

# Computer simulation of many-body dynamics

**Even the very simplest model fluid exhibits such characteristics of macroscopic nonequilibrium flow as irreversibility, shear thinning and dilatancy.**

William G. Hoover

The 300-year-old discipline of Newtonian mechanics is still the basis for today's computer calculations at our national laboratories. However, computers are prompting important changes within mechanics itself. Versions of atomistic mechanics now under development save time by matching numerical techniques to computer capabilities, which—even with the fastest, newest machines—are quite limited when compared to the complexities inherent in modeling the real world.

In this article I illustrate the new computer methods that are based on a modified mechanics. As an example I use a very simple model fluid—three particles in a steady nonequilibrium shear flow. We will see that even this small system is large enough to exhibit important macroscopic characteristics of nonequilibrium fluids and to enhance our understanding of such fluids. After a few words on the history of computational mechanics, I will describe some of the computer simulation techniques that investigators are now using to understand macroscopic properties of materials in terms of behavior on the atomic level. We will see that the effort to model real systems forces us to pay close attention to constraints, in particular, to nonholonomic constraints, which we do not often encounter in textbook problems in classical mechanics. Then I will discuss nonlinear nonequilibrium molecular dynamics, looking at the extreme example of shockwaves and the interesting question of reversibility in two- and three-body systems.

**Computational mechanics emerges.** Newton's original formulation of the

"many-body problem" stimulated two correlated advances in applied science. Not only was mechanics developed to describe a wide range of astronomical and mechanical problems, but applied mathematics also had to be invented to obtain numerical solutions of these problems. Numerical techniques of approximation were required because even such a simple system as three interacting particles was then, and still is, analytically intractable. The men who followed Isaac Newton (1643–1727) in developing mechanics—Leonhard Euler (1707–1783), Joseph Lagrange (1736–1813), Karl Gauss (1777–1855) and William Hamilton (1805–1865)—also constructed the applied mathematics necessary to extract numerical results from the analytic formulation. The methods they created to solve the differential equations of motion—Newton's, Lagrange's or Hamilton's—are still in use today.

Much of twentieth-century refinement of these venerable numerical methods has taken place at our national laboratories, where the best possible computers have supported the weapons and energy programs and have also been available, on the side, for other kinds of physics problems. However, the proliferation of computers in the last decade has narrowed the gap between the large laboratories and university centers, which now contribute a major share of computational advances.

Our computers are now about one billion times quicker than humans, but they are still a billion times too slow to simulate the real-time dynamics of a cube of gas only one millionth of a meter on a side! Even today the dynamical behavior of many-body quantum systems lies well beyond the capacity of computer simulation. Limited computer speed also rules out straightforward atomistic simulations of common but complicated flow phenomena, such as turbulence, detona-

tion and plastic deformation—problems that involve too many microscopic degrees of freedom. Whether we use numerical or analytic methods, we can treat these complicated problems more effectively using continuum—as opposed to atomistic—mechanics. Macroscopic continuum mechanics, too, was pioneered by Newton and his early followers, and is now being applied by hundreds of thousands of scientists and engineers. Indeed, for most engineering problems that treat real materials instead of simplified models, only continuum mechanics is relevant.

## Computer simulations

The computer simulations I describe here are not directly concerned with engineering problems such as stress analysis and stability. They are not continuum but atomistic. That is, they deal with matter made up of individual particles rather than viewed as a continuous body. There is an essential difference of scale between the atomistic and continuum views. The more detailed atomic view of the processes underlying macroscopic behavior is necessary to a fundamental understanding of continuum physics.

Laboratory experiments designed to analyze particle behavior help test and support computer work based on the atomistic view. Such experiments include the ingenious shear-flow apparatus of figure 1, in which film records the actual motion of a few hundred real macroscopic particles. The experiment produces a flow record that is very much like the results of computer simulations of shear flow. Computer simulations, however, allow more precise control of flow variables and also yield more elaborate, fine-grained descriptions of the fluid's behavior. By comparing the results of computer and lab experiments, we can improve and refine the techniques of computer simulation as well as the theoretical models of nonlinear flow.

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The underlying goal of atomistic computer simulation is, of course, to understand the macroscopic properties of materials in terms of the behavior of their constituent microscopic particles. What sorts of macroscopic behavior can computer simulations allow us to study? For a start, think about everyday actions such as opening a can, lighting a match or boiling water. These three macroscopic operations correspond, on an atomic level, to the breaking of bonds and the motion of lattice defects, frictional heating and chemical reaction, and a phase change induced by thermal motion. We can analyze the fundamental microscopic processes underlying these large-scale events by computer simulations on a scale of a few hundred or thousand atoms.

It is true that such simulations involve a very small number of atoms compared to the total number in a can, matchstick or cup of coffee, but the number of atoms is still much greater than we can deal with using pencil-and-paper mathematics. For analysis by hand, even a three-body problem—predicting where three interacting particles will go as a result of their mutual interactions—is too much. The importance of the atomistic models solved by computation is that the few hundred particles we can study and thereby understand are enough to give a faithful picture of atomic behavior.

Atomistic simulation can follow the details of accreting water molecules in the formation of rain drops, the relative sliding motion of iron atoms in a nail bending under a hammer blow, or the separation of atoms from one an-

other as a crack advances in a china plate. One can incorporate these underlying mechanisms into the macroscopic models that describe cloud formation, plastic flow and fracture.

