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Nonequilibrium Molecular Dynamics [1]

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Abstract

MOLECULAR DYNAMICS has been generalized in order to simulate a variety of NONEQUILIBRIUM systems. This generalization has been achieved by adopting microscopic mechanical definitions of macroscopic thermodynamic and hydrodynamic variables, such as temperature and stress. Some of the problems already treated include rapid plastic deformation, intense heat conduction, strong shockwaves simulation, and far-from-equilibrium phase transformations. Continuing advances in technique and in the modeling of interatomic forces, coupled with qualitative improvements in computer hardware, are enabling such simulations to approximate real-world microscale and nanoscale experiments.

1. OVERVIEW

Equilibrium molecular dynamics has been around ever since Fermi applied computers to the many-body problem, at Los Alamos during the Second World War. Molecular dynamics began as the routine solution of Newton's equations of motion using simple two-body perturbed-oscillator and hard-sphere force laws. Nonequilibrium molecular dynamics was developed a generation later, in order to simulate *non*equilibrium and nonlinear flows of simple fluids as well as to check an apparent disagreement between the linear Green-Kubo transport coefficients and experimental data. At present we can simulate the motions of several million particles, even with the more complex several-body forces typical of metals and covalently-bonded glasses. We can also follow the ground-state electronic motions for somewhat smaller systems. But atomistic simulation is still limited to micron and nanometer length scales and to microsecond and picosecond time scales. These lengths and times are increasingly relevant to experimentalists. Near-term increases of another three [or maybe six, once optical computers become a reality] orders of magnitude in computer capacity promise further qualitative changes in the problems we can solve and an even more intensive confrontation of simulation with laboratory experiments.

I cannot judge the present and future utility and applicability of such simulation techniques to nuclear physics, but I feel that our experience in imposing constraints on problems in classical many-body dynamics, by using the ideas of Gauss, Jaynes, and Nosé might stimulate parallel advances in nuclear dynamics. Here I describe progress in understanding the connection between microscopic reversible mechanics and macroscopic irreversible thermodynamics and hydrodynamics as well as state-of-the-art applications to simulating shockwaves, fracture, and plastic flow, including nonequilibrium grain growth.

2. NONEQUILIBRIUM MOLECULAR DYNAMICS[1]

In the equilibrium case atomistic motions are governed by Newton's differential equations of motion. For particles with masses {m} at locations {q} with momenta {p}, "equilibrium molecular dynamics" means the time-history {q(t),p(t)} solution of the ordinary differential equations of motion:

$$\{\, dq/dt \equiv \dot{q} = p/m \,;\, dp/dt \equiv \dot{p} = m\ddot{q} = F/m = [F_A + F_B]/m \,\}\,,$$

where I indicate explicitly both atomistic [A] and boundary [B] forces. These *conservative* forces are typically functions $F = F(q)$ of coordinates. The atomistic forces F_A link each particle with several of its neighbors. The boundary forces F_B serve to contain atoms within a specified region.

For simulations designed to measure bulk properties periodic boundaries are usual. In this case no container walls are necessary and the dynamics is governed solely by the atomistic forces F_A. Calculations have gradually progressed from the simple pair potentials $\phi_{12} = \phi(q_1-q_2)$ to more elaborate angle-dependent potentials describing covalent bonds[2,3], $\phi_{123} = \phi(q_1,q_2,q_3)$, to embedded-atom potentials[4] describing metal interactions, $\phi_1(\rho_1\{q\})$, where the density function ρ_1 depends upon the locations of the many near neighbors of Particle 1. The most recent and more nearly fundamental development[5] is Car and Parrinello's, which follows the detailed motions of the ground-state electrons which underly the empirical atomistic interactions. This last approach has the most to gain from further expected increases in computer speed because typical timesteps are a thousand times smaller than those based on few-atom empirical potentials. In all of these cases the coupled nonlinear equations of motion are easily solved numerically, and can provide a useful route to accurate equilibrium "equations of state" which interrelate the macroscopic pressure, temperature, energy and volume. Simple mechanical considerations provide the microscopic recipes for temperature [See Section 3 and Reference 1] and pressure as functions of particle coordinates and momenta.

