

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36

TITLE. COMPUTER SIMULATION OF NONEQUILIBRIUM PROCESSES

LA-UR--85-2473

AUTHOR(S) Duane C. Wallace, X-4

DE85 015708

SUBMITTED TO A.P.S. Topical Conference on Shock Waves in Condensed Matter,
Spokane, July, 1985

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

By acceptance of this article the publisher recognizes that the U S Government retains a nonexclusive royalty-free license to publish or reproduce the published form of this contribution or to allow others to do so, for U S Government purposes

The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U S Department of Energy

Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

COMPUTER SIMULATION OF NONEQUILIBRIUM PROCESSES

Duane C. Wallace

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

ABSTRACT

The underlying concepts of nonequilibrium statistical mechanics, and of irreversible thermodynamics, will be described. The question at hand is then, How are these concepts to be realized in computer simulations of many-particle systems? The answer will be given for dissipative deformation processes in solids, on three hierarchical levels: heterogeneous plastic flow, dislocation dynamics, and molecular dynamics. Application to the shock process will be discussed.

I. STATISTICAL FOUNDATIONS

We begin by reviewing the underlying concepts of statistical mechanics, both nonequilibrium and equilibrium, and of thermodynamics, both irreversible and reversible. These concepts are rather old, and are hardly taught in school nowadays; undoubtedly many of the younger students will be surprised (startled?) to learn that there exists a well-established and logical framework for treating general nonequilibrium processes. While the essential points will be covered in the present paper, additional details can be found in two recent references of a review nature.^{1,2}

Nonequilibrium Statistical Mechanics

In order to define the various statistical and thermodynamic theories, and to see their regions of applicability and their interconnections, it is easiest to start with the most general theory, namely nonequilibrium statistical mechanics. For this discussion, the system we consider is a nearly-ideal gas; it is composed of atoms whose only important interactions are binary elastic collisions. The gas is divided into a large number of cells, each with a constant total mass. (Alternatively, one can choose the cells to have constant volume, it is merely a convention.) Each cell contains a large number of atoms, and is treated as a statistical subsystem. Let $\{p\}$ represent the atomic momenta, and let M be the mass of one atom. The momentum distribution for the cell located at position r , at time t , is $f(\vec{p}, t)$. The important mechanical properties of a cell are its density $\rho(\vec{r}, t)$, its mean velocity $\vec{v}(\vec{r}, t)$, and its total energy $\epsilon(\vec{r}, t)$:

$$\rho(\vec{r}, t) = \int f(\vec{r}, \vec{p}, t) d\vec{p} \quad (1)$$

$$M\vec{v}(\vec{r}, t) = \frac{1}{\rho(\vec{r}, t)} \int \vec{p} f(\vec{r}, \vec{p}, t) d\vec{p} \quad (2)$$

$$e(\vec{r}, t) = \frac{1}{\rho(\vec{r}, t)} \int \frac{\vec{p}^2}{2M} f(\vec{r}, \vec{p}, t) d\vec{p} \quad (3)$$

Since we are dealing with a nearly ideal gas, the energy is entirely kinetic energy.

We now inquire about a nonequilibrium process for a system, subject to initial conditions and boundary conditions on the momentum distribution $f(\vec{r}, \vec{p}, t)$. For a nearly ideal gas, the process will be completely described by the Boltzmann equation, which gives the evolution of $f(\vec{r}, \vec{p}, t)$. This evolution is consistent with conservation of mass, momentum, and energy, and also contains a time-irreversible term, namely the collision integral. For a nongaseous system, there does not at present exist a transport equation capable of describing the evolution of the momentum distribution. For such a system, a partial description of a nonequilibrium process is obtained from the equations of continuum mechanics, which are the equations for conservation of mass, momentum, and energy, locally applied to the densities $\rho(\vec{r}, t)$, $\vec{v}(\vec{r}, t)$, and $e(\vec{r}, t)$. The continuum mechanic equations are always correct, but they alone are not sufficient to determine a process.