Temperature, stress, internal energy and heat flux are typical macroscopic properties of interest in our simulations. On a microscopic level, temperature corresponds to the kinetic energy of particles; stress, to the flow of momentum; and heat flux, to the flow of energy.

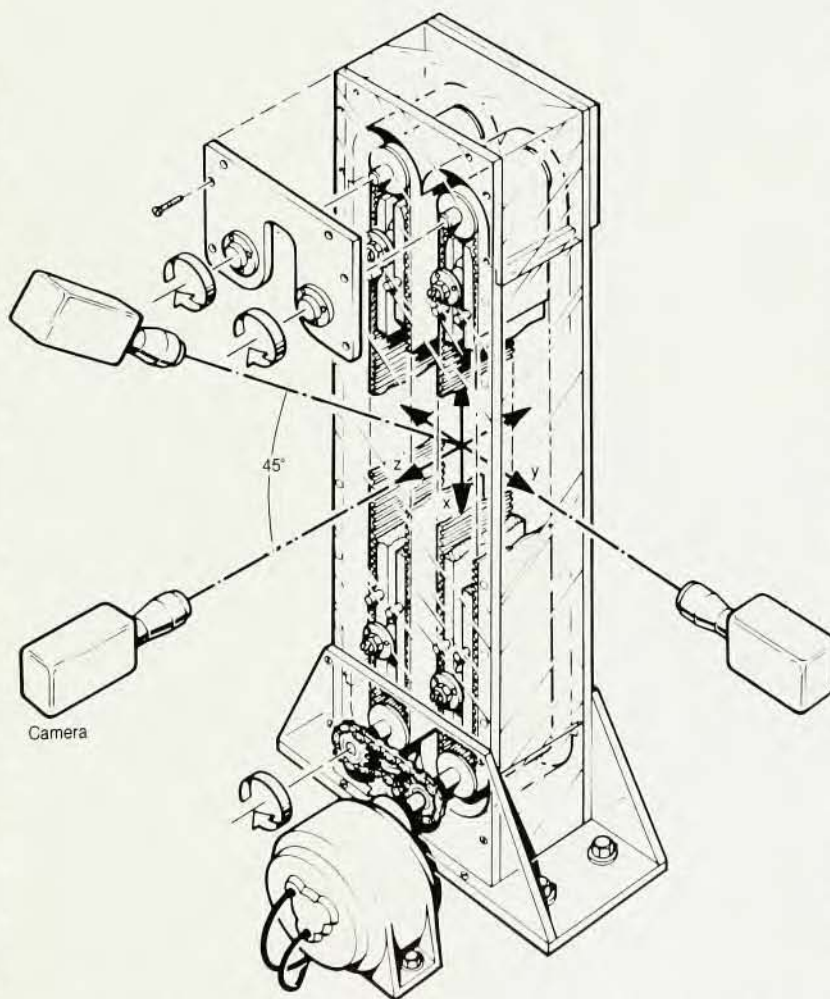
With a fast computer, measuring these constitutive properties of microscopic systems is straightforward. One can express dynamic variables, such as

energy, temperature and the pressure tensor, as simple functions of particle coordinates and velocities. Averaging these functions over time or space leads to the macroscopic equation of state. Entropy is not a dynamical variable, and has to be determined indirectly, by thermodynamic integration.

For simplicity, I restrict the discussion here to monatomic point-mass particles with short-range forces. However, one can apply similar techniques to long-range Coulomb forces and polyatomic molecules. Models of simple metals and ionic melts, as well as water, benzene, substituted methanes and other small molecules have all been treated successfully.

**The algorithms.** A computer simulation involves tracing out the motion of from two to a million particles. The particles advance through space according to discrete "difference equation" approximations to the differential equations of motion. Thus the "motion" is described as a series of snapshots. In a steady-state case, just as at equilibrium, we can accumulate time averages during the calculation. Nonsteady noncyclic phenomena require a different averaging: Several replications of the calculation, with slightly different initial conditions, have to be averaged together.

A typical calculation includes millions of discrete time intervals. We must make these time intervals small enough so that we can interpolate particle trajectories between them as low-order polynomials in time. For a time step  $\Delta t$  small enough to replace the particle's position  $r(t)$  by a quadratic, we can re-



**Apparatus** for a large-scale macroscopic experiment simulating shear in polymer solutions. The experiment simulates a polymer solution with quarter-inch plastic spheres—the "polymer molecules"—in a viscous liquid. In the center of the apparatus, the "solution" is sheared by motor-driven belts moving in opposite directions. Experiments with this device at Los Alamos National Laboratory have measured the clustering of the "polymer molecules" as a function of strain rate and packing density. The results correlate well with experimental data for smaller particles. The apparatus is about one meter in height. (From reference 10.)