Systems can be coupled to external sources of work and heat to simulate equilibrium isobaric and isothermal systems. With two or more sources the simulation of nonequilibrium systems is possible. Nonequilibrium systems can be driven away from equilibrium by using moving thermostatted boundaries or by imposing the corresponding momentum and heat fluxes, P and Q, the pressure tensor and the heat flux vector. The nonequilibrium forces required to establish these boundary values can include both constraint forces [C] and driving forces [D] which serve to exchange heat and work between an otherwise Newtonian system and the outside world. These forces typically depend upon both coordinates and momenta: $F_C = F_C(q,p)$; $F_D = F_D(q,p)$. In what follows I will consider in detail a constraint force which imposes the temperature T on one or more degrees of freedom. Local versions of such forces can induce a steady-state heat flow.

In any nonequilibrium case "mechanical" equation of state variables [those which do not involve entropy] can still be defined and used, just as at equilibrium. With the addition of nonequilibrium forces, numerical solutions can still be generated using a numerical antique, Störmer's leapfrog algorithm[6,7]:

$$q(t+dt) - 2q(t) + q(t-dt) \equiv (dt)^2[F_A(t) + F_B(t) + F_C(t) + F_D(t)]/m .$$

This algorithm has several advantages beyond simplicity in programming. It is particularly stable, as might be expected from its patently time-reversible nature. It requires the minimum computer storage, just three locations per coordinate. It can easily be generalized to include the driving and constraint forces used in nonequilibrium simulations[7]. The notation (t) on the right hand side of this difference equation indicates that the forces are functions of the coordinates and momenta of the system at time t. Typically the constraint and driving forces, F_C and F_D, involve momenta, apparently complicating the solution algorithm. But such a constrained dynamics can still be solved, with little additional effort, by the judicious use of a centered-difference representation of velocity: $p(t)/m \equiv v(t) \equiv [q(t+dt) - q(t-dt)]/2dt$. The resulting constrained equations of motion can then be solved, explicitly, for the new coordinates $\{q(t+dt)\}$ in terms of past and present values.

The size of feasible molecular dynamics simulations is still increasing rapidly. We have come from Fermi, Pasta, and Ulam's small systems[8] of 16 and 32 atoms in 1945, Alder and Wainwright's 870 atoms[9] in 1965, Holian's 4000 in 1980[10], and Abraham's 161,604 in 1985[11] to the million-atom simulations of the present[12-14]. Today it is no longer a hard problem to solve these differential equations for the motion of millions of atoms; billions are on the horizon. Computer speed, which limits the number of time steps, has increased much more slowly. Typically, and throughout the forseeable future, a "long" calculation involves millions of time steps and consumes a few weeks or months of computer time. To keep costs down, the increase in capacity is being obtained mainly by parallel calculations, as illustrated by Tony De Groot's SPRINT computer[15], a 64-transputer machine matching the performance of a CRAY at the cost of an automobile, and the Chudnovsky brothers' home-built parallel supercomputer, the first to compute two billion digits of π[16].

With increasing computer power, models for the underlying atomistic forces have gradually become more elaborate. The earliest three-dimensional calculations used hard-sphere billiard-ball interactions; eventually these gave way to pair potentials with attractive forces, for instance various truncated forms of the Lennard-Jones potential, $\phi(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^{6}]$. The attractive forces made it possible to simulate liquids in addition to gases and solids. Good agreement was obtained for the equilibrium and transport properties of the rare gases. More recently, collective [many-body] embedded-atom potentials[4] have been developed to describe metals and their alloys. With increasing computer power, the use of angle-dependent potentials characterizing covalently-bonded materials like silicon and water has become common. Car and Parinello's breakthrough[5] in simulating electronic motions provides even more realistic interactions, though at the expense of a much smaller time step.

The simulation and interpretation of boundary-driven nonequilibrium problems involving heat transfer requires mechanical definitions of stress and temperature[1,17]. Stress is a mechanical momentum flux so that its microscopic formulation is straightforward and accepted. Temperature is less universally understood and remains a potential source of controversy.