Equilibrium

For uniform boundary conditions, e.g. an isolated system with a fixed volume, the system will approach an equilibrium state. In discussing equilibrium, we take the mean velocity of the system to be zero, or else transform to center-of-mass coordinates, thus eliminating one parameter. Then for a nearly ideal gas, the Boltzmann equation tells us that the equilibrium momentum distribution is constant in space and time, and is merely a function of the momentum magnitude $p = |\vec{p}|$, and of two scalar parameters β and ρ :

$$f_0(p; \beta, \rho) = c(\beta, \rho) e^{-\beta p^2/2M} \quad (4)$$

$c(\beta, \rho)$ is a normalizing function, such that the system density is ρ ,

$$\rho = \int f_0(p; \beta, \rho) d\vec{p} \quad (5)$$

Then β turns out to be related to the kinetic energy density:

$$e = \frac{3}{2\beta} \quad (6)$$

At this point, it is worthwhile to recall the relations among the whole family of equilibrium theories. First, the Boltzmann equilibrium limit is equivalent to the ensemble theory of equilibrium statistical mechanics. The Boltzmann distribution $f_0(p; \beta, \rho)$ corresponds directly to the canonical ensemble, in which phase-space averages are performed for a fixed density with the canonical weight function $e^{-\beta H}$. Equilibrium thermodynamics (which is often called "thermodynamics" for short) is made equivalent to equilibrium statistical mechanics through the identification of β with the temperature T :

$$\beta = \frac{1}{kT} \quad (7)$$

where k is Boltzmann's constant. Equilibrium thermodynamics then describes reversible processes, since by definition these are processes which are constrained to pass continuously through equilibrium states. Incidentally, the customary notion that a process will be reversible if it is done slowly enough is not always correct, as is shown by the example of elastic-plastic deformation in a solid.²

Irreversible Thermodynamics

Let us suppress the position and time variables, and write the momentum distribution simply $f(\vec{p})$. In the function space for $f(\vec{p})$, the equilibrium functions $f_0(p; \beta, \rho)$ occupy an extremely small part, only a two-dimensional surface (β and ρ) in an infinite-dimensional space. This is an important observation, because it is only on the equilibrium surface that the equilibrium quantities are defined. In particular, the temperature T and the entropy S are defined only on the equilibrium surface.

We now consider processes which are close to equilibrium. Specifically, this means that $f(\vec{p})$ is locally given by

$$f(\vec{p}) = f_0(p; \beta, \rho) + \delta f(\vec{p}) \quad , \quad (8)$$

where $\delta f(\vec{p})$ can be treated as a perturbation. Hence $f(\vec{p})$ is still restricted to a very small part of the total function space: it is close to the equilibrium surface. Within this region, however, the equilibrium quantities are defined approximately, and the thermodynamic relations among these quantities still hold approximately. This is the region of irreversible thermodynamics. In other words, an irreversible-thermodynamic process is one which passes through states which are sufficiently close to equilibrium so that the thermodynamic quantities can be meaningfully defined. Irreversible thermodynamics thus represents a very small part of the theory of nonequilibrium statistical mechanics.

Irreversible thermodynamics is characterized by dissipative force-flow processes. The force-flow relation is called the constitutive equation. For example, in heat conduction, the force is the temperature gradient $\vec{\nabla}T$, the flow is the heat current \vec{J} , and the constitutive equation is

$$\vec{J} = -\kappa \vec{\nabla}T \quad , \quad (9)$$

where κ is the thermal conductivity of the material in question. Note that constitutive equations are not contained in any equilibrium theory. The dissipation produces entropy; in the case of heat conduction this is given by

$$TdS = dQ \quad , \quad (10)$$

where Q is the quantity of heat transported. To calculate an irreversible process, one needs a complete set of equations. For a process such as a shock, where material is accelerated, the complete set of equations consists of the equations of continuum mechanics, the constitutive equation, or whatever irreversible processes are driven by the shock (e.g. plastic flow, heat transport), the entropy-production equation, and some thermodynamic relations. Note that an entropy-production inequality, $TdS > \text{something}$, is not sufficient for irreversible thermodynamics.

The question arises, how can one tell if irreversible thermodynamics is in fact a valid theory for a given process in a given material? For a nearly-ideal gas, this question can be answered by checking irreversible thermodynamics against the Boltzmann equation. It is known in general that

the near-equilibrium solution of the Boltzmann equation is just the irreversible-thermodynamic solution for a viscous heat-conducting gas.¹ For other systems, computer simulations may eventually take the place of the Boltzmann equation. Or else one can first calculate the process from irreversible thermodynamics, then compare the spatial and temporal rates of change with appropriate relaxation lengths and times, to see if the system could in fact remain near equilibrium throughout the process.

