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# FLOWS FAR FROM EQUILIBRIUM VIA MOLECULAR DYNAMICS

*Denis J. Evans*

Research School of Chemistry, Australian National University,  
Canberra, A.C.T. 2601, Australia

*William G. Hoover*

Department of Applied Science, University of California at Davis-  
Livermore, and Lawrence Livermore National Laboratory, Livermore,  
California 94550

## 1. INTRODUCTION

The basic concepts—mass, force, and acceleration—were first correctly interrelated by Newton. Three hundred years ago he explained the regular motion of the planets about the Sun on the basis of pairwise-additive gravitational forces. The possibility of solving Newton's equations of motion for  $N$ -body systems of atoms or molecules had to wait until 1953, when suitable computers had become available at Los Alamos.

On a human time scale, the night sky has a relatively stable appearance. It is amusing that, from a mathematical viewpoint, gravitational  $N$ -body systems are much less "stable" than the molecular systems studied by molecular dynamics. Mathematical stability can be monitored by observing the separation between two neighboring trajectories. In a stable case, the separation grows linearly with time. In the typical *unstable* case, this distance increases exponentially with time. This "Lyapunov" instability is a ubiquitous feature of interesting dynamical systems. Whether or not it affects other properties of such systems in any important way is a

fascinating unresolved problem. Interest in astronomical problems, the original focus of many-body studies, is still an active field of research (Lightman & Shapiro 1978).

Molecular dynamics has come to mean the numerical solution of classical differential equations of motion for many-body problems. The number of particles  $N$  has varied from 2 to the current world record of  $N = 161,604$  (Abraham et al. 1984). The first serious efforts in this field involved simple one-dimensional systems with  $N = 16$ . These studies were suggested by Fermi (Fermi et al. 1955).

Fermi's early calculations (Tuck & Menzel 1972) were designed to illustrate the approach toward equilibrium of an anharmonic one-dimensional chain. The failure of such chains to equilibrate led to a still-growing industry: chaos, solitons, and catastrophes. Fermi et al. evidently also solved some two-dimensional dynamical problems in their exploratory work (Miller 1964, 1971). Within five years, both solid-phase (Gibson et al. 1959) and fluid-phase (Alder & Wainwright 1956) simulations in three dimensions appeared. Recent "large" dynamic simulations (Meiburg 1985) of 40,000 flowing gas particles, 59,573 vibrating solid particles (Kinney & Guinan 1982), and 161,604 adsorbed atoms (Abraham et al. 1984) on a graphite substrate are about four orders of magnitude "larger" than those Fermi inspired in 1953.

The deterministic nature of the underlying differential equations simplifies intercomparisons and checks of the work, but this determinism should not be taken too seriously, since Lyapunov instability interferes. Thus the "true" trajectory is not followed for long. Lyapunov instability complicates the lives of physicists seeking help from mathematicians in analyzing their problems. Mathematicians suspect that the instability is responsible for whatever bizarre behavior the physicist finds (Fox 1983). Physicists know that no significant features of the systems they study can be grossly altered by this sensitivity to small perturbations.

G. A. Bird's "direct-simulation method" takes advantage of the macroscopic insensitivity to exact microscopic details. With this approach and its many variants (Nanbu 1983a), pairs of particles collide statistically rather than deterministically. The resulting simulations are somewhat cheaper than those of true molecular dynamics. Millions of gas-phase particles can be treated with these techniques (Potter 1973).

As with any computer technique, molecular dynamics can furnish excruciating detail (Raveché et al. 1972). Any reproducible features of the calculations can be used to test and expand theories and to curtail misguided hunches.

Molecular dynamics, when coupled with graphic displays, is useful in unraveling unexpected phenomena and mechanisms that are not under-

stood (Erpenbeck 1984). Flow visualization is simplest in two-dimensional systems. In three-dimensional systems, a slow rotation is useful in presenting solutions in movie form.

