

ATOMISTIC NONEQUILIBRIUM COMPUTER SIMULATIONS*

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Newton's, Lagrange's and Hamilton's equations of motion have been modified to include the effects of constraints, nonequilibrium fluxes, and gradients. These nonclassical equations provide estimates of the linear transport coefficients and, through nonlinear dissipative terms, can also simulate nonequilibrium steady states. To illustrate the modified equations of motion, we apply them to a simple three-oscillator problem. The new methods have also been used to study nonlinear problems with large coupled gradients. We describe two examples: the coupling of heat flow with rotation and the simulation of strong shockwaves in dense fluids.

1. Introduction

The nonequilibrium hydrodynamic behavior of a dense fluid is described by its transport coefficients: the shear and bulk viscosities and the thermal conductivity. Thirty years ago Green¹⁾ formulated the linear transport coefficients in terms of atomistic autocorrelation functions. At about that time the development of molecular dynamics at Livermore²⁾ made it possible to evaluate the "Green-Kubo" expressions numerically. After some initial discussion³⁾ these expressions were generally accepted as the correct path to dense-fluid transport theory.

Still, occasional questions⁴⁾ continued to be raised about the validity of Green's expressions. The first viscosity and thermal conductivity calculations using a "realistic" force-law, a Lennard-Jones potential describing liquid argon, were somewhat disappointing. First, the calculations were slow to converge. Second, the triple-point thermal conductivity deviated from the known experimental value by about a factor of two. These difficulties led to a search for fresh approaches to the computer simulation of atomistic transport processes, principally shear viscosity.

Shear viscosity was studied more extensively than the conductivity because it is intrinsically simpler. The driving force "causing" a shear stress can be reproduced in a homogeneous periodic system—see fig. 1. A constant temperature gradient, on the other hand, cannot occur in a periodic, boundary-

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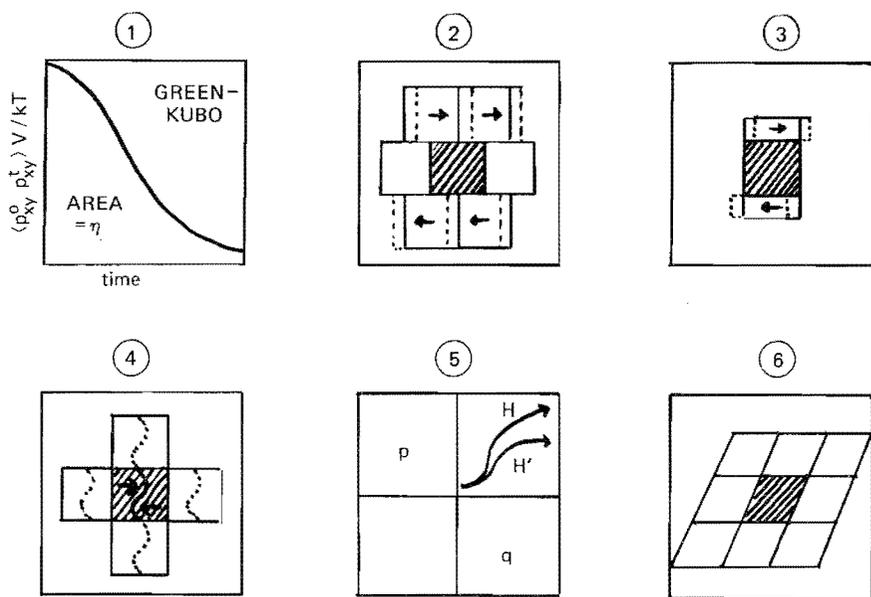
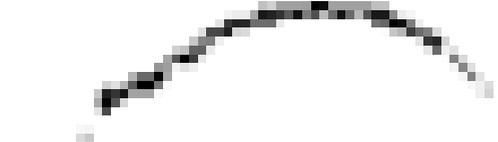