Figure 1



place Newton's equation of motion,  $m\ddot{r} = F(r)$ , by Verlet's time-reversible difference equation

$$m[r(t+dt) - 2r(t) + r(t-dt)]/(dt)^2 = F(r(t))$$

A typical time step  $dt$  for liquid argon at its triple point, using Verlet's equation, corresponds to 10 femtoseconds of real time. We can use Verlet's equation to compute the position of a particle at time  $(t+dt)$  in terms of its earlier positions  $r(t)$  and  $r(t-dt)$ . From this coordinate information we can calculate interpolated velocities using either

$$v(t) = [r(t+dt) - r(t-dt)]/(2dt)$$

or, more accurately, but more expensive in terms of storage,

$$v(t) = [r(t-2dt) - 8r(t-dt) + 8r(t+dt) - r(t+2dt)]/(12dt)$$

There are a variety of software packages that one can use to perform integration and interpolation efficiently.<sup>1</sup>

There are two types of molecular dynamics simulations: equilibrium<sup>2</sup> and nonequilibrium.<sup>3</sup> Equilibrium simulations use regular Newtonian equations of motion, without modification, to determine the thermodynamic equation of state. Nonequilibrium simulations, which we will discuss in the second half of this article, use modified Newtonian equations to determine the state of a system. The equation of state relates the pressure, energy, volume and temperature of an isolated system whose energy and volume do not change with time. Equilibrium calcu-

lations, which reflect the simplest states of a system, naturally developed first and were fairly well perfected before any nonequilibrium simulation began. The experience gained from work on equilibrium simulation made it possible later to venture into the more complicated realm of systems away from equilibrium, which are characterized by inhomogeneities, gradients, flows, external forces, dissipation and heat reservoirs.

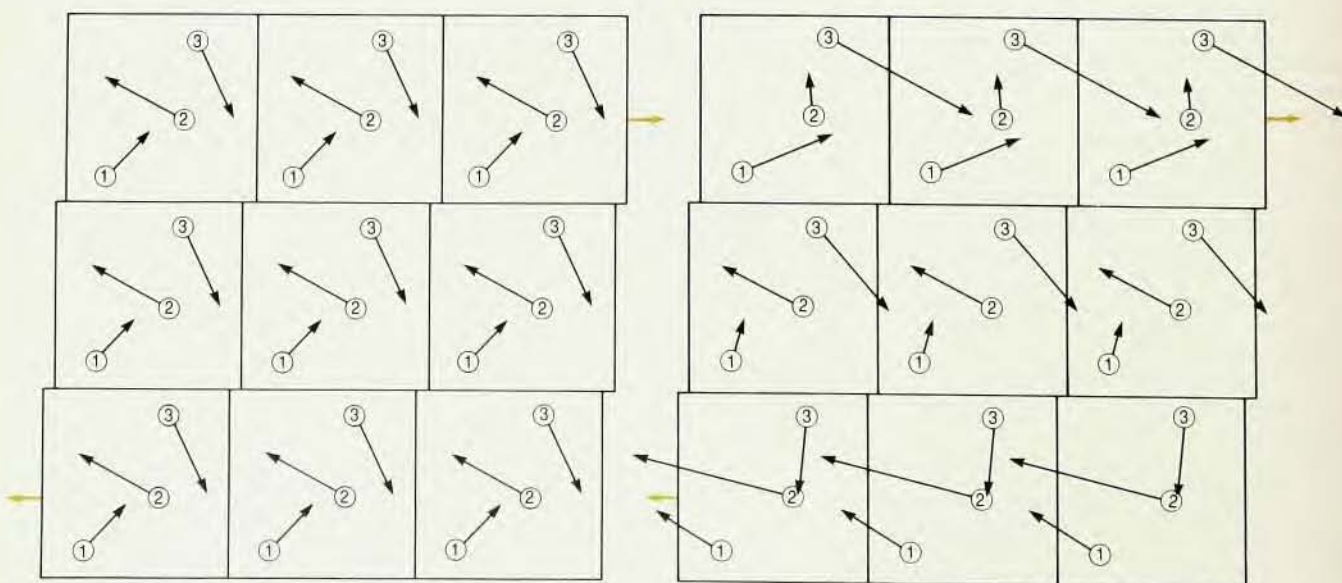
Approximate numerical solutions often provide unexpected insight into fluid behavior. Feigenbaum's universality theory, which deals with difference equations,<sup>4</sup> is a well-known example of this. (See "Roads to chaos," by Leo Kadanoff, December, page 46.) Difference equations were originally developed to give approximate numerical answers to differential equations; nonlinear problems give rise to simple difference equations that have a complex, rich topological structure, where very small changes in the equations lead to startling patterns of wide change in the results. Motivated by numerical solutions, Feigenbaum showed that the simplest nonlinear equations have a chaotic behavior that is optimistically called "universal"—applicable to a wide range of physical phenomena.

Computer simulation gives the researcher virtually unlimited flexibility in varying the parameters in a calculation. With this numerical experimentation one can do much more than with ordinary laboratory experiments to clarify patterns of behavior in physical phenomena. An example is the sur-

prising discovery that even simple two- and three-body systems already clearly embody the irreversible dissipative behavior described by the second law of thermodynamics, which is ordinarily written for macroscopic systems. Among the many-body phenomena that computer simulations have revealed are the failure of slightly anharmonic chains to equilibrate, the slow decay of velocity autocorrelation functions in fluids (see the article by Berni Alder and W. Edward Alley on page 56), and the universality of the melting transition. A more recent example is the surprising non-Newtonian flow behavior of "simple fluids," discussed by Denis Evans, Howard Hanley and Siegfried Hess in their article on page 26.