How is temperature to be defined? One of the two definitions which are valid, and equivalent, at equilibrium, $T \equiv (\partial E/\partial S)_V$, cannot work at all away from equilibrium without a nonequilibrium definition for the entropy S. Gibbs' equilibrium definition of entropy, $S \equiv -k\langle \ln f \rangle$, can diverge in nonequilibrium steady states, because these states inhabit (multi)fractal phase-space structures, "strange attractors", which have zero volume[18,19]. These attractors have a dimensionality which varies with the departure from equilibrium. As an example, the information dimension of the phase-space attractor characterizing a dense boundary-driven few-body two-dimensional shear flow drops by more than 7 as the strain rate is increased[20]. Thus entropy offers no simple route to nonequilibrium temperatures. A second possibility for defining temperature can be based on *energy* rather than *entropy*, the kinetic energy of an ideal-gas thermometer. Because temperature is of fundamental importance in characterizing not only equilibrium, but more importantly nonequilibrium, systems and their boundaries, I sketch the details in the next Section. At least for classical systems, a useful nonequilibrium temperature can be based on this approach, with a firm basis in mechanics, thermodynamics, and kinetic theory[21].

3. MECHANICAL DEFINITION OF TEMPERATURE

The classical ideal gas links temperature to pressure and thereby links macroscopic thermodynamics and hydrodynamics to microscopic mechanics. A fundamental and operational approach to equilibrium thermodynamics regards the pressure registered by an ideal-gas thermometer in contact with a system as a definition of that system's temperature. In an ideal gas the momentum flux tensor [pressure tensor] components can be visualized as local sums of velocity products. For instance, the instantaneous average, over a box of volume V, of the mechanical fluxes of x and y momentum flowing in the direction of the x axis are:

$VP_{xx} \equiv \Sigma m\dot{x}^2$ and $VP_{xy} \equiv \Sigma m\dot{x}\dot{y} \equiv VP_{yx}$.

From the standpoint of a mechanical *gedanken* experiment, P_{xx} represents the time-averaged force per unit area, in the x direction, resulting from elastic collisions exerted on massive walls erected perpendicular to the x direction and bounding the infinitesimal volume V. Thus the instantaneous ideal-gas pressure, $P_{ideal} \equiv (P_{xx} + P_{yy} + P_{zz})/3 \equiv \Sigma mv^2/3V$, is a direct measure of kinetic energy or, by definition, temperature.

For an isolated classical system with a separable Hamiltonian, $H(\{q,p\}) \equiv \Phi(\{q\}) + \Sigma(p^2/2m)$ equilibrium statistical mechanics arrives at this same definition of temperature, $T \equiv \langle p_x^2 + p_y^2 + p_z^2\rangle/(3mk)$. In Gibbs' statistical mechanics this result follows from the maximum-probability distribution over phase-space states. The same definition can be usefully extended and applied to any classical separable system, not just ideal gases, even far from equilibrium. To make the usefulness of this broader definition apparent, I use kinetic theory to analyze the interaction of an individual system particle [mass M] with an ideal-gas thermometer. I show that defining a system temperature in this way is consistent with intuition. With this definition thermal evolution behaves correctly, with the system absorbing heat from any hotter thermometer and giving off heat to any colder one. The ideal-gas thermometer should be visualized as a collection of light particles [mass m] with the equilibrium Maxwell-Boltzmann velocity distribution characteristic of the temperature T. These light particles measure the temperature of a degree of freedom by making frequent impulsive elastic collisions.