II. MOLECULAR DYNAMICS

Ordinary MD

The procedure in ordinary MD is to place N particles in a computational cell, specify the potentials of interaction among the particles, and calculate the motion of the particles by numerically integrating the classical equations of motion (Newton's law). The calculation is usually done with periodic boundary conditions, in which the computational cell is surrounded by identical image cells, and particle interactions are allowed to cross cell walls. Periodic boundary conditions eliminate the large surface effects, of relative order $N^{-1/3}$, and introduce smaller effects of relative order N^{-1} . An extensive discussion of ordinary-MD techniques may be found in a recent review.³

There are two types of differences between an MD calculation and real nature. The first type of difference is in the interatomic potentials, which we never know exactly. The second type is due to computer artifacts, i.e. specific properties of the computer system which are not present in nature. This includes small- N effects: in natural systems N is enormous, while on

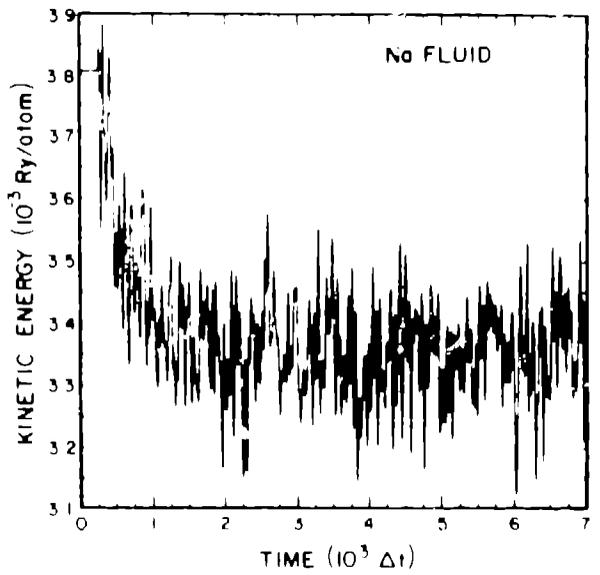


Fig. 1. Time development of the kinetic energy per atom for an MD system of sodium atoms. Initially the atoms are on bcc lattice sites, with a distribution of kinetic energies; the system evolves to an equilibrium fluid.

the computer we have $N \sim 10^3$. Another computer artifact is numerical integration with a finite timestep Δt ; I do not know how nature integrates the classical motion of a many-particle system, but it is probably not with a finite Δt . A group of us at Los Alamos has carried out extensive calculations of equilibrium thermodynamic properties of solid and fluid metallic sodium,⁴⁻¹² a material for which we have a good representation of the interatomic potentials.¹³ For equilibrium calculations, computer artifacts appear to be under control. The situation in nonequilibrium calculations is not yet known.

For an ordinary MD system of 686 sodium atoms, the evolution of the kinetic energy is shown in Figure 1. The calculation was started with the atoms at the equilibrium sites of a bcc lattice, and with a random Maxwellian velocity distribution. When the system comes to equilibrium, i.e. when the mean and bandwidth of the signal become essentially constant, the sodium is in the fluid phase. While this is an ordinary everyday graph of an ordinary MD run, it is to me a fascinating result. From a nonequilibrium initial state, the computer finds and establishes the correlations appropriate for the fluid equilibrium state. Furthermore, it is at least possible that the timescale of the approach to equilibrium, as seen in Figure 1, is a physically meaningful relaxation time for real metallic sodium.

Exotic MD

While it is a difficult problem to effectively simulate nature on a computer, it is no trouble at all for the computer to do things which are quite beyond nature's wildest imagination. It is this circumstance which has led to the statement,

"There used to be two realities in the world of physics:
Experiment and Theory. Now there are three, and the third one
is The Computer."

Of course, the computer's role is a legitimate one, and the computer will be of enormous help to us in many-particle problems. The point which will always require care is in properly interpreting what we do with the computer.

A major variation of molecular dynamics, which has achieved wide popularity in recent years, is to direct the computer to make specific changes in particle positions and/or velocities, at specific timesteps. Andersen¹⁴ proposed "MD at constant temperature," achieved by altering the momentum of random particles at random instants of time, and "MD at constant pressure," achieved by rescaling particle positions at each timestep. By means of a more general rescaling of particle positions, involving changes in shape as well as volume of the computational cell, Parrinello and Rahman¹⁵ extended Andersen's method to "MD at constant stress." Still another way of rescaling particle positions and velocities has been used by Abraham.^{16,17} This general variation of molecular dynamics is fine as a technique for sampling phase space, in the same way that the systems of an ensemble represent a sampling of phase space. The specific rule according to which particle positions and/or velocities are changed will then define the type of ensemble which is represented. However, this variation of molecular dynamics does not give the real physical evolution of a nonequilibrium system.