Fig. 1. Six methods for determining the shear viscosity using molecular dynamics. The first is based on integrating the Green-Kubo integrand, as illustrated in ref. 5. The second and third methods drive a bulk system with moving boundaries, either images of the system itself or independent sets of particles with fixed center-of-mass velocity^{6,8}). The fourth approach uses a sinusoidal external field to generate a sinusoidal shear flow⁷). The fifth approach uses a small perturbation, and studies the offset of the unperturbed and perturbed trajectories in qp space¹⁰). The last method, based on Doll's tensor, shears the system homogeneously, while simultaneously extracting heat to maintain constant temperature¹¹) or energy¹⁹)

free system. Five new nonequilibrium methods were soon developed for simulating dense-fluid shear flows. Lees and Edwards⁶) used moving periodic images, above and below a dense-fluid system to drive the fluid into a state of shear. Gosling, McDonald, and Singer⁷) used a sinusoidal transverse force to support a periodic standing shear wave. In both these early approaches irreversible heating caused the fluid to heat up as time passed. Ashurst and Hoover⁸) used external reservoir regions, composed of particles separated from the bulk fluid, to drive the shear. In these latter calculations the temperature was also held fixed at the reservoirs, making it possible to extract the viscous heat and produce a steady flow.

Ashurst and Hoover⁹) next developed a truly homogeneous periodic-shear method with very little number dependence. In this work each particle was displaced in the x -direction by an extra displacement proportional to its y -coordinate, at every time step. The four methods just described all simulate strain rates much greater than those found in conventional laboratory experiments. A fifth method more closely resembles the Green-Kubo small-



gradient approach. Jacucci, Ciccotti, and McDonald¹⁰⁾ concentrated on developing methods for treating very small perturbations, examining the offset between unperturbed and perturbed qp -space trajectories. This offset was used to estimate the linear transport coefficients. All five nonequilibrium shear-flow techniques are sketched in fig. 1.

The numerical results from these shear-viscosity investigations, and from less extensive simulations of heat flow, reinforced the validity of Green's original formulation. The factor-of-two disagreement in the autocorrelation calculation of the thermal conductivity was traced to an arithmetic error. In the end, including the Green-Kubo method, half a dozen different methods were available for measuring shear viscosity or thermal conductivity in dense fluids. The major difficulties uncovered were computational: number-dependence, wavelength-dependence, and gradient-dependence. In a word, non-linearity.

The nonequilibrium techniques developed in transport work led to the systematic study of nonlinear problems. The nonlinear case is intrinsically complicated by the presence of boundaries necessary to drive the system away from equilibrium, and, in a steady state, to transport out of the system the irreversibly-generated heat. A great deal of the pioneering nonlinear work has been carried out by Denis Evans and Howard Hanley.

In the last two years some of the new nonequilibrium methods have become embedded into the theoretical structure of statistical mechanics. Almost ten years after the original simulations, we now know that the homogeneous periodic shear flows can be described, analytically, by a modification of Hamiltonian mechanics in which the sheared fluid exchanges heat with an unseen reservoir¹¹⁾. A corresponding modification of Lagrangian mechanics has also been developed. Andersen¹²⁾ discovered the hydrostatic version of these new Lagrangian equations of motion.

Formal understanding of heat reservoirs has also developed slowly. In 1973 Ashurst used "momentum rescaling" to maintain a constant value of the kinetic temperature in the boundary regions of his nonequilibrium shear-flow and heat-flow simulations. Almost ten years passed before it was discovered that this momentum rescaling corresponded analytically to new differential equations of motion. These new "isothermal" equations of motion, Langevin-like modifications of Hamilton's equations, were discovered simultaneously and independently in 1981, by Evans and Hoover. A slightly different approach, based on conventional constrained Lagrangian dynamics¹³⁾, is compared to the Hamiltonian-based equations in section 2.