To begin with a one-dimensional illustration, consider the impulsive [instantaneous] headon collision of a relatively heavy [nonideal] system particle, having mass M and x velocity component $\dot{X}$, with a light ideal-gas-thermometer particle, having mass m and x velocity component $\dot{x}$. The resulting x velocity components which satisfy conservation of momentum and [kinetic] energy are:

$$\dot{X}' = (M-m/M+m)\dot{X} + 2(m/M+m)\dot{x}\ ;\ \dot{x}' = (m-M/M+m)\dot{x} + 2(M/M+m)\dot{X}\ .$$

Even in a general three-dimensional collision occuring parallel to the x axis, these same relations hold for the three-dimensional particles' x velocity components, with the y and z velocity components unchanged. The *averaged* velocity change, $\langle(\dot{X}'-\dot{X})\rangle$, averaged over a light-particle Maxwell-Boltzmann distribution is proportional to the heavy-particle acceleration. It can be expressed as the collision-averaged value of a power series in the mass ratio m/M. The various terms in this expansion all lead to simple Gaussian integrals. The first nonvanishing term comes from the Taylor's series expansion of two integrals:

$$\ddot{X} \propto \int|\dot{X}-\dot{x}|(\dot{X}'-\dot{X})\exp(-m\dot{x}^2/2kT)d\dot{x}/\int|\dot{X}-\dot{x}|\exp(-m\dot{x}^2/2kT)d\dot{x} \rightarrow -4(m/M)\dot{X}\ .$$

The arrow indicates the limit $m << M$. Thus the ideal-gas thermometer furnishes a frictional force proportional to the massive particle's speed. The denominator integral is proportional to the collision rate so that the frictional acceleration could be written $-(m/M)\dot{X}/\tau$.

For equilibrium *thermo*dynamics, where temperature corresponds to kinetic energy, the averaged (kinetic) energy change is relevant. The same correspondence holds away from equilibrium, as we now show in detail. The kinetic energy change depends only upon the massive particle's [nonequilibrium] speed *relative to the [equilibrium] thermal speed.* For a collision taking place along the x axis the averaged energy change for the massive particle is:

$$<\dot{E}>_{1D} \propto \int|\dot{X}-\dot{x}|(M/2)(\dot{X}'^2-\dot{X}^2)\exp(-m\dot{x}^2/2kT)d\dot{x}/\int|\dot{X}-\dot{x}|\exp(-m\dot{x}^2/2kT)d\dot{x} \rightarrow$$

$$4(m/M)[kT - M\dot{X}^2],$$

where again the arrow → indicates the limit $m << M$. An average over all three space directions gives the result:

$$<\dot{E}>_{3D} \propto (m/M)[3kT - m\dot{X}^2 - m\dot{Y}^2 - m\dot{Z}^2].$$

Thus a classical mechanical ideal-gas thermometer [which we visualize as a collection of many light particles with a Maxwell-Boltzmann velocity distribution] provides a unique and consistent definition of temperature, even for a *single* particle *arbitrarily far from equilibrium.* With a thermometric bath at temperature T the [averaged] effect of collisions is to heat any cooler particle and to cool any hotter particle. For an atom in a classical system the [averaged] direction of thermometric heat flow is invariably from hot to cold. The details of the fluctuations around the limiting $[m/M \rightarrow 0]$ averages could be analyzed from the standpoint of the Fokker-Planck equation.

It might well be argued that both this kinetic-theory derivation and the limit $[m/M \rightarrow 0]$ are superfluous, for the following reason: collisions leading to equilibrium must [ultimately] force any atom, whether it is heavy or not, to take on a time-averaged kinetic energy $3kT/2$; an atom with greater energy must (on the average) lose energy in coming to equilibrium, while a less energetic one must gain. But the fact that the direction of the energy change, system to bath or bath to system, is the same, no matter how far from equilibrium the system atom might be, bolsters the adoption of the ideal-gas temperature scale for classical nonequilibrium systems.

For the direction of heat flow to depend only upon the kinetic temperature it is essential that the thermometer have the Maxwell-Boltzmann distribution. A simple mixture made up of light particles ($m=1$) with two equally likely velocities, $\{-1,+1\}$, combined with heavy particles ($M=2$) with velocities $\{-1,0,+1\}$ with weights $\{1/4,1/2/,1/4\}$, leads to a transient cooling off of the light gas and a heating up of the heavy one if the two interact statistically.

The situation is evidently different in standard quantum mechanics[22]. Bohr emphasized the paradox that measurement is an essentially classical process which cannot be assimilated in the Schrödinger equation. The absence of feedback in the quantum mechanics seems to preclude the treatment of nonequilibrium problems or of measurement, except as approximations. Hence we can consider only the classical case. Because quantum mechanics conserves mass, momentum, and energy too, a correct quantum calculation could hardly lead to different results.