**Constraints become important.** Equations of motion, and ways to solve them, underwent little change for 250 years. Equivalent formulations of Newtonian, Lagrangian and Hamiltonian mechanics all agreed, provided that isolated conservative systems were treated and that all degrees of freedom were explicitly included. With the advent of computer calculations, difficulties associated with fluctuations and boundaries in small systems became important concerns. Physicists developed methods to include these effects efficiently, or to eliminate them altogether by imposing special constraints on the equations of motion.

The perturbing influence of container walls extends so far into a fluid that it is not practical on our computers to consider systems large enough to make boundary effects negligible. To eliminate the influence of the container,



**Two views** of a periodic three-particle system undergoing steady shear at constant temperature. Colored arrows show the direction of the shear. In the left half of the figure, arrows show the thermal motion

of the particles measured relative to the local comoving velocity. At the right, arrows show velocities of the same particles, this time measured relative to an observer at the center of the picture. Figure 2



researchers have adopted the periodic boundary conditions used in lattice dynamics, as indicated in figure 2. One can picture a periodic system either as extending infinitely far in all directions, or as a finite system in which opposite sides are artificially coupled together. These special periodic mechanical boundaries greatly improve the rate of convergence to the large-system limit. Note that the layered structure induced by boundary surfaces is not *always* unrealistic: Granular materials, such as gravel or grain, do exhibit a fairly well-defined boundary layer that extends only half a dozen particle diameters from the container wall. One can use computer simulations to study the flow properties of granular materials, too.

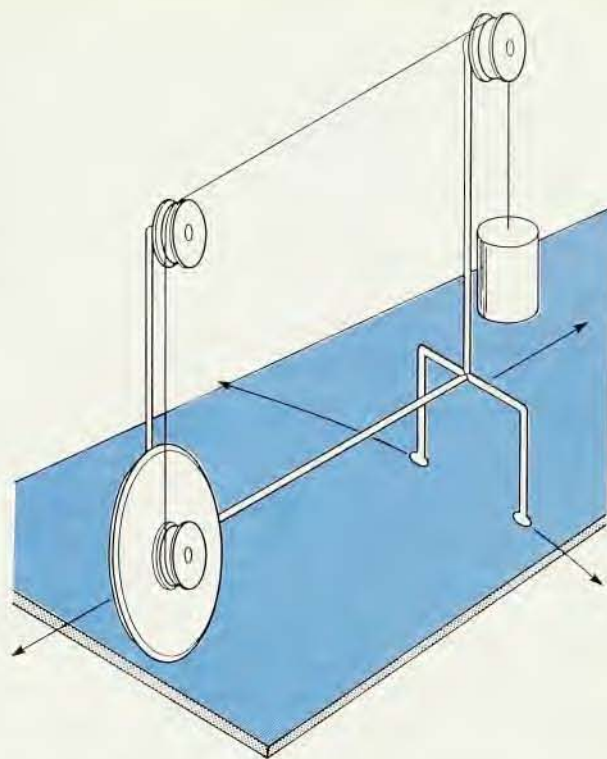
When one imposes special constraints to handle the difficulties associated with fluctuations and boundaries in small systems, the constrained versions of the equations of motion can be based upon the "holonomic" and "nonholonomic" constraints explained in textbooks on classical mechanics.<sup>5</sup> Holonomic constraints involve only coordinates and time, and have the form  $f_h(q,t) = 0$ . Nonholonomic constraints involve velocities, and have the form  $f_n(q,\dot{q},t) = 0$ . The most common holonomic constraints are those used to fix bond distances or angles in rigid polyatomic molecules. The use of holonomic constraints has made possible the study of both rigid and flexible molecules. Computer time requirements have limited quantitative studies of the constitutive relations for polyatomic molecules, but these studies are proceeding through use of the same basic techniques described here for monatomic simple fluids.

Nonholonomic constraints, which involve velocities, typically occur in mechanical problems with rolling contacts. The resulting linear constraints are straightforward to treat. Until recently, the only nonlinear nonholonomic constraint discussed in the literature<sup>6</sup> was that governing the motion of the front-wheel-drive cart shown in figure 3.

Scientists in countries around the world are now studying many types of nonlinear nonholonomic constraints. In atomistic simulations, constraints fixing temperature, energy, pressure or heat flux involve both the coordinates and the velocities in a nonlinear inhomogeneous way. Temperature and kinetic pressure are quadratic in the velocities. The kinetic heat-flux vector is cubic. It isn't clear how to constrain temperature, pressure or heat flux using classical, unmodified Newtonian mechanics. There are two complications. First, dissipative constraints

"Appell's cart." This device, driven by a falling weight, is the classical example of a mechanical system with nonlinear nonholonomic constraints involving velocities. Such constraints typically occur in systems with rolling contacts. As the arrows indicate, the cart can run forward or backward and rotate about the lowest point on its knife-edged wheel.

Figure 3



cause the energy to vary with time because the forces that induce the constraints do work—such constraint forces are ordinarily avoided in textbook classical mechanics. Second, once we allow energy changes, the many trajectories satisfying nonlinear nonholonomic constraints frustrate a straightforward Lagrange-multiplier approach, which no longer uniquely describes the motion.