In comparing molecular-dynamics results with true laboratory experiments, not only forces but also boundary conditions must be specified. Even in the largest simulations, the fraction of surface particles would be a few percent if a real boundary were present. For this reason, techniques reducing the influence of boundaries, or eliminating them altogether, have been extensively studied. This effort has generated interest in many familiar ideas: viscous damping, smoothing, and Gaussian noise. Many of the schemes used to carry out constant-temperature or constant-energy simulations are straightforward examples of "control theory." Even so, a lack of diligence, candor, or curiosity has led to a wide variety of ill-conceived techniques, which G. Stell refers to as "setbacks in physics."

Systems "far from equilibrium" occur whenever nonequilibrium properties vary in just a few mean free paths or over a very few collision times. Most of the nonequilibrium simulations using molecular dynamics are far from equilibrium. Otherwise, the interesting flow phenomena being studied would be obscured by thermal and statistical fluctuations. In fluid mechanics, typical examples include Knudsen gases and shock waves, as well as interfacial regions bounding rapidly vaporizing or condensing phases. If such systems could be explained from a theoretical point of view, then there would be no point in simulating them. So far, theory is of little use in predicting the nonlinear aspects of flows far from equilibrium.

In this review, we begin by considering the current state of the theory and pointing out directions in which it might soon be improved. The computer simulations play an important role in furnishing detailed information on which theoretical developments can be based. We next describe the simulation techniques, emphasizing the relatively new idea of constraining macroscopic variables at fixed instantaneous or average values.

As an illustration, we apply several (nine) techniques to the simulation of heat flow in the simplest possible system, a three-particle one-dimensional chain. From this simple model some features common to the more complex systems of interest far from equilibrium are revealed.

We then focus on problems—shock waves, shear flow, and heat flow—in which the result is in doubt from a continuum viewpoint. An area of interest in this sense is the principal of material frame indifference (Lumley 1970, Jaynes 1980). This "principle," really just an approximation, has led a long life, in large part owing to the difficulties in performing unambiguous experimental tests. Molecular dynamics furnishes such tests. Finally, we close this review, which reflects mainly the areas of our own research interests, with speculations on future developments.

## 2. THEORY OF SYSTEMS FAR FROM EQUILIBRIUM

So far, little is known about systems far from equilibrium. Even the Boltzmann equation, which applies at densities low enough that three-body collisions and two-body correlations can be ignored, has to be solved numerically in all but the simplest cases.

Of course, very general scaling or similarity arguments can be applied to nonequilibrium systems, yielding restricted forms of the principle of corresponding states. The idea of scaling, and scale models, is familiar in mechanical engineering. Consider a material in which stress depends only upon strain. In this case the macroscopic equation of motion,

$$\rho \, du/dt = \nabla \cdot \sigma, \quad (1)$$

can be written in a scaled form by multiplying by a characteristic macroscopic length  $L$ . If the time is scaled by the same multiplicative factor—proportional to a sound traversal time—then the scaled equation of motion is independent of  $L$ . Thus the fact that scale models do not exactly mimic full-scale experience is a consequence of exceptions to the assumed dependence of stress on strain. The effects of strain rate and temperature on stress complicate real behavior.

The microscopic equations of motion are ordinary, rather than partial, differential equations, but these too can satisfy scaling relationships. If the coordinates and velocities in two systems differ by only a scale factor, and if the forces also give the same scaled accelerations, then the detailed time developments of the trajectories in the two systems will correspond. A similar correspondence, but with a scaled *time*, holds if the coordinates and accelerations differ by independent scale factors. The two scales can be combined if the force law is an inverse power. The usual range runs from Maxwellian particles (inverse fourth-power potential) to hard spheres.

To obtain corresponding microscopic trajectories in the most general nonequilibrium case, each of the terms in the nonequilibrium equations of motion,

$$dp/dt = F_a + F_b + F_c + F_d, \quad (2)$$

must obey the same scaling relation. Here  $F_a$  indicates the “applied” forces derived from an interparticle potential  $\Phi$ ,  $F_b$  the “boundary” forces,  $F_c$  the constraint forces, and  $F_d$  the driving forces.