4. INCLUDING TEMPERATURE IN MOLECULAR DYNAMICS

Temperature can most elegantly be incorporated in molecular dynamics by using a constraint force, $F_C \equiv -\zeta p$. This form of the constraint force, linear in the momentum p, follows from Gauss' principle of least constraint[17,23]. The "friction coefficient" $\zeta(q,p)$ can then be determined in either of two ways. If Gauss' principle is used to keep kinetic energy constant, $\dot{K} = 0$, the result is a differential feedback expression for ζ_{GAUSS}:

$$\zeta_{GAUSS} \equiv -\dot{\Phi}/2K \, ; -\dot{\Phi} \equiv \Sigma p\cdot F/m \, ; K \equiv \Sigma p^2/2m \, ,$$

where Φ is the potential energy. That this choice maintains the kinetic temperature follows directly from the equations of motion:

$$(d/dt)(3NkT/2) = (d/dt)\Sigma p^2/2m = \Sigma(p\cdot F/m) - \Sigma(p\cdot\zeta p/m) =$$
$$[(\Sigma p\cdot F) - 2K(p\cdot F/2K)]/m \equiv 0 \, .$$

Nosé developed a very clever way to incorporate temperature into dynamics by using *integral* rather than differential feedback[24]. His goal was to generate Gibbs' canonical distribution dynamically. Just as in the differential case, Nosé's constraint force is linear in momentum. In my own work I have emphasized the utility of a particular form of Nosé's equations. In this single-variable form the so-called "Nosé-Hoover" friction coefficient is given by an integral expression:

$$\zeta_{NOSÉ\text{-}HOOVER} = \int[(K'/\langle K\rangle) - 1]dt' \, .$$

For an isolated system, this definition is consistent with Gibbs' canonical distribution. Small systems, with only a few degrees of freedom, often lack the required ergodicity and mixing to achieve the complete canonical distribution, occupying instead a small subset of phase-space states.

Bulgac and Kusnezov[25], Winkler[26], and Martyna[27] have all showed, very recently, and in very different ways, that more elaborate dynamical thermostats, involving two or more variables rather than one, can enhance the necessary mixing and lead to a complete canonical distribution, even for systems as simple as the one-dimensional harmonic oscillator.

Perhaps parallel ideas would be useful in nuclear physics? For the (three-dimensional) Fermi distribution we would have to satisfy the constraints $<p^2> = 3/5$; $<p^4> = 3/7$; $<p^6> = 3/9$, for instance. To implement all of these constraints in the equations of motion

$$\{ dp/dt = F - \alpha p - \beta p^3 - \chi p^5 \} ,$$

we would need to find the Lagrange multipliers α, β, and χ satisying the three linear equations:

$$\Sigma F \cdot p = \alpha <p^2> + \beta <p^4> + \gamma <p^6> ;$$

$$\Sigma F \cdot p^3 = \alpha <p^4> + \beta <p^6> + \gamma <p^8> ;$$

$$\Sigma F \cdot p^5 = \alpha <p^6> + \beta <p^8> + \gamma <p^{10}> .$$

Perhaps it would be simpler to achieve this goal by imposing a maximum speed (the Fermi speed) on the velocity distribution, while simultaneously constraining the second moment of the distribution.

5. SECOND LAW OF THERMODYNAMICS

Adopting the ideal-gas temperature scale has benefits beyond the possibility of far-from-equilibrium simulations. It allows the [irreversible] Second Law of Thermodynamics to be deduced directly from [reversible] (Nosé-Hoover) mechanics[28]. The demonstration is possible because Nosé-Hoover mechanics allows an exact calculation of the evolution of the phase-space distribution function $f(q,p,\zeta)$. The continuity equation for the flow in phase space relates the change in comoving phase-space volume $\otimes$ and the change in comoving phase-space probability density f: $d\ln f/dt + d\ln\otimes/dt \equiv 0$. The phase-space volume $\otimes$ can be visualized as an infinitesimal hypersphere centered on a typical phase-space trajectory. The long-time deformation of the hypersphere [it becomes a hyperellipsoid] can be described in terms of the growth and shrinkage rates of the hyperellipsoid's principal axes. The steady-state set of rates $\{\lambda\}$ is called the "Lyapunov spectrum" of the system in question.