At present these new nonequilibrium methods, developed originally to check Green's work, are being applied to the more complicated nonlinear hydrodynamic problems. Functions in qp space other than energy, tem-

perature, and strain rate can be constrained to constant values. The heat flux vector, the moments of angular velocity, and the pressure tensor are examples.

The new methods could be used to impose "quiet boundaries" on systems initially out of equilibrium. Gibson et al.¹⁴⁾, in one of the first "realistic" simulations, used special energy-absorbing boundaries in following the dynamics of a small crystal initially excited by a hot-atom collision.

Steady states far from equilibrium have been studied. In 1978 Holian et al.¹⁵⁾ simulated a very strong dense-fluid shockwave, in which a hundredfold temperature increase occurred in a distance of only a few interatomic spacings. Another very small-scale steady-state system with correspondingly large gradients was studied by Hoover et al.¹⁶⁾. By studying the radial flow of heat in a very rapidly rotating dense fluid, they were able to show that Coriolis' forces change the direction of heat flow. The nonlinear coupling of the heat flow with rotation leads to an interesting violation of Fourier's law.

Here we first review the structure of the nonequilibrium methods. Then we discuss some results.

2. Atomistic mechanics with constraints

Classical mechanics connects "states" (sets of coordinates q and momenta p) in the qp space through the dynamical equations of motion. The dynamical equations, Newton's, Lagrange's, or Hamilton's, can be used to describe equilibrium or nonequilibrium systems. In most nonequilibrium cases some interaction with the outside world is required. Typically a boundary capable of furnishing particles, momentum, or energy to the system is included. Such a boundary is macroscopically small. Its structure can be ignored in laboratory experiments. But in computer experiments the extent of the boundary influence is large enough¹⁷⁾ to produce noticeable size-dependence. To avoid this size-dependence, it is logical to try to do without boundary regions altogether, by substituting for the boundary, a homogeneous collective force that will provide the essence of the boundary effect, but do it more gently. Since the normal atomistic equations of motion need boundaries to treat transport problems, they must be modified to induce flow or temperature fields, when periodic boundaries are used.

Once the idea of modifying the classical equations of motion is accepted—and this takes time—only the pragmatic criteria of simplicity, economy, and style can guide the physicist. Ideally, the modification should lend itself to theoretical analysis and should reduce the number-dependence of the property being studied. In order that the results be comparable to real laboratory

experiments the modification must also vanish in the limit that the system becomes large. Because the simplest nonequilibrium problems are steady-state ones, a logical beginning is to develop modified equations of motion which stabilize particular phase functions. Equations of motion ordinarily stabilize energy. The nonclassical equations of motion can stabilize temperature, the strain-rate tensor, energy or temperature in the presence of a fixed strain-rate tensor, the pressure tensor, and the heat-flux vector. Each of these quantities can be described in terms of q 's and p 's, the ingredients of the equations of motion.

The details of such schemes are not particularly intricate. The ordinary differential equations required to induce a shear flow while simultaneously maintaining constant temperature are illustrated below, in eqs. (5).

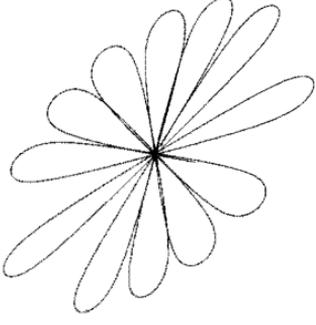
That particular set of equations, and its three-dimensional generalization, showed that the "isothermal" dynamical schemes work very nicely for two- and three-dimensional fluids and solids with several hundred particles. I wondered how small and simple a dynamical system could be and still respond stably to the new constraints. A one-dimensional chain of Hooke's-law oscillators is perhaps the simplest system. If the center of mass is fixed then the constraint of fixed kinetic energy leads to an instability—divergence of the energy—for a two-particle chain. Neither particle can slow down, and each must move as a free particle would, so that the total energy rises as the square of the time, for long times. With a three-or-more-particle chain the situation is different. Any of the three particles can reach a turning point, with zero velocity, because the two others can share the kinetic energy. Fig. 2 illustrates the three-particle case, with periodic boundaries.