It would be appealing if J. W. Gibbs’ equilibrium statistical mechanics could be easily extended to the nonequilibrium case. Jaynes (1980) has

rightly suggested that nonequilibrium ensembles could be constructed by restricting the phase space to regions consistent with macroscopic knowledge. In practice, this prescription is somewhat barren because it is not easily applied. For instance, consider a system undergoing planar Couette flow with an average shear stress  $\langle \sigma \rangle = -\langle P_{xy} \rangle$ . Jaynes' prescription leads to a phase-space distribution function somewhat different from the equilibrium  $f_0$ :

$$f/f_0 = \exp(-\lambda\sigma), \quad (3)$$

where  $\lambda$  is a Lagrange multiplier chosen to reproduce the average stress  $\langle \sigma \rangle$ . We know that this distribution function (3) is oversimplified. The true steady-state distribution function

$$f(t = \infty)/f_0 = \exp\left[-(\gamma V/kT) \int_0^\infty \sigma(-t) dt\right] \quad (4)$$

for the special case of adiabatic plane Couette flow has been known since the work of Yamada & Kawasaki (1967). For dilute gases, the corresponding Boltzmann equation result has been known since 1935 (Chapman & Cowling 1970). If an external field  $F_e$  induces a dissipation

$$dH_0/dt = JF_e, \quad (5)$$

then it is possible to show that the nonequilibrium distribution function takes the form

$$f(t)/f_0 = \exp\left[-\int_0^t \beta J(-s)F_e ds\right], \quad (6)$$

where  $\beta = 1/kT$ . Surprisingly, this formal expression remains valid even in thermostated systems (Morriss & Evans 1985). In this case the *thermostated* field-dependent equations of motion must be used to compute  $J(-s)$  from the initial coordinates and velocities.

One of the important families of relations that has been discovered for transport coefficients is that due to M. S. Green & R. Kubo. The Green-Kubo relations relate a transport coefficient  $L$ , where  $J = LF_e$ , to the decay of equilibrium fluctuations:

$$L \approx \int_0^\infty \langle J(t)J(0) \rangle_0 dt. \quad (7)$$

As we shall see, these expressions have played a major role in the development of algorithms for computing transport coefficients.

The Green-Kubo relations suggest an obvious strategy for computing transport coefficients from computer simulations. One could simply perform an equilibrium simulation and by time averaging compute the required time correlation function  $\langle J(t)J(0) \rangle_0$ . It turns out that such an approach is very inefficient. The results depend strongly and nonmonotonically on system size (Holian & Evans 1983). Furthermore, such calculations must be carried out to very long simulated times in order to achieve convergence of the Green-Kubo integrals (Evans 1981a).

### 3. ATOMISTIC SIMULATION TECHNIQUES

In equilibrium molecular-dynamics simulations, periodic boundaries are used to reduce finite size effects. With this choice, the size dependence of the energy per particle and the pressure is typically  $1/N$ . In nonequilibrium systems, special boundaries have to be considered if mass, momentum, or energy are to be introduced at a physical boundary. A convenient way of adding mass in dense systems has yet to be developed. Momentum and energy can be added in several ways. The most rudimentary technique is to reset the velocities of particles colliding with the "wall" (Lebowitz & Spohn 1978). New velocities are chosen from a Maxwell-Boltzmann distribution with specified mean and mean-squared velocities. A more sophisticated approach is necessary in dense fluids to combat the tendency of particles to order parallel to such boundaries. For this purpose, Ashurst (1973) used "fluid walls" in which the velocities of a few dozen wall particles were constrained to have fixed first and second moments. This was done by an ad hoc scaling process equivalent to using a constraint force  $F_c = A + B \cdot v$ , with  $A(t)$  and  $B(t)$  chosen to maintain the first and second moments unchanged.

An alternative is to use additional "stochastic" forces in reservoir regions. The reservoirs impose a mean temperature (through the second velocity moment) on the reservoir particles. This approach has been used successfully by Karplus and his coworkers (Brooks & Karplus 1983).

More recently, homogeneous techniques using periodic boundaries have been used both to drive and thermostat nonequilibrium flows. Homogeneous algorithms are particularly useful in reducing the number dependence of computed results.

For both heat and momentum flow, the simulation methods can be viewed as employing fictitious driving forces  $F_d$ . These forces homogeneously interact with the molecules in such a way as to mimic precisely the bulk response of a real system to externally imposed temperature or velocity gradients. Statistical-mechanical theory is used to prove the equivalence (Evans & Morriss 1984a) of (a) the *mechanical* response to the

driving force and (b) the *thermal* response to the applied thermodynamic gradient. The latter is described, at least in the linear regime close to equilibrium, by a Green-Kubo relation. This represents one of the most useful applications of these relations. For shear flow it has been possible to develop exact homogeneous methods for simulating flows far from equilibrium.

