrobenzene is described in the next section.

III. HEXANITROBENZENE

Hexanitrobenzene, $(CNO_2)_6$, is a crystalline high explosive, about twice the density of water, first synthesized and characterized in Russia[17]. Initial attempts to make this material in the United States failed. Later, when it became clear that hexanitrobenzene is sensitive both to water and to light, military interest in it subsided. Nevertheless, from the scientific standpoint this substance is extremely interesting. Because it contains no hydrogen it is reasonable to use a classical description for its motion.

The molecules have sixfold rotational symmetry, but with the nitro groups aligned like blades of a propellor to alleviate steric repulsion of neighboring oxygens. The crystal structure was described in 1966 by Akopyan, Struchkov, and Dashevskii. For reasons that are not clear the sixfold symmetry is broken in the crystalline phase. The molecules are arranged in layers with nearly hexagonal symmetry, with each nearly-equilateral triangle of molecules having a "long" side about one percent longer than its two "short" sides. These nearly hexagonal sheets are stacked, in a nearly-face-centered-cubic arrangement: ABCABCABC..., with a spacing between planes 4.08Å, considerably smaller than the lengths of the triangle legs, 9.05 and 9.13Å.

Discussions with quantum chemists indicated that a reliable simulation of the breakup of a hexanitrobenzene molecule is beyond the state of the art. A likely mechanism is the breakup, due to bending, of one of the six nitro groups. Faced with a lack of detailed information on the breakup mechanism we modelled the molecule as six carbon atoms and six nitro groups, with 6x3+6x3=36 degrees of freedom per molecule. Interactions within the molecules can be treated in the quasiharmonic approximation. Interactions between molecules were based on a truncated Lennard-Jones potential to which a Hooke's-law potential was added in such a way as to bring both the potential and its first derivative (minus the force) to zero at the potential cutoff.

Exploratory calculations, in two dimensions, established that the energy was lowered by about 7% if the molecules were allowed to rotate. In these calculations the Lennard-Jones potential was cut off at twice the distance to the potential minimum which was in turn three times the C-C or C-NO_2 separation distance. In the three-dimensional case both the nearly-hexagonal and nearly-face-centered forms of the structure were studied. The least-energy rotation, just over 8 degrees, was approximately equal to that found in two dimensions. The intermolecular and interplanar spacings were 8.75Å and 2.67Å, respectively. The corresponding experimental values are (9.05, 9.05, 9.13)Å and 4.08Å. The energies of the two forms studied agreed to four-figure accuracy. Because the range of the potential exceeds twice the interplanar spacing the numbers are in fact slightly different.

A final investigation was designed to match the experimental spacings of hexanitrobenzene, 9.08Å and 4.08Å. A stress-free unit cell was constructed using a potential minimum at 4.56Å and a C-C + C-NO_2 separation of 2.79Å. Again the two forms of crystal agreed in energy to four-figure accuracy. A well depth of 9.6×10^{-14} ergs was chosen approximately to reproduce the estimated heat of vaporization of the crystal. A detailed report of these calculations is in preparation[18].

IV. RECOMMENDATIONS

It is recommended that a study of the normal-mode energies, bond displacements, and angular distortions in the model of hexanitrobenzene be studied as a function of initial temperature, shockwidth and strength of shockwave. These calculations would be useful in assessing the validity of competing theories of vibrational relaxation, as described by Holian[16] and in further developing techniques for predicting the sensitivity of new explosive chemicals to detonation.

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