The two nonzero modes have the same frequency in this three-particle problem, so that the usual constant-energy dynamics would trace out an ellipse in the three-dimensional qp space describing the system with fixed center of mass. That periodic motion is illustrated in fig. 2.

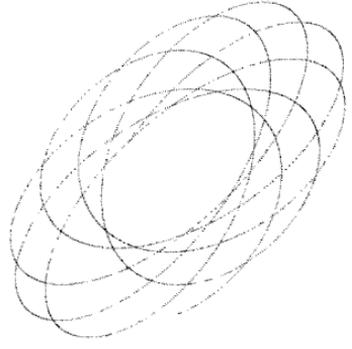
How can we study the dynamics of this simple system at fixed temperature? There are many ways. The simplest involve constraining the kinetic energy by modifications of Lagrangian or Hamiltonian dynamics. The traditional Lagrangian approach¹³⁾ introduces the fixed-temperature constraint through a Lagrange multiplier. Eliminating that multiplier from the equations then yields the following set

$$\dot{q} = (p/m) \left(2mKE / \sum p^2 \right)^{1/2}; \quad \dot{p} = F. \quad (1)$$

In this set of equations the "momentum" p is no longer $m\dot{q}$. Numerical solution shows that the system is stable and that the average potential energy



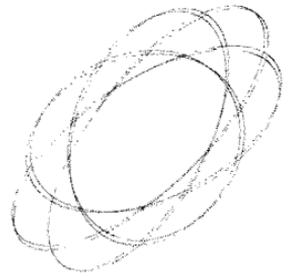
HAMILTONIAN



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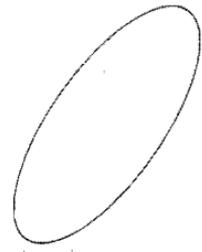
LAGRANGIAN



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is somewhat greater than the value predicted by equipartition. Typical trajectories are shown in fig. 2.

Another approach to the constant-temperature constraint can be based on Hamilton's equations. A frictional force resembling Langevin's in form, but varying relatively rapidly with time, can be introduced to constrain the kinetic energy, $\Sigma(p^2/2m)$, to a fixed value

$$\dot{q} = p/m; \quad \dot{p} = F - \zeta p; \quad \zeta = \Sigma(pF) / \Sigma p^2. \quad (2)$$

As shown in fig. 2c, numerical simulation indicates that the system of equations (2) is stable. This time the average potential energy is somewhat closer to the value predicted by equipartition.

In scheme (1) above only the \dot{q} equation was changed. In scheme (2) only the \dot{p} equation was changed. These two different schemes could be viewed as limiting cases of a general modification of Hamilton's equations in which coordinates and momenta are simultaneously modified.

The schemes just outlined can easily be generalized to simulate moving isothermal boundaries. In scheme (2) for instance, a collective force, $- \langle F \rangle$, can be added to the \dot{p} equation to maintain a boundary's velocity in the presence of unbalanced forces.

Many alternative schemes could be based upon constraining momenta of the velocity distribution higher than the second. All such schemes are possible methods for carrying out isothermal molecular dynamics. In fact, the second set of equations described above is exactly equivalent to Ashurst's velocity-rescaling approach used in 1973 to simulate viscous and heat flows! But the equivalence was only recently discovered.