A steady state can be driven away from equilibrium only through steady heat exchange. Thus, for a nonequilibrium steady state the time average of the friction coefficient sum, $\Sigma\zeta \equiv -\Sigma\lambda \equiv d\ln f/dt \equiv -d\ln\otimes/dt$, cannot vanish. As a consequence the comoving phase-space volume $\otimes$ must approach either zero or infinity, exponentially fast. Straightforward integration of the Nosé-Hoover equations of motion then shows that the comoving phase-space volume $\otimes$ can be bounded (in fact, approaching zero volume) only if the density f diverges:

$$df/dt = -\Sigma[f(\partial\dot{q}/\partial q) + f(\partial\dot{p}/\partial p) + f(\partial\dot{\zeta}/\partial\zeta)] = 0 + \Sigma\zeta f + 0 \Rightarrow$$

$$\otimes(t)/\otimes(0) \equiv f(0)/f(t) \equiv \exp[-\int\Sigma\zeta(t')dt'] \to 0 \, .$$

This exact result leads to the interpretation of the unidirectional evolution of nonequilibrium steady states as indicating the collapse of phase-space probability onto a strange attractor. Pictures showing typical attractors for few-body systems can be found in References 18 and 28.

The topology of many-body phase-space motion has been analyzed too, by borrowing the necessary tools from nonlinear dynamics. It is now well established that the combination of *stretching* motion characteristic of chaotic systems (where nearby trajectories separate exponentially fast with time) and the *bending* motion required by a bounded phase space, lead together to beautiful fractal structures. The prototype of this motion is called the "Smale horseshoe". It is highly interesting that the exponential spreading instability, called "Lyapunov instability", has roughly the same form, as characterized by the spectrum of orthogonal Lyapunov exponents, for equilibrium and nonequilibrium systems, be they fluid or solid. It is interesting, and possibly discouraging[29] that the instability spectrum for atoms looks about the same as the instability for turbulent continuum flows[19]. Thus the hope that turbulent flows could be described by only a few degrees of freedom should be abandoned.

6. EXAMPLE RESULTS

6.1 Transport Coefficients

The first extensive nonequilibrium simulations were devoted to checking the hydrodynamic transport coefficients for diffusion, viscous flow, and heat conduction[30]. In a typical simulation particles in one region of space are constrained to have a temperature hotter than those in another. The resulting heat flow can be used to compute the conductivity in two equivalent ways, in terms of the thermodynamic dissipation or in terms of the measured heat flux. Consistent calculations of this kind have been carried out for all of the transport coefficients. It was observed, and also proved, that the linear response theory results could be recovered from the nonlinear simulations by reducing the driving forces[31]. The nonlinear effects turned up in the exploratory simulations were most interesting. For instance, it was thus observed that the shear viscosity measured in simulations typically decreases with increasing strain rate. This decrease in viscosity is reasonable from a physical viewpoint. As planes of fluid flow over one another the induced spatial correlations act to reduce interplanar drag, lowering viscosity. Although the topological picture is sound, the expectation that viscosity drops with increasing strain rate is not generally valid. The shear stress measured in strong shockwaves corresponds to an increase rather than a decrease in viscosity, as explained below.

6.2 Shockwaves

Shockwaves were one of the first nonequilibrium problems to be simulated[32]. A shockwave is a highly irreversible transition region linking a cold low-density initial state to a hotter higher-density final state. In the early shockwave simulations cold particles were fed into one end of the shockwave region while hot particles were extracted from the opposite end. Because a steady shockwave is subsonic relative to the hot material the wave is not entirely free of boundary influences. Quantitative results became available about ten years later and were based on simulations in which a long periodic parallelepiped was compressed longitudinally. The resulting steady shockwave profiles show an *increase,* rather than a *decrease,* in the shear stress, corresponding to an increase in viscosity. This example shows how hard it is to generalize nonlinear problems.