### Nonequilibrium molecular dynamics

The first atomistic fluid simulations at Los Alamos and Livermore established two interesting points: First, a dilute many-body hard-sphere gas reaches thermal equilibrium rapidly, after just a few collisions per particle, confirming the low-density behavior predicted by the Boltzmann equation. Second, the ensuing equilibrium properties agree with the predictions of the Mayer virial-series approach, namely, that one can calculate the equilibrium pressure and energy by summing each particle's two-body interactions, three-body interactions, and so on. These initial successes clarified the regions of usefulness of both the gas-phase nonequilibrium and the fluid-phase equilibrium theories. E. G. D. Cohen describes the gas-phase theory in his article on page 64.

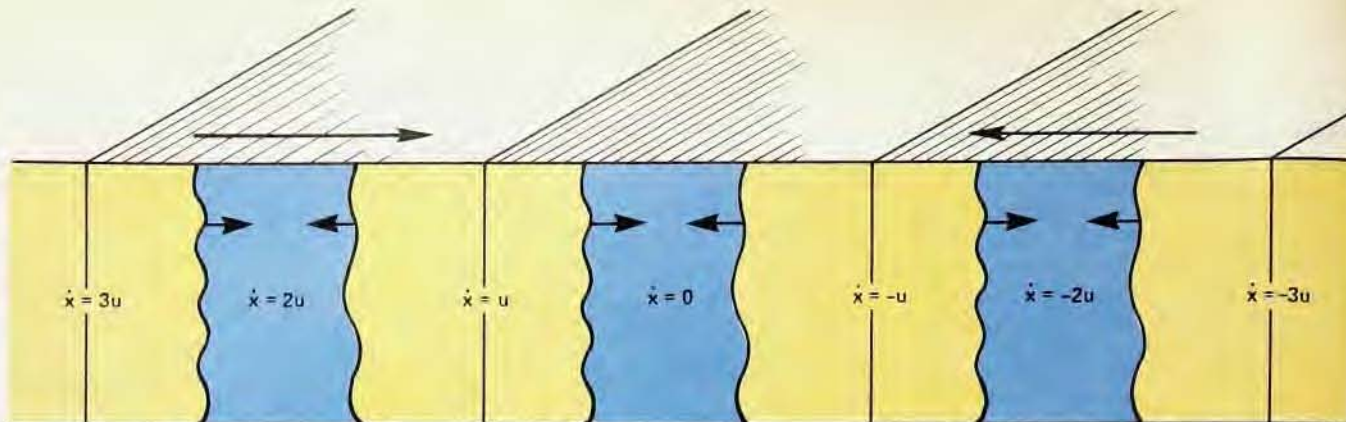
While we can make direct comparison between theoretical analyses and simulations for dilute gases, both at equilibrium and away from equilibrium, for dense nonequilibrium fluids we have had very little useful theory. Hence, for dense fluids the computer experiments have acted as helpful pi-

lots in correlating microscopic atomic forces with macroscopic nonequilibrium phenomena. The principal such phenomenon of interest to simulation is nonequilibrium flow. A fluid's *shear viscosity*—its resistance to changes in shape—helps characterize its macroscopic flow. Viscous flow, first described by Newton, is an irreversible flow in which a fluid is heated by internal friction occurring during deformation. Alder and Alley, in their article on page 56, describe the generalization of viscosity that takes account of linear frequency and wavelength dependence.

The second law of thermodynamics distinguishes between reversible processes, which can be seen as a sequence of equilibrium states, and irreversible entropy-producing nonequilibrium flows, in which there is usually energy conversion—work into heat. This conversion normally occurs in the process of transporting mass, momentum or energy from one place to another. Thus, most nonequilibrium problems are also "transport problems." In Newtonian viscous flow, stress is proportional to the strain rate; that is, the force per unit area is proportional to the relative deformation rate. In heat flow, the flow per unit area and time is proportional to the negative of the temperature gradient. The proportionality coefficients for these flows—the viscosity and thermal conductivity—are "transport coefficients."

A major goal of theory and simulation is to generate transport coefficients and to correlate these with the results of the appropriate laboratory





**A pair of shockwaves**, generated by compressing a fluid with two moving periodic images of itself. Mean velocities  $\dot{x}$  in the shocked and unshocked (blue) material are expressed in terms of the piston velocity  $u$ . Small arrows show shockwave motion. Figure 4

experiments. Alder and Alley discuss the definition and utility of generalizations of the hydrodynamic transport coefficients when those generalizations take into account frequency and wavelength dependence. Now that we have reliable methods for simulating nonequilibrium flows and for deriving macroscopic constitutive relations, we can expect to see more quantitative comparisons with high-frequency short-wavelength experiments in the years ahead.

Ten years ago it was established that a standard method for estimating transport properties, the "Green-Kubo fluctuation method," converged very slowly for dense fluids.<sup>2</sup> The Green-Kubo approach requires integration of a correlation function that describes the decay of velocity fluctuations about equilibrium and is computationally more cumbersome than the accumulation of steady-state averages. The stage was set to seek better methods, and indeed, starting with work at Livermore in 1974, the development of steady-state computer simulations began. In these, the underlying idea is to simulate steady flows—flows that do not change with time—to avoid the inefficient alternative of waiting for equivalent equilibrium fluctuations.