Which of the many possible isothermal schemes is best? Because perturbing \ddot{q} is gentler than perturbing \dot{q} a little reflection suggests that the set (2) is superior to the set (1). In addition, the set (2) has a remarkable statistical property: It maintains a canonical distribution in qp space¹⁸. Although Liouville's theorem is violated for this non-Hamiltonian set of equations, the change in the qp -space density with time is exactly that required to maintain

Fig. 2. Two sets of qp -space trajectories for three masses joined by springs, calculated according to the two constant-temperature schemes outlined in the text. The abscissa and ordinate are the coordinates of two masses. In each set all three trajectories correspond to the same initial conditions. The first trajectory corresponds to Newton's energy-conserving equations of motion. The second and third correspond to modifications of Lagrange's and Hamilton's equations of motion according to schemes (1) and (2) of the text. The modification of Hamilton's equations maintains a canonical qp -space distribution and has recently been used in simulating solid-phase plastic deformation¹⁸).

the equilibrium distribution:

$$d \ln f/dt = - \sum \partial \dot{p} / \partial p = - \dot{E}/kT. \quad (3)$$

More complicated constraints have recently been introduced. Doll's tensor, Σ_{qp} , is fundamentally related to the pressure tensor and to the strain-rate tensor ∇u . By adding the tensor product, $\nabla u : \Sigma_{qp}$, to an equilibrium Hamiltonian function, new equations of motion result with the strain rate ∇u fixed. These new equations satisfy identically the thermodynamic relation describing adiabatic deformation¹¹⁾

$$\dot{q} = (p/m) + q \cdot \nabla u; \quad \dot{p} = F - \nabla u \cdot p; \quad \dot{E} = -VP : \nabla u. \quad (4)$$

With the new adiabatic equations either dilatational or shear flows can be simulated. In either case the system will gradually heat up. Therefore a combination of the shear deformation du_x/dy and the isothermal friction-coefficient approach — scheme (2) above — can be used to study steady shears

$$\begin{aligned} \dot{x} &= (p_x/m) + (du_x/dy)y; & \dot{y} &= (p_y/m); & \dot{p}_x &= F_x - \zeta_x p_x; \\ \dot{p}_y &= F_y - (du_x/dy)p_x - \zeta_y p_y; & \zeta_x &= \sum (p_x F_x) / \sum (p_x p_x); \\ \zeta_y &= \sum [p_y F_y - (du_x/dy)p_x p_y] / \sum (p_y p_y). \end{aligned} \quad (5)$$

These equations successfully generate steady shear in either fluids or solids¹⁸⁾ and have substantially reduced number dependence. Evans¹⁹⁾ has recently carried out constant-energy shear simulations, in which total, rather than kinetic energy is fixed in a system on which irreversible work is being performed. The nonlinear effects are very similar.

If the strain rate du_x/dy is chosen to stabilize the pressure tensor then constant-pressure simulations can be carried out. In the work done so far a relaxation time has been used instead²⁰⁾ so that it is not known to what extent the truly constant-pressure simulations are stable.

The heat flux vector, like the pressure tensor, can be written as a sum of potential and kinetic contributions¹⁶⁾. Once again the modification of Hamilton's equations necessary to make the heat flux vector constant can be found in terms of a momentum-dependent force. Calculations using this constant-flux idea should be carried out for comparison with the several alternative approaches¹⁹⁻²¹⁾ that have recently evolved.

What is the evidence that these ad hoc modifications of Newton's achievement are worthwhile? First, numerical study shows that the approach to the large-system limit is regular and well-behaved. Second, the nonequili-

brium methods converge more rapidly than does the Green-Kubo approach, with a corresponding savings in computer time. Third, the transport coefficients obtained using the new dynamical equations agree with experimental data and with alternative computer experiments in which the collective forces present in the systems (1), (2), and (5) are replaced by special boundaries.

Finally, there is evidence which will appeal to kinetic theorists who pursue, for the most part, transport in low-density gases. It is possible to show that the new dynamical equations in eqs. (2) produce exactly the same flow field, to first order in the strain rate, as is found in a system driven by external boundary forces.