An entire field of nonequilibrium molecular dynamics has been developed, largely from the pioneering work of Bill Hoover.¹⁸⁻²⁰ Hoover's technique is to apply macroscopic forces to the MD system, from an external source, or through the boundary conditions, and also to modify the equations of motion by the addition of frictional forces applied to the individual particles. These two effects are then balanced so that the MD system remains in a nonequilibrium steady state. In this way, the system behavior can be simulated in states far from equilibrium. Of course, the question arises as to the

true source of irreversibility. In contrast to the usual point of view, where the equations of motion are reversible, and irreversibility presumably results from nonintegrability, Hoover uses equations of motion which are intrinsically irreversible. Since one does not have a physical justification for frictional forces in the atomic equations of motion, the physical meaning of Hoover's technique is at present unclear.

III. SOLID DEFORMATION ON THREE LEVELS

The three levels refer to different scales of size and time. The finest scale is the atomic scale, where the motions of individual atoms are studied; the intermediate scale is dislocation dynamics, where moving and interacting dislocations are studied; and the macroscopic scale is the continuum field theory of heterogeneous plastic flow. These scales form a hierarchy, because physical properties are related between neighboring levels.

Heterogeneous Plastic Flow

Let us begin by describing the "solid-dominant model" for plastic flow.² Consider a single crystal of material, containing one edge dislocation, as shown by the left drawings in Figure 2. This single crystal may be the entire sample under study, or it may be a small element inside a much larger sample. When a shear stress τ is applied to the surface of this crystal, it deforms elastically, as shown in Figure 2. Elastic forces are present throughout the crystal; these forces support elastic strain everywhere except at the dislocation core, and there the elastic forces drive the dislocation. When the dislocation moves, the top half of the crystal slides over the bottom half; the amount of this sliding is the plastic strain ϕ . The relation between the plastic strain rate $\dot{\phi}$ and the applied shear stress τ is the plastic constitutive relation for the crystal.

Now replace the entire slip plane of the dislocation by a shear band, as illustrated in the drawings on the right of Figure 2. When the same shear stress τ is applied, the crystal deforms elastically, with exactly the same elastic strain as before. Elastic forces are again present throughout the crystal, supporting elastic strain everywhere except in the shear band, where the elastic forces drive dislocations. Again the top half of the crystal slides over the bottom half, but now the sliding is presumably much faster than with only one dislocation present; $\dot{\phi}$ is much greater than before. Hence the essential difference between the presence of one dislocation, and a shear band, is a difference in the plastic constitutive relation.

We can summarize the main points of the solid-dominant model, as follows. Elastic strain and plastic strain are both present, and are independent variables. The shear stress satisfies simultaneously the elastic stress-strain relation, and the plastic constitutive relation. Work is done by stress driving strains; elastic work is reversible, and plastic work is mostly irreversible.

It is useful to contrast the behavior of a fluid with that of a solid. For a viscous fluid there is only one strain variable, namely the total strain, and the constitutive relation sets the shear stress proportional to the shear strain rate. The fact that fluid behavior does not contain an independent plastic strain variable is sufficient to show that an elastic-plastic solid cannot be represented by a fluid. Consider again the crystal illustrated in Figure 2. The drawings on the right are still correct if the shear band is replaced by a thin layer of viscous fluid; the crystal still has independent elastic and plastic strains, and the only thing that changes is the plastic constitutive relation. In order to eliminate the plastic strain as

an independent variable, one has to go all the way to the "fluid-dominant model," in which the material is supposed to be a fluid with some bits of solid distributed in it. Only in this limit will the material behave more like a fluid than a solid.

With a computer, we can calculate (simulate) a macroscopic process involving heterogeneous plastic flow, by numerically integrating the complete set of coupled differential equations. This set is composed of the equations of continuum mechanics, the plastic constitutive equation, the entropy production equation, and some equilibrium thermoelastic relations. Such a computation is generally called hydrodynamics, although solid dynamics would be a more accurate term. Note that it is possible in principle to resolve the heterogeneities, such as shear bands or growing voids, which may appear in a solid-dynamic process. This will certainly be done in the future. In the meantime, the practice is to replace the heterogeneities by a homogeneous model. Such a model contains parameters which represent the properties of the inhomogeneities, for example their density and their constitutive behavior. This approach is represented by the work of Lee Davison and co-workers,^{21, 22} and of James Johnson.²³

As a summary of the macroscopic theory of heterogeneous plastic flow, we list the essential input and output of this theory. The input is the complete set of coupled differential equations, together with the appropriate material properties, namely the thermodynamic and constitutive data. The output is a description of a macroscopic flow process, as e.g. a shock process.