These methods have been successfully applied to fluids and solids over the entire range of temperatures and densities (Ladd & Hoover 1983, Hanley 1983, Hoover et al. 1984, Gillan & Dixon 1983, Evans 1982a, Hoover et al. 1982).

#### 4. CONTROL OF HYDRODYNAMIC AND THERMODYNAMIC VARIABLES

“Feedback” allows the regulation of a “control variable”  $\zeta$  in terms of an error variable  $\Delta(t)$ . The simplest dependence is linear in  $\Delta$  and its time derivative or integral:

$$\zeta = a \, d\Delta/dt + b\Delta + c \int^t \Delta(s) \, ds, \quad (8)$$

where the coefficients  $a$ ,  $b$ , and  $c$  could be chosen either arbitrarily or so as to satisfy a variational principle such as Gauss’ (Pars 1979). A series “RLC” circuit is described by Equation (8). In this case,  $\zeta$  corresponds to voltage and  $\Delta$  to current. The coefficients  $a$ ,  $b$ , and  $c$  describe inductive, resistive, and capacitive circuit elements, respectively.

A damped oscillator is another simple illustration. If the oscillator velocity were to be controlled, then  $b$  would be a friction coefficient and  $a$  would correspond to an effective mass. Linear relations of the form (8) have been studied extensively because they can be solved easily with Laplace transforms.

Consider now a many-body system to be studied at constant kinetic energy. If the kinetic energy is calculated in a comoving “Lagrangian” coordinate frame, then fixing the kinetic energy is equivalent to controlling the temperature. Gauss’ principle (Pars 1979) suggests that the appropriate control variable is the friction coefficient  $\zeta$ , where Newton’s equations of motion are extended to

$$dp/dt = F(q) - \zeta p. \quad (9)$$

If  $\zeta$  were a control variable, then the simplest energy-based relations for

its time development would be

$$\begin{aligned} d\zeta/dt &\propto d[E(t) - E_0]/dt, \\ &\propto [E(t) - E_0], \\ &\propto \int_0^t [E(s) - E_0] ds. \end{aligned} \tag{10}$$

Relations similar to these have been used for carrying out "isothermal" molecular dynamics (Hoover et al. 1982, Evans 1983) (in which kinetic energy  $K$  rather than total energy  $E$  is fixed). The control variable  $\zeta$  is proportional to the negative time derivative of the potential energy  $\Phi$ . Ashurst (1974) used an equivalent "velocity-scaling" technique in his extensive study of dense-fluid transport properties. Alternatively,  $\zeta$  could be chosen to be proportional to the kinetic-energy error  $K - K_0$  as in Berendsen's more recent effort (Berendsen et al. 1984), or to the time integral of the kinetic-energy error as in Nosé's (1984a,b) method. The Nosé relations are of special interest because in an ergodic system they should generate the canonical distribution. Of the three choices, only Berendsen's is not time reversible. This irreversibility leads to substantial theoretical difficulties. For instance, the equilibrium distribution generated by time-averaging Berendsen trajectories is not known. The time-dependent properties of Berendsen dynamics are also *very* difficult to analyze. In contrast, the fundamental statistical properties of isothermal dynamics and Nosé dynamics are basically understood (Morriss & Evans 1985, Evans & Morriss 1984b, Evans & Holian 1985). If, in the absence of external fields, any of these schemes is applied to total energy, rather than to kinetic or potential energy, the equations of motion eventually generate the micro-canonical ensemble.

An alternative to the steady-state approaches was developed by Ciccotti et al. (1979). They suggested analyzing the linear response to very small external driving forces. The random noise that would normally make such a calculation impossible was reduced by performing pairs of simulations, with and without the external driving field. Differencing the response from the two calculations substantially reduces the short-time noise. Unfortunately, the intrinsic Lyapunov instability requires substantial and computationally expensive ensemble averaging over the initial phases before even reasonably accurate results can be obtained. These difficulties become insurmountable at longer times.