The usual streaming terms in the Boltzmann equation are easily evaluated

$$\partial f/\partial t + \dot{q}\partial f/\partial q + F\partial f/\partial p = -(mv_x v_y/kT)(du_x/dy)f_0, \quad (6)$$

if the local equilibrium distribution function f_0 is used. Exactly the same streaming term results, from $F(\partial f/\partial p)$ rather than $\dot{q}(\partial f/\partial q)$, if the velocity-dependent external force, $-(du_x/dy)p_x$ in eq. (4), is applied to the local equilibrium distribution.

Thus the new nonequilibrium equations of motion are stable, economical, have relatively small number-dependence, agree with the Boltzmann equation at low density, and are thermodynamically self-consistent.

3. Results and prospects

What has been accomplished with the nonequilibrium simulations? They have provided our *only* reliable estimates for the magnitude of nonlinear effects. In most cases where these effects have been predicted theoretically, the magnitudes are not understood.

The early simulations of shear flow and heat flow established that these processes are not linear. The coefficients changed with the magnitude of the strain rate or temperature gradient. The viscosity always appears to decrease as the strain rate is increased^{22,23}). The thermal conductivity can either increase or decrease as the magnitude of the temperature gradient is increased²²). It is particularly valuable to have these results for known force-laws, without the additional complexities caused by intramolecular degrees of freedom.

Denis Evans has established that the viscosity results are "understood" in the sense that mode-mode coupling theory predicts correctly the power-law form of the nonlinearity. But the orders-of-magnitude disagreement in the size of the nonlinearity indicates that the basic physics is not understood. It seems

likely that theoretical analyses of our steady-state dynamical equations will eventually lead to quantitative estimates..

There are related and unresolved problems in understanding the structure of shockwaves in dense fluids. Here again the computer experiments are valuable because they furnish detail at a small scale beyond the reach of current laboratory experiments. In fig. 3 we illustrate the dependence of the longitudinal pressure P_{xx} on volume during a strong steady shock compression. These states are the "Rayleigh Line." The particular shockwave considered here compresses a Lennard-Jones model of liquid argon at the triple point, to a final pressure of nearly half a megabar at a temperature of 12,000 K. The straight-line dependence of longitudinal pressure on volume follows from conservation of mass and momentum. The transverse component