Understanding of nonlinear flow behavior has been advanced by Loose and Hess[33]. In shockwaves the shear stress is greater, rather than less, than the Newtonian prediction. From the standpoint of continuum mechanics the shockwave geometry is different, with a shear deformation described by compression in one direction $\varepsilon_{xx} = -\varepsilon$ and expansion in the other two, $\varepsilon_{yy} = \varepsilon_{zz} = \varepsilon/2$, superposed on an additional overall compression. Simulations of shockwaves show the opposite behavior. Strongly compressed fluids, either dense or dilute, show shockwidths greater than the linear-transport predictions of the Navier-Stokes equations[34,35].

Molecular dynamics simulations have shown that shockwaves can still be described quite well with the linear (Navier-Stokes) hydrodynamic theory. The measured heat and momentum fluxes at strain rates of terahertz and pressure gradients of 10^{15} bars/meter deviate from linear transport theory by only 30%. This work has recently been extended to chemically-reacting flows[36]. Reference 36 contains sample frames from an interesting videotape showing the shock-induced dissocation of a dense diatomic fluid.

6.3 Indentation and Broken Symmetry

Simulation is most valuable for problems whose outcome is uncertain. Examples, in which macroscopic physics cannot predict the outcome, include flows in which symmetry is broken: fracture, fragmentation, and plastic flow. Such problems involve real surfaces rather than periodic boundaries, and are at last becoming more common. With the current and projected increases in computer power it is possible to identify failure modes and to measure the kinetics of processes which lie outside macroscopic theory. The dynamics shows flow behavior consistent over time scales ranging from the macroscopic to the microscopic.

Indentation is a physical test which incorporates both elastic and plastic deformation in an interesting way. In our exploratory two-dimensional indentation simulations we found that indentation and fracture are problems in which the microscopic chaos of the motion equations has macroscopic consequences. Starting out with a workpiece which is a single crystal with perfect left-right symmetry, that symmetry is promptly lost. The seed of infinitesimal thermal displacements coupled to the Lyapunov instability of the equations of motion provides an overall macroscopic symmetry breaking.

6.4 Other Applications

There are hosts of other applications of molecular dynamics which have been carried out recently. These are mere suggestions of the possibilities which will open up as computer power increases by another six orders of magnitude. The collisional properties of Bucky Balls, including the production of diamonds[37], and the dynamic behavior of two-phase interfaces[38] are two examples. Bucky Balls, like high temperature superconductivity, turned out to be much more easily explained than predicted. These two examples show why simulation will never run out of interesting problems[39].

7. GOALS FOR THE FUTURE

The goals of nonequilibrium molecular dynamics coincide with the goals of physics: explanation of known phenomena and prediction of new ones. 35 years ago freezing was explained and illustrated by hard-disk and hard-sphere simulations. Gradually the problems attacked became more specialized. Brad Holian's shockwave movies, the surface reconstruction of crystals [Giulia De Lorenzi was responsible for the film], and the flow of a two-dimensional fluid around a cylinder [shown by Larry Hannon] were among the early significant problems whose solutions I remember seeing at research conferences. They reminded me strongly of Bragg's movie of dislocation motion in bubble rafts and Alder and Wainwright's early movies of H-Theorem flows and two-phase equilibria. For nonlinear problems such visual displays of simulation provide the conceptual cause-effect links that inspire and facilitate subsequent theoretical analyses. With the simple gas-liquid-solid phase behavior reproduced with simple pair potentials much more complex systems, even biological ones, are current research areas.

It is an interesting challenge to explore the extent to which behavior of interesting materials like silicon can be reproduced by simulation. Silicon exists in an amorphous form as well as in two different crystalline structures, one conducting. Among its interesting features are a squirting phenomenon seen in indentation[40], a transformation from crystalline to amorphous under indentation[41], and an explosive crystallization caused by the difference in free energies of the amorphous and crystalline phases[42]. The three-dimensional indentation simulations currently underway will show whether or not these interesting features can be reproduced with existing force models[43].

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