It is possible that this long-time difficulty with "differential non-equilibrium molecular dynamics" could be alleviated by constraining the system to eliminate unwanted fluctuations. It would probably be worthwhile to also consider the response of systems to the simultaneous application of both a momentum gradient and a heat flux.

In the following section we apply the three types of control—differential, proportional, and integral—to the one-dimensional heat-flow problem. This problem is artificial, but interesting nonetheless.

## 5. AN EXAMPLE: HEAT FLOW IN A THREE-BODY PERIODIC CHAIN

With Hooke's law forces, the Hamiltonian  $H$  for a three-particle chain is

$$H = \sum p_i^2/2m + (\kappa/2)[(x_1 - x_2)^2 + (x_2 - x_3)^2 + (x_3 - x_1)^2], \quad (11)$$

where the  $x_i$  are the displacements from equally spaced rest positions. This system has two independent normal-mode vibrations,

$$x_1 = A \sin(\omega t), \quad x_2 = A \sin(\omega t \pm 2\Pi/3), \quad x_3 = A \sin(\omega t \pm 4\Pi/3), \quad (12)$$

which represents right-moving (minus signs) and left-moving (plus signs) phonons.

If we set the stress-free interparticle spacing, the force constant  $\kappa$ , and the atomic mass  $m$  all equal to unity, the phonon wavelengths are 3 and the frequency is  $\omega = 3$ . A convenient property of the phonons (12) is that their kinetic and potential energies are constants of the motion. Thus the phonons (12) are solutions of the control relations (10) specifying steady values for the kinetic, potential, or total energies.

In the presence of a driving force  $F_d$ , the three methods (integral, proportional, differential) lead to different results. Consider the force used by Evans and Gillan to generate a heat current (Gillan & Dixon 1983, Evans 1982b). In the one-dimensional case, this force depends on the contribution of each particle to the energy and to the pressure tensor:

$$F_d \propto [\Delta E + \Delta P_{xx}^\Phi V], \quad (13)$$

where  $\Delta E$  is the difference between the  $i$ th particle's energy and the mean  $E/N = E/3$ . Likewise,  $\Delta P_{xx}^\Phi$  is the contribution of each particle to the potential part of the pressure tensor, again relative to the instantaneous value  $\langle P_{xx}^\Phi \rangle = \sum P_{xx}^\Phi/3$ . If the three-particle chain were in a state of motion corresponding to the right-moving phonon (12), then the pressure-tensor terms from (13) would drive the motion of each particle with a frequency twice the normal-mode frequency.

This driving force gradually excites the phonon (12) with minus signs and causes the chain to heat up. The heating can be prevented in nine different ways, according to the suggestions displayed in (10). That is, the total, kinetic, or potential energy can be stabilized by a derivative, proportional, or integral thermostat.