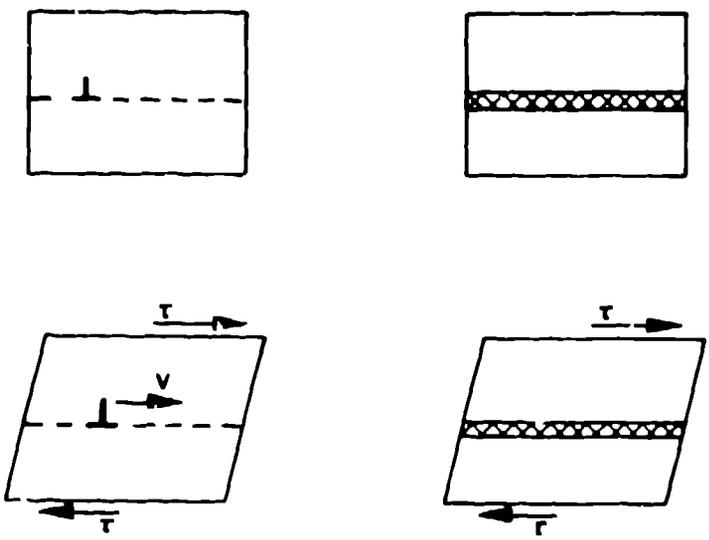


Fig. 2. On the left, a single crystal with an edge dislocation whose slip plane is the dashed line; application of a shear stress τ (lower diagram) causes the crystal to deform elastically, and causes the dislocation to move with velocity v . On the right, the same crystal with the slip plane replaced by a shear band; the same shear stress τ causes the same elastic deformation.

Dislocation Dynamics

8

We now want to simulate solid deformation on a different level, namely by studying the motion of individual dislocations. To do this, we construct a computer model of a system of dislocations and obstacles, as illustrated in Figure 3. The obstacles may be any physically appropriate barriers to dislocation motion, including other dislocations. To calculate the dislocation dynamics, we have to construct an equation of motion for the dislocations. The equation of motion contains a driving force, which results from a stress applied to the material, and a dislocation line tension, and terms representing interactions with the barriers, including barrier penetration probabilities. The equation of motion can also contain a dislocation drag term, and mechanisms to generate and annihilate dislocations. The procedure then is to numerically integrate the equation of motion, to simulate the dislocation dynamics. Realistic simulations for steady-state flows can be accomplished with current computer technology; such simulations are represented by the work of Schwarz and Labusch.²⁴⁻²⁶

In summary, the essential input and output for the computer simulation of dislocation dynamics is as follows. The input consists of a dislocation equation of motion, and the basic properties of a dislocation or dislocation system, namely its energy, its interaction with all sorts of barriers, and its generation and annihilation mechanisms. The output consists of the plastic constitutive properties of the material, in terms of dislocation density, the nature of the barriers, the temperature and so on. This output information becomes the input for a heterogeneous plastic flow calculation.

Atomic Dynamics

The ultimate level on which one can simulate solid deformation is the atomic level. Figure 4 illustrates the arrangement of atoms on the cross-sectional plane of an edge dislocation in a simple-cubic lattice. What we would like to do is construct a three-dimensional system of atoms on the computer, in the arrangement of a crystal lattice containing a single dislocation, then specify the potentials of interactions among the atoms, and calculate the motion of the atoms in the system. This is in fact an ordinary MD simulation, as we discussed in Section II. What can be learned from such a

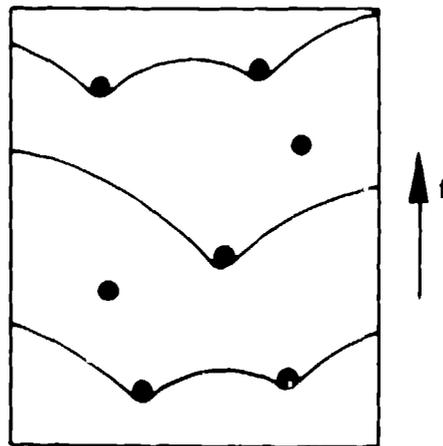


Fig. 3. Dislocations (lines) moving through an array of obstacles (dots). f is the force per unit length on a dislocation.

simulation? First of all, for the static lattice, which represents a crystal at zero temperature but without zero-point motion (since the theory is classical), one can find how the atoms relax their positions around a dislocation; hence the dislocation core structure and energy can be calculated. In the same way, the structure and energy can be calculated for related defect configurations, such as dislocation jogs and dislocation partials. Further, the effect of temperature on these defect configurations can be studied by doing ordinary MD simulations at finite temperatures, right up to the melting temperature of the material under consideration. One can apply a shear stress to the MD system, and watch the dislocation move. The interaction of a moving dislocation with the lattice can thus be studied. Finally, in principle, the interaction of a dislocation with an impurity, with a point defect, or with another dislocation can be determined by means of ordinary MD simulations.