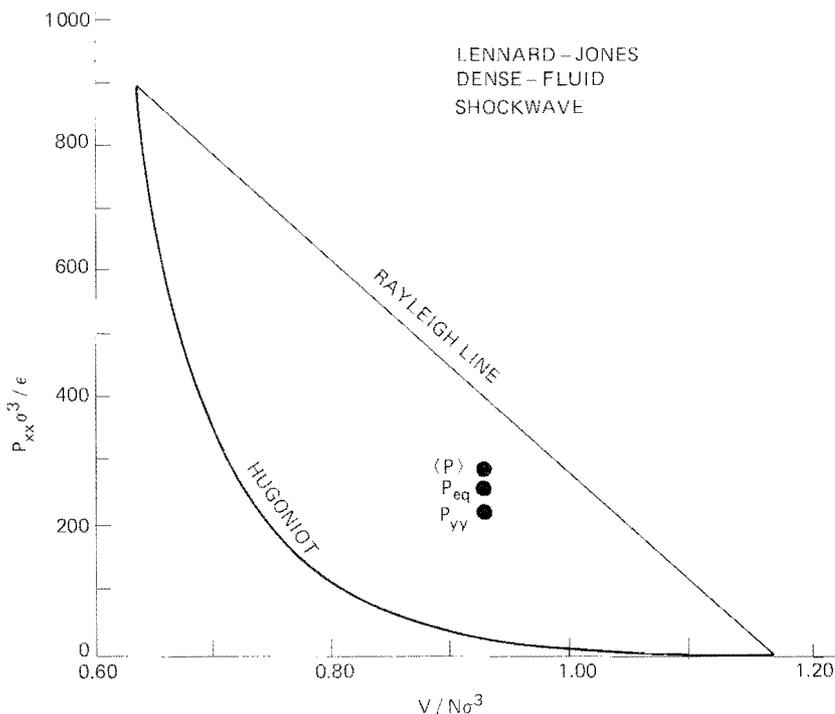


Fig. 3. Pressure-volume states in a steady shockwave linking the triple point to a high-pressure state as described in ref. 15. The steady wave proceeds through states along the Rayleigh line. In the center of the shockwave, where the velocity gradient reaches its maximum value, the average pressure, equilibrium pressure (pressure calculated using the local average temperature), and transverse pressure-tensor component are all indicated. The molecular dynamics results and Navier-Stokes results agree within the size of the plotting symbols. The "Hugoniot" curve lying below all these points is the locus of equilibrium states which can be reached by shockwaves starting from the triple point state, σ and ϵ are the Lennard-Jones potential collision diameter and well depth, respectively.

of the pressure tensor $P_{yy} = P_{zz}$ lags behind P_{xx} , with the difference between these components proportional to the shear viscosity. The points near the middle of the Figure indicate the mean pressure, $(P_{xx} + P_{yy} + P_{zz})/3$, as well as the "equilibrium pressure" characteristic of the temperature $(T_{xx} + T_{yy} + T_{zz})/3$, and the transverse pressure-tensor component $P_{yy} = P_{zz}$, all measured in the central steeply raising part of the shockwave. These shockwave data were generated using 4800 atoms with a modification of the Lees-Edwards scheme⁶). The neighboring periodic images of the basic dynamical cell were moved toward one another so as to compress, rather than shear, the basic cell.

Within the size of the plotting symbols, the results from this nonequilibrium shockwave simulation agree with the predictions of the Navier-Stokes equations of continuum mechanics, in which Newtonian viscosity and Fourier heat conduction are assumed. A more detailed look reveals a fly in the ointment. The computer-generated temperature and velocity profiles are less steep than the corresponding calculated profiles from the Navier-Stokes equations. The difference is about thirty percent. Thus the hydrodynamic viscosity and conductivity are in fact smaller than those inferred from the directly-measured shockwave profile. On the other hand, all of the nonlinear effects so far characterized — wavelength, frequency, and gradient dependence suggest that the shocked material's transport coefficients should lie below the hydrodynamic ones. This qualitative discrepancy remains unexplained. I believe it is likely to be due to the finite range of interparticle forces. On a continuum basis, this would be called nonlocality.

Shockwaves are particularly interesting nonequilibrium states because they require no special nonequilibrium boundaries to preserve them. The similarity between the observed structure of strong shockwaves and the Navier-Stokes predictions suggests that shockwaves could logically be used to *define* nonlinear transport coefficients. A systematic study of the combinations of temperature and velocity gradients available through shockwave compression, based on the Navier-Stokes equations, would be useful.

Finally, a case in which theoretical analysis is in good agreement with the nonlinear computer simulations should also be mentioned¹⁶). The Boltzmann equation predicts a violation of Fourier's linear law of heat conduction at high rotational velocities. This is because Coriolis' accelerations affect particle trajectories in a velocity-dependent way. Even in the absence of a particle current, the heat current is affected by Coriolis' accelerations. Computer simulation of this nonlinear problem, with heat flowing (nearly, but not quite) radially in a rotating annulus, has shown semiquantitative agreement with the predictions of Boltzmann's equation, applied to a dense fluid by using the Enskog theory.

Certainly the additional complications associated with polyatomic molecules deserve the intensive study they are receiving. But our limited understanding of even the simple nonlinear behavior that we see for the simplest conceivable systems, suggests that nonlinear fluid phenomena will be an exciting field for some time.

Note added in proof. Jim Haile is preparing a comprehensive study of the various isothermal equations of motion. Denis Evans and G.P. Morriss have implemented the constant-pressure equations of motion for a many-body soft-sphere system. The equations were well-behaved. We thank Drs. Evans and Haile for communicating these results prior to publication.

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