**Shockwaves.** One can adapt steady-state simulations to the analysis of shockwaves.<sup>7</sup> Figure 4 shows the basic geometry. Shockwaves are an extreme case of nonlinear fluid flow, and as such reveal interesting new aspects of flow in general. They involve abrupt, violent changes in all of the fluid's thermodynamic properties. Gone are the smooth, gentle gradients of normal fluid flow—the pressure can rise millions of atmospheres in little more than one atomic vibration time! Heat flow occurs in a shockwave in the presence of shear, or changes in shape. The combined effect of compression, heating and shear is *nonlinear*, not simply a sum of individual contributions.

Shockwaves, because of the speed and size of their gradients, have important applications in metallurgical and

chemical syntheses. Computer simulation may be able to explain the use of shockwaves to produce macroscopic specimens of metallic glasses and to induce chemical reactions. Computer simulations of shockwaves have already shown that nonlinear effects on even the monatomic transport coefficients are relatively small, but significant. A shockwave compressing liquid argon from the triple-point liquid state to a much denser fluid state at 400 kilobars causes viscous stresses only 30% different from those based on the Navier-Stokes model of Newtonian viscosity. Fourier's law, which states that the flow of heat is proportional to the temperature difference, also applies with similar corrections under these conditions. Interestingly, the shockwave effect on the transport coefficients is in the opposite direction from that found in the simpler (but still nonlinear) case of plane Couette flow, shown in the figure on page 29. In Couette flow, the velocity  $u_x$  of the fluid varies linearly with displacement  $y$  in the direction perpendicular to that of the flow:  $u_x = (du_x/dy)y$ .

A plane shockwave is a particularly clean nonlinear problem because the only boundaries needed to confine it are equilibrium liquid states. The two boundaries, made up of shocked and unshocked particles, differ in velocity, density and temperature. Computer simulations of shockwaves are complicated by the need to resolve velocity, stress, energy and heat flux spatially and in a moving coordinate system. Even so, a shockwave simulation requires only a few hundred lines of FORTRAN.

### Describing nonequilibrium states

We specify the "state" of a many-particle system by listing its properties; our list should be sufficiently detailed so that any other interesting property necessarily follows from those listed. The simplest states are equilibrium fluid states, which are completely specified by only a few variables—pressure, temperature and composi-

tion. Equilibrium thermodynamics relates the work and heat involved in reversible changes between states.

As we move away from equilibrium, we need additional variables to describe a state. In "linear" nonequilibrium situations that are still relatively close to equilibrium, it is sufficient to specify the flow of mass, momentum and energy, that is, the particle current, the shear stress and the heat flow. Far away from equilibrium, where conditions become nonlinear, it is not known what constitutes a complete set of state variables. For isothermal Couette flow, Evans, Hanley, and Hess suggest that density, temperature and strain rate are sufficient. In Couette flow viscosity *decreases* with increasing strain rate, as figure 5 indicates; this behavior is known as "shear thinning." On the other hand, for sufficiently large deviations from equilibrium, a complete description would require that the pressure tensor and heat flux vector in a shear flow be specified too. In a shockwave the viscosity generally *increases* with increasing strain rate. Thus even the *sign* of the nonlinear shear behavior depends upon more than the local thermodynamic state and the strain rate. The mechanisms underlying this complex behavior aren't yet known.

Edwin T. Jaynes of Washington University in St. Louis has emphasized the need for a complete description of state in formulating nonequilibrium statistical mechanics. However, identification of the relevant state variables continues to be a major difficulty, hindering progress in nonequilibrium statistical mechanics. For simulations of nonequilibrium molecular dynamics, we can specify the additional state variables that are needed by imposing boundary conditions or by imposing constraints on the dynamical trajectories. The use of external physical boundaries is relatively undesirable in computer simulations because these boundaries cause geometric inhomogeneities and increase the dependence of calculated thermodynamic and hy-



hydrodynamic properties on the size of the system. The use of specially constrained equations of motion that maintain steady values of state variables help to avoid these boundary effects.

**Gauss's principle** of least constraint<sup>5</sup> occupies an obscure corner of classical mechanics, but is extremely useful for solving nonequilibrium problems. Gauss enunciated this principle two years after developing the mathematical least-squares technique. He stated that the forces of constraint  $F_c$  acting on a system should be made as small as possible, in a least-squares sense, minimizing  $\Sigma F_c^2/m$ . This leads to the Newtonian equations of motion. Models of molecular structure have long used Gauss's principle to impose geometric "holonomic" constraints, but it has only just recently been observed that the principle is also effective for constraining the much more complicated hydrodynamic and thermodynamic functions in nonequilibrium systems.