Such calculations are enormously difficult. They are difficult for two reasons. In the first place, the elastic deformation of the lattice around a dislocation is long range, hence the atomic simulation of a dislocation requires an extremely large computational cell. Present-day computer technology is just barely able to do a realistic dislocation simulation. Secondly, we aren't quite sure of how to construct the interatomic potentials which operate in the region of a defect. To explain this problem, consider simple metals, for which pseudopotential perturbation theory applies.²⁷ The effective potential between ions operates through the conduction electrons, and the conduction electron density is nearly constant in space. This theory gives us good potentials for the vibrating ions in a nondefect crystal,¹³ up to the melting temperature,^{4,5,8} and even for the moving ions in the fluid.⁷ However, if a defect is present in a crystal, the conduction electron density might have a large variation in the vicinity of the defect; if this happens, we do not know how to calculate the interionic potential in that region. The interionic potential then has to be found self-consistently with the ionic structure. This is a problem which I recommend to the theorists.

In spite of the difficulty of doing computer simulations of dislocations on the atomic level, this technique offers great promise for learning about

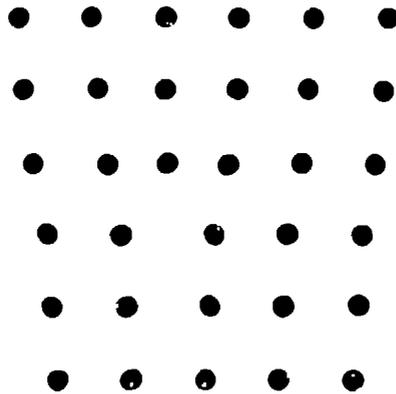


Fig. 4. View of the atoms in a planar cross section of an edge dislocation in a simple-cubic lattice.

atomic properties of dislocation in the future. Current state of the art is represented by the work of Vitek and collaborators, who have simulated the core structure and the motion of dislocations in bcc metals and in ordered alloys.²⁸⁻³¹ In these calculations, the long range deformation of the lattice in directions transverse to the dislocation line is represented by elastic-continuum boundary conditions for atoms outside the computational cell.

In summary, the essential input for the atomic simulation of dislocations is the atomic equation of motion and the interatomic potentials; the output is the basic properties of a dislocation in the crystal, its energy and its interactions with the lattice and with other defects. This output information becomes the input for dislocation dynamics simulations.

IV. APPLICATION TO SHOCKS

Nature of a Shock in a Solid

Let us first consider sound waves, which in first approximation are adiabatic elastic waves (where adiabatic means isentropic). When a small-amplitude elastic wave is generated in a solid, a large number of dissipative processes are driven. For example, because the local density and temperature vary in the presence of an elastic wave, the conduction electrons and the phonons are continually changing their distributions in an effort to stay in equilibrium, and this process is dissipative. Also because of the local temperature gradients, there is dissipative heat conduction. The sound wave scatters from defects, impurities, and grain boundaries; the free segments of pinned dislocations are caused to vibrate; domain walls are caused to move; these and many other dissipative processes are driven by an elastic wave in a solid. But the important point is, for a small-amplitude elastic wave in a solid, all of the dissipation effects are small. We know this from the following simple observation. A real sound wave, in the sonic or ultrasonic frequency range, is an adiabatic elastic wave clothed with all the accompanying dissipative processes. And real sound waves in solids normally travel for many wavelengths without significant attenuation.

The nature of a shock in a solid can be seen by contrasting a shock with a sound wave. For a sound wave, we can neglect dissipation entirely, and still have the essential physics, in terms of reversible thermoelastic theory. For a shock, the dissipative transfer of mechanical work into heat is an essential part of the process. Since in a solid this transfer takes place by plastic flow, we conclude that stress relaxation by plastic flow has to occur in the shock front. Here, plastic flow is used in the general sense, to include stress-relaxing structural changes, such as twinning. Other characteristics of a shock, such as the presence of an elastic (or partly elastic) precursor, and the presence of dissipation mechanisms in addition to plastic flow, should not obscure the fact that the existence of plastic flow is crucial to the shock process in a solid.