In Figure 1 we exhibit the results of numerical calculations using these

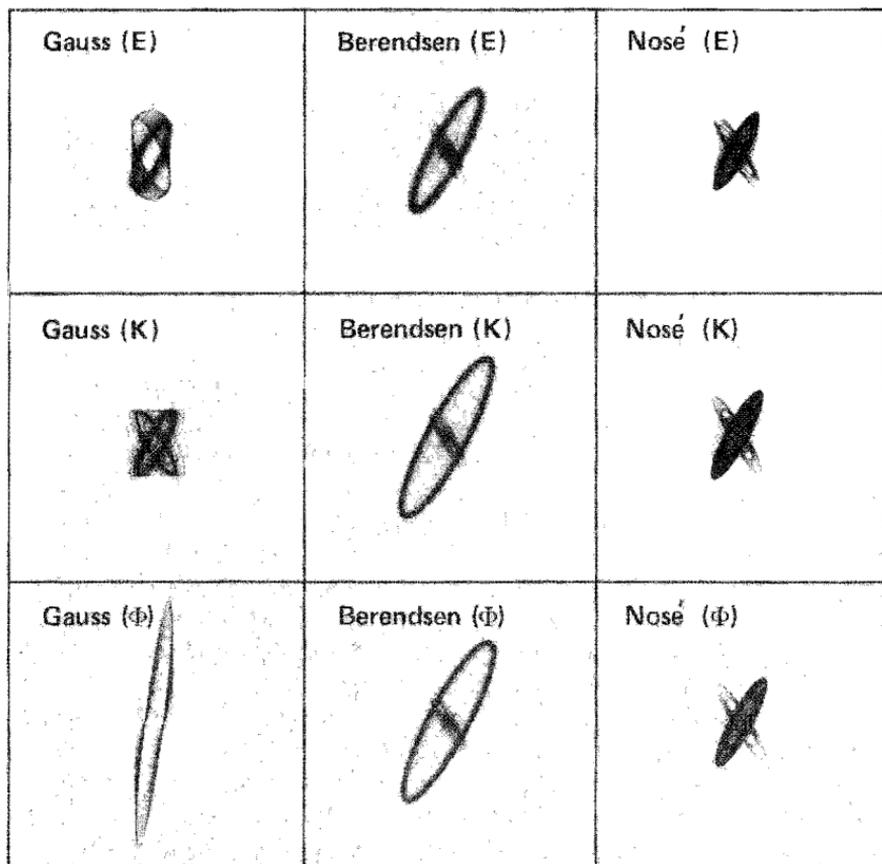


Figure 1 Trajectories for heat flow in a one-dimensional three-particle chain, with periodic boundaries. Numbering the particles from left to right, the abscissa corresponds to the coordinate of particle 1, and the ordinate represents the velocity of particle 2. The amplitude of the displacements is initially  $1/15$ , where the particle masses, force constants, and average interparticle spacings are all set equal to unity. The driving force on each particle has the form  $0.1(\Delta E + \Delta P^{\Phi}V)$ . The initial conditions are given by Equation (12) with plus signs (corresponding to a left-moving phonon). The three simulations shown in the first column were carried out with the total (E), kinetic (K), or potential ( $\Phi$ ) energies constrained at their initial values. The last of these calculations is unstable, which is indicated by the gradual divergence of the amplitude of particle 2's velocity. This calculation was followed for a reduced time of 100. The others were all followed to 1000. In the second column, each of the three energies in turn obeys the "Berendsen" relaxation equations suggested by the Rayleigh and van der Pol equations. In the final column, the friction coefficient is calculated by integrating the total, kinetic, or potential energy with respect to time.

nine techniques. Those that have been used before—Gauss ( $E$  or  $K$ ), Berendsen ( $K$ ), and Nosé ( $K$ )—to stabilize the total or kinetic energy all work in this case, as do all but one [Gauss ( $\Phi$ )] of the rest of the methods stabilizing the total or potential energies. If the potential energy is stabilized by the differential method (Gauss' method) and is made a constant of the motion, the coupling to the chain's kinetic energy is not strong enough to prevent the rapid divergence of the total energy. This is evidenced by the relatively rapid kinetic-energy increase shown in Figure 1. Of the other techniques, the relaxation technique used by Berendsen allows somewhat greater fluctuations than the rest. It is interesting that this technique, applied to a one-dimensional harmonic oscillator, results in the Rayleigh equation if the kinetic energy is controlled,

$$d^2x/dt^2 = -x - dx/dt[(dx/dt)^2 - 1], \quad (14)$$

and in the van der Pol equation if the potential energy is controlled:

$$d^2x/dt^2 = -x - dx/dt(x^2 - 1). \quad (15)$$

These two equations are closely related and have been intensively studied. The van der Pol equation (for the velocity rather than the coordinate) results if the Rayleigh equation is differentiated with respect to time.

In the simple example studied here, all of the convergent methods for generating steady flows gradually force the three-body system into a nearly pure state corresponding to a phonon propagating in the positive direction. In Figure 1, this corresponds to a nearly elliptical orbit with foci in the first and third quadrants. In the more physically reasonable examples where a scattering mechanism allows energy to flow out of excited modes, this natural decay would be offset by the driving force  $F_d$ . Here the driving force  $F_d$  and the thermostat  $F_c$  balance because no decay mechanism is present in harmonic systems.