To illustrate Gauss's principle, consider temperature. The kinetic temperature of a classical  $D$ -dimensional  $N$ -particle system is proportional to the kinetic energy:

$$DNkT \equiv \Sigma(p^2/m)$$

If we hold the kinetic temperature to a constant, Gauss's principle produces the equations of motion

$$\begin{aligned}\dot{p} &= F + F_c \\ F_c &= -\xi p \\ \xi &= \Sigma F_c(p/m)/\Sigma(p^2/m)\end{aligned}$$

Here  $F$  represents the applied forces. The "friction coefficient"  $\xi$  varies with time, changing sign and magnitude in such a way that temperature remains fixed. To see that these constrained equations of motion satisfy the constraint of fixed temperature, multiply both sides of the  $\dot{p}$  equation by  $p/m$  and sum over all particles. The left-hand

side is then the time derivative of the kinetic energy, and the right-hand side is identically equal to zero. The constrained equations are stable and effective in keeping the temperature constant for systems of two or more particles (three or more in one dimension). One can also apply Gauss's principle to shear flow, diffusion, electrical conduction and heat conduction.

### Simulating shear and heat flows

The stress tensor from two-particle nonequilibrium calculations exhibits shear-thinning and dilatant behavior similar to the many-particle effects discussed by Evans, Hanley and Hess. The viscosity decreases, and the pressure increases, with increasing strain rate. In the two-particle case, the motion can be treated as that of a single reduced-mass particle moving in a time-dependent field. Application of the Boltzmann equation to the two-particle Lorentz gas problem produces a very similar shear-thinning behavior, as shown in figure 5.

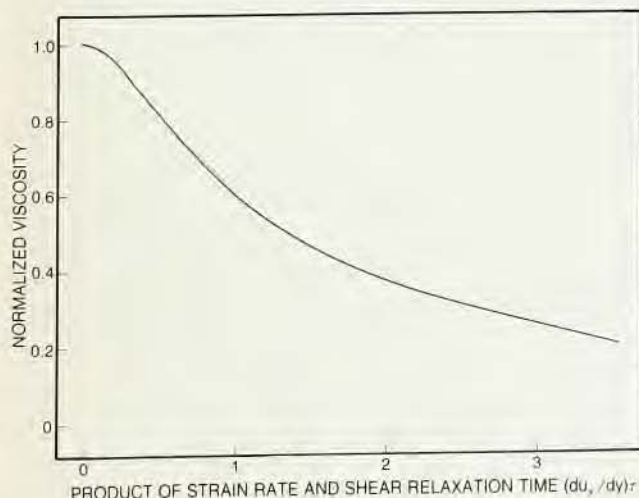
Heat flow has been more difficult to study than shear flow. The simplest heat-flow model requires three bodies. One can carry out simulations of homogeneous periodic heat flow with external forces that induce a heat current. The amplitude of the external force, analogous to the voltage driving an electric current, can be kept fixed or, using Gauss's principle, adjusted to maintain a constant heat current. The dissipation associated with this current not only matches that calculated for the system's linear response to small currents, but it also allows one to estimate the system's nonlinear response. Evans<sup>8</sup> has shown that the external-force approach to heat flow dramatically reduces the fluctuations inherent in alternative methods.

There is no reasonable doubt that the computer flow simulations reproduce

correctly the *linear* diffusive, viscous and conductive transport phenomena. The accuracy of computer simulations of *nonlinear* properties is currently being investigated, mainly by comparison with less restrictive simulations and with experiment. To the extent that disagreement is found, we must expand our list of nonequilibrium state variables to include new constraints, as Jaynes has emphasized. (Particular fluctuations could also be imposed through Gauss's principle.) So far the indications are that we can determine the nonlinear stress tensor, at least semi-quantitatively, by nonequilibrium isothermal or isoenergetic simulations. For instance, normal stresses calculated from isothermal "homogeneous shear" equations of motion (see figure 6c) agree with predictions of the Boltzmann equation for low-density systems.

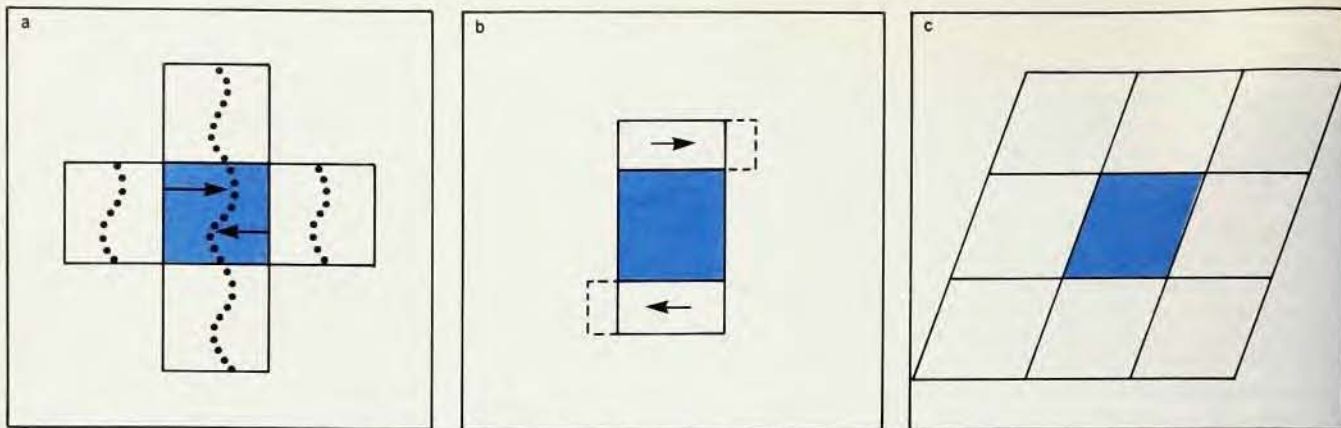
**Reversibility.** The equations of motion for nonequilibrium simulations are characteristically "reversible in the time."<sup>9</sup> This means that a movie of the nonequilibrium motion, run backwards, would show a "reversed" motion obeying the *same* equations of motion. However, macroscopic hydrodynamics insists that the conversion of work to heat is irreversible. This macroscopic view is correct, even for two or three bodies! Formally, reversibility implies that the viscosity and thermal conductivity can change sign. Newton's, Lagrange's and Hamilton's classical equations of motion all share this reversibility property, but the hydrodynamic equations, which include the irreversible production of entropy, with viscosity and conductivity always positive, do not share this property. Thus, real life movies make little sense when run backwards. This lack of reversibility results from the instability inherent in the microscopic equations of motion—the equations of motion of point masses.