Heterogeneous Plastic Flow

A few years ago, we applied the continuum equations of thermoelastic-plastic flow, in the solid-dominant model, to the process of weak planar shocks in solids.^{32,33} The assumption made in this application is that the space- and time-scales of the heterogeneities in the plastic flow are small compared to the space- and time-scales of the shock process. If this were not the case, the shock wave would break up into different structures at different locations, on a plane of constant distance from the impact surface. In the visual experiments on 6061 aluminum,³⁴ there was no indication of such macroscopically inhomogeneous wave structure, within the spatial

and temporal resolution of the instrument. It was therefore appropriate to analyze these experiments with the above mentioned theory. In particular, by combining the experimental data with known thermoelastic properties, the plastic constitutive behavior of 6061 aluminum, averaged over the shock-induced heterogeneities, was obtained.³² This analysis is difficult, and is subject to errors in the numerical integration, and errors in the input experimental data, but not significant errors in the underlying theory.

Grady has stressed the existence of shear-band structures in samples recovered from shock experiments.^{35,36} In the case of aluminum, and 6061 aluminum, the spatial scale of these structures appears to be of order or less than the width of the plastic wave.³⁵ The existence of shear bands has led Grady to propose for the shock process a set of equations which are more representative of fluid behavior than they are of solid behavior. Let ϵ denote the total compression induced by the shock, the compression in the Hugoniot state. For a solid, ϵ contains both elastic and plastic contributions, hence ϵ is not the variable for specifying plastic strain, nor plastic dissipation, as Grady does (Ref. 35, eqs (1) and (3)). For the energy dissipated in a weak shock, Grady uses fluid theory (Ref. 35, eq. (3)), which gives a dissipation of order ϵ^3 , while for a solid the dissipation is formally of order ϵ^2 , as we have shown.³⁷

In the weak shock regime, the decrease in shock risetime with increasing shock strength is a plastic strainrate effect: higher shear stresses drive plastic flow at higher rates. By extending the equations of thermoelastic plastic flow to overdriven shocks in metals,^{38,39} we expect the risetime to be of order 10^{-12} s for shocks up to a few Mbar. We are also able to show that heat transport is necessary for the existence of an overdriven steady-wave shock.³⁸ Finally, for shock strengths above a few Mbar in metals, the electrons and phonons will not be able to remain near equilibrium, and hence irreversible thermodynamics will break down.^{39,40}

MD Simulations

There have been a number of computer simulations of supported waves in one-dimensional chains of interacting atoms.⁴¹⁻⁴³ These waves are generated by simulating planar impact experiments; such experiments generate shocks in real materials. But the computer simulations generate nonsteady waves, characterized by a continually growing length of nonequilibrium material immediately following the wave front. This result has led to the suggestion that the steady-wave jump conditions cannot be used to interpret experiments on shocks in solids.⁴¹ But such a conclusion is not warranted, because waves in a one-dimensional atomic chain have no plastic flow. The computer-simulated waves are not shocks, but are damped nonlinear elastic waves.

The same situation can appear in computer-generated waves in three-dimensional lattices. Thus, the computed nonsteady profiles of MacDonald and Tsai⁴⁴ are not shocks, and conclusions about real shocks in real materials cannot be drawn from these computer simulations. But a realistic shock can be generated in a three-dimensional lattice, as shown by the simulations of Holian and Straub.⁴⁵ For a sufficiently strong compressional wave, a highly specific mode of plastic flow is driven, namely a stress-relaxing dissipative structural transition. The resulting wave structure is a decaying elastic precursor, followed by a plastic compression to a steady state.⁴⁶

Finally, we note that MD simulation of dissipative stress-relaxing flow in a viscous fluid is in principle much simpler than for an elastic-plastic crystalline solid. This is because viscous fluid flow occurs on the atomic scale, while plastic flow usually occurs on the scale of dislocations. Hence, computer simulations of shocks in fluid are already in reasonably good agreement with continuum irreversible thermodynamics.^{47,48}