Calculations of transport and thermodynamic properties of steady states are much more complex for three-dimensional systems. There is evidence that the temperature is best stabilized by Gauss' differential method in three dimensions. This method is about one order of magnitude more efficient than the proportional or integral methods (Evans & Holian 1985).

## 6. EXAMPLE APPLICATIONS TO FLUID MECHANICS

### 6.1 *Strong Shock Waves*

Molecular dynamics has been successfully applied to the simulation of simple fluid shock waves (Klimenko & Dremin 1980a,b, Niki & Ono 1977,

Holian et al. 1980, Yen & Ng 1974). In this work chemical reactions, radiation transport, and electronic transport are all omitted. In the most comprehensive simulation (Holian et al. 1980), a twofold compression of liquid argon, starting at the triple point, was simulated. A periodic rectangular parallelepiped, with an aspect ratio of about 20 and containing 4800 particles, was compressed, with periodic images of the system used as pistons. The resulting pair of 400-kbar shock waves ran toward the box center. The density, heat flux, and pressure tensor were measured in coordinate frames moving along with the shock waves. Comoving profiles of the longitudinal and transverse temperatures were also accumulated.

The results indicated that the effective viscosity and thermal conductivity at the shock-wave center exceed the Newtonian and Fourier values by about 30%. In this region the longitudinal temperature exceeds the transverse temperature by a factor of two. Because the gradients in such a strong shock wave are so much larger than those found in other flow problems, it can be concluded that truly nonlinear transport coefficients are relatively small.

In dilute gases the Boltzmann equation can be used to describe highly nonlinear flows, such as shock waves. The equation can be solved directly, by introducing suitable grids in velocity and coordinate space (Yen 1984). The equation can also be "solved" in G. A. Bird's more physical way, by introducing gas particles in macroscopic physical zones and allowing these to undergo "stochastic" long-range collisions. Because the Boltzmann equation describes the collisions of particles at the same space point, Bird's longer-range collisions between pairs are carried out in an approximate way. Particles in the same space zone are allowed to collide, with a randomly chosen impact parameter and a collision probability proportional to their relative velocity and cross section. Between stochastic collisions, the particles are advanced along noninteracting trajectories described by the streaming terms in the Boltzmann equation. (The trajectories are straight lines in the absence of gravitational or electromagnetic fields.) For an example application to shock-wave propagation, through a mixture of gases in the presence of a wall, see the paper by Schmidt et al. (1984).

Bird's stochastic-collision approach, elaborated by Nanbu (1983a,b, 1984), conserves energy and linear momentum but not angular momentum. Two spatially separated particles traveling clockwise around a point in their common cell can suffer a head-on "stochastic" collision and travel *counterclockwise* after that collision. Meiburg (1985) carried out an interesting comparison of Bird's technique with molecular dynamics on a large-scale problem—40,000 hard spheres flowing past an inclined plate. Figure 2 shows the resulting flow, calculated using the two different methods. Molecular dynamics reveals vortex generation at the plate

boundaries. The vortices did not appear using the stochastic-collision approach. Hybrid methods (using molecular dynamics where small vortices are important, and stochastic collisions elsewhere) could combine the realism of the molecular-dynamics model with the efficiency of Bird's approach.

## 6.2 Plane Couette Flow

Of all the flows involving shear, plane Couette flow (with  $u_x = \gamma y$ , for instance) is the simplest. The volume remains constant. Periodic boundaries taking the strain rate  $\gamma$  into account are easy to implement. Simulations in which boundary regions induce the flow can be used (Tenenbaum et al. 1982), but they lead to greater dependence of the stress on system size and to a layering of particles parallel to the walls.

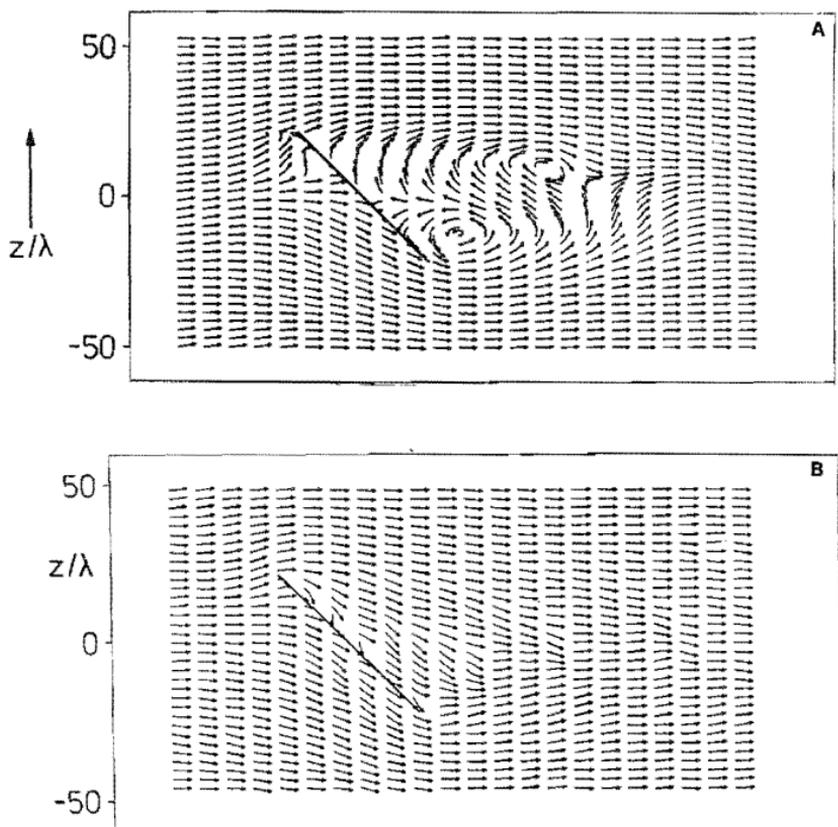


Figure 2 Flow patterns generated using (a) molecular dynamics and (b) G. A. Bird's stochastic-collision model. In both cases a dilute hard-sphere gas flows past an inclined plate and is confined, at the top and bottom of the channel, by reflecting boundaries. The vortices shown in the molecular-dynamics simulation are absent in the stochastic model. In both cases the arrows represent averages of the velocity directions of the particles occupying the corresponding spatial zones.

The periodic and rigid-wall simulations have provided reliable viscosities for a variety of short-ranged force laws. For a recent corresponding-states treatment of the linear viscosities, see Rosenfeld (1977). Systems with long-ranged Coulomb forces are harder to treat. A straightforward cutting off of the potential's range leads to substantial number dependence, even in equilibrium simulations. It seems likely that P. P. Ewald's technique could be used to carry out corresponding shear simulations for plasmas, metals, and ionic melts.

In the nonlinear regime the flow becomes so rapid that the viscosity is changed—usually decreasing with higher rates—and the pressure tensor becomes anisotropic, with  $P_{yy} > P_{xx} > P_{zz}$ . The details of the thermostat used to impose steady-state conditions can affect the normal-stress results (Ladd & Hoover 1985). An isotropic constraint force

$$F_c = -\zeta p \quad (16)$$

produces normal stresses consistent with the Boltzmann equation and with nonlinear-response theory (Ladd & Hoover 1985, Evans & Morriss 1984b). The friction coefficient  $\zeta$  depends upon time in such a way as to make either the temperature or the energy constant. "Temperature" is proportional to the second moment of the velocity-distribution function

$$3NkT = \sum m[(v_x - \gamma y)^2 + v_y^2 + v_z^2]. \quad (17)$$

There are many other interesting flows to study in elucidating the nonlinear dependence of shear and normal stresses on the mode and rate of deformation. Hess (1984) considered the relaxation of fluids initially deformed by twofold longitudinal compression. The volume-preserving transverse expansion was treated in two different ways, which Hess promises to compare in a later publication.

Other flows, incorporating more complicated rotations than does plane Couette flow, could be studied using either Bird's or Meiburg's (1985) approach. "Four-roller" periodic flow is an interesting possibility.

Recently, Rainwater et al. (1985) used another approach to model flows that are more complex than planar Couette flow. Their approach is to take planar-flow simulation data and to use these as inputs to strictly macroscopic hydrodynamical calculations of flow properties in more complex geometries. One of the interesting results of their work is the realization that conventional rheological hydrodynamics fails to take *any* account of shear dilatancy—the isothermal/isobaric expansion