Quantitatively, the accuracy required in the initial conditions varies *exponentially* with the length of time over which the trajectory is to be reversed. Reversing the motion of atmospheric-pressure argon gas for one second would require initial conditions known to a trillion decimal places. In a very short time from the macroscopic viewpoint—a few collision times—the work and heat terms in a reversed flow, as well as the viscous stress, change sign and exhibit macroscopic irreversible dissipation. It is extremely interesting that deterministic two- or three-body problems already contain the dynamical complexity required to thwart formal microscopic reversibility and to obey—on a time-averaged basis—the second law of thermodynamics instead.



**Viscosity** of a two-body system as a function of strain rate. The data come from a numerical solution of the Boltzmann equation for a two-body system of hard disks. Figure 5





**Inducing a shear flow** in three different ways. These are the methods commonly used in computer experiments. In **a**, shear flow is driven by a spatially-dependent external force, a sinusoidal field. In **b**, boundar-

ies are constrained to move as indicated. In **c**, periodic images of the system itself provide homogeneous deformation; heat may be extracted to maintain constant temperature or energy. **Figure 6**

When Gauss's principle is applied to two- or three-body shear flows, not only are the few-body viscosities positive, but they also exhibit nonlinear shear thinning, where the viscosity is a decreasing function of strain rate, as in figure 5. The mean pressure, on the other hand, shows a rapid increase with strain rate, a behavior known as "dilatancy." Both shear thinning and dilatancy are well-known macroscopic properties. The appearance of these nonlinear phenomena in two- and three-body problems promises to simplify our theoretical understanding of them.

### Nonequilibrium simulations

While researchers have put the main emphasis on the determination of linear and nonlinear transport coefficients, they have done considerable work on spatial distribution functions in shear flows and in shockwaves. Although many of the simulations correspond to conditions more extreme than those ordinarily encountered in the laboratory, most are typical of the violent deformation of materials caused by laser heating or strong, explosively-driven shockwaves. It is only a matter of time before more careful analyses will make possible a direct confrontation between simulation and experiment. Already, light scattering from sheared polymer systems has shown qualitative agreement with the nonlinear shear effects seen in computer simulations. Larger-scale, truly macroscopic experiments<sup>10</sup> at Los Alamos have simulated the shear of polymer solutions. These experiments show the clustering of "polymer molecules"—quarter-inch plastic spheres—suspended in a viscous fluid sheared by moving belts (figure 1). Data showing this clustering as a function of strain rate and packing density correlate very nicely with experimental data for

smaller particles and should stimulate corroboratory computer simulations.

The results obtained so far indicate that the transport coefficients depend relatively little on the driving gradients. However, the small dependence isn't uniform. The coefficients either increase or decrease, depending upon the particular conditions of the simulation. In strong shockwaves the effective transport coefficients exceed their small-gradient values. In simple shear flow such as that indicated in figure 5, the viscosity lies below the low-gradient value. Even the relatively small decrease seen in shear flow greatly exceeds current theoretical predictions. The reason for this disagreement is not yet understood.

The computer simulations of "simple shear" in "simple fluids" have revealed unexpectedly complicated stress states. The "normal stresses,"  $-P_{xx}$ ,  $-P_{yy}$  and  $-P_{zz}$ , all depend upon the shear strain rate  $du_x/dy$  in a complicated way. We can ascribe the compressive  $zz$  stress to an overall energetic distortion of the fluid's structure, induced by shear. The  $xx$  and  $yy$  stresses include not only a similar distortion, but also the effect of "stress rotation." Because Couette flow is a rotational flow—clockwise for  $du_x/dy$  positive—any  $xy$  shear stress present in the fluid has a tendency to rotate clockwise through an angle  $(\tau/2)du_x/dy$ , where  $\tau$  is the shear relaxation time. This rotational memory should increase the normal stress  $-P_{xx}$  relative to the normal stress  $-P_{yy}$ , and this increase is in fact observed in computer simulations of dense fluids.

As the pace of activity in computer simulation has quickened, the need for frequent international gatherings to communicate findings and to avoid duplication has become more pronounced. The Gordon conferences and the National Bureau of Standards con-

ferences in this country, and the Centre Européen De Calcul Atomique et Moléculaire workshops and the Collaborative Computational Project workshops abroad, have been particularly valuable forums for the exchange of information.

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