REFERENCES

1. H. J. Kreuzer, Nonequilibrium Thermodynamics and its Statistical Foundations (Clarendon Press, Oxford, 1981).
2. D. C. Wallace, Thermoelastic-Plastic Flow in Solids (LA-10119, Los Alamos National Laboratory, Los Alamos, 1983).
3. D. C. Wallace, in Electronic Structure, Dynamics, and Quantum Structural Properties of Condensed Matter, edited by J. T. Devreese and P. Van Camp (Plenum, New York, 1985), p. 521.
4. G. K. Straub, R. E. Swanson, B. L. Holian, and D. C. Wallace, in Ab Initio Calculation of Phonon Spectra, edited by J. T. Devreese (Plenum, New York, 1983), p. 137.
5. R. E. Swanson, G. K. Straub, B. L. Holian, and D. C. Wallace, Phys. Rev. B25, 7807 (1982).
6. B. L. Holian, G. K. Straub, R. E. Swanson, and D. C. Wallace, Phys. Rev. B27, 2873 (1983).
7. G. K. Straub, S. K. Schiferl, and D. C. Wallace, Phys. Rev. B28, 312 (1983).
8. G. K. Straub and D. C. Wallace, Phys. Rev. B30, 3029 (1984).
9. D. C. Wallace, S. K. Schiferl, and G. K. Straub, Phys. Rev. A30, 616 (1984).
10. D. C. Wallace and G. K. Straub, Phys. Rev. A27, 2201 (1983).
11. D. C. Wallace, B. L. Holian, J. D. Johnson, and G. K. Straub, Phys. Rev. A26, 2882 (1982).
12. S. K. Schiferl and D. C. Wallace, Phys. Rev. B31, 7662 (1985).
13. D. C. Wallace, Phys. Rev. 176, 832 (1968).
14. H. C. Andersen, J. Chem. Phys. 72, 2384 (1980).
15. M. Parrinello and A. Rahman, J. Appl. Phys. 52, 7182 (1981).
16. F. F. Abraham, in Proc. Intern. Conf. on Ordering in Two Dimensions, edited by S. K. Sinha (North-Holland, New York, 1980), p. 133.
17. F. F. Abraham, Phys. Reports 80, 339 (1981).
18. W. G. Hoover and W. T. Ashurst, in Theoretical Chemistry, edited by H. Eyring and E. Henderson (Academic, New York, 1975), Vol. 1, p. 1.
19. W. G. Hoover, Ann. Rev. Phys. Chem. 34, 103 (1983).
20. W. G. Hoover, Physics Today 37, 44 (1984).
21. L. Davison, in Shock Waves in Condensed Matter - 1983, edited by J. R. Asay, R. A. Graham, and G. K. Straub (North-Holland, Amsterdam, 1984), p. 181.
22. L. Davison, A. L. Stevens, and M. E. Kipp, J. Mech. Phys. Solids 25, 11 (1977).
23. J. N. Johnson, J. Appl. Mech. 105, 393 (1983).
24. R. B. Schwarz and R. Labusch, J. Appl. Phys. 49, 5174 (1978).
25. R. B. Schwarz, Phys. Rev. B21, 5617 (1980).
26. R. B. Schwarz, Acta Met. 29, 311 (1981).
27. D. C. Wallace, Thermodynamics of Crystals (Wiley, New York, 1970).
28. V. Vitek, Crystal Lattice Defects 5, 1 (1974).
29. V. Vitek, Proc. Roy. Soc. (London) A352, 109 (1976).
30. M. Yamaguchi, V. Paidar, D. P. Pope, and V. Vitek, Phil. Mag. A45, 867 (1982).
31. V. Paidar, M. Yamaguchi, D. P. Pope, and V. Vitek, Phil. Mag. A45, 883 (1982).
32. D. C. Wallace, Phys. Rev. B22, 1477 (1980).
33. D. C. Wallace, Phys. Rev. B22, 1487 (1980).
34. J. N. Johnson and L. M. Barker, J. Appl. Phys. 40, 4321 (1969).
35. D. E. Grady and J. R. Asay, J. Appl. Phys. 53, 7330 (1982).
36. D. E. Grady, in Shock Waves in Condensed Matter - 1983, edited by J. R. Asay, R. A. Graham, and G. K. Straub (North-Holland, Amsterdam, 1984), p. 363.
37. D. C. Wallace, Phys. Rev. B22, 1495 (1980).
38. D. C. Wallace, Phys. Rev. B24, 3597 (1981).
39. D. C. Wallace, Phys. Rev. B24, 5607 (1981).

40. D. C. Wallace, Phys. Rev. A25, 3290 (1982).
41. D. H. Tsai and C. W. Beckett, J. Geophys. Res. 71, 2601 (1966).
42. B. L. Holian and G. K. Straub, Phys. Rev. B18, 1593 (1978).
43. G. K. Straub, B. L. Holian, and R. G. Petschuk, Phys. Rev. B19, 404^a (1979).
44. R. A. MacDonald and D. H. Tsai, Phys. Reports 46, 1 (1978).
45. B. L. Holian and G. K. Straub, Phys. Rev. Lett. 43, 1598 (1979).
46. G. K. Straub, private communication.
47. W. G. Hoover, Phys. Rev. Lett. 42, 1531 (1979).
48. B. L. Holian, W. G. Hoover, B. Moran, and G. K. Straub, Phys. Rev. A22, 2798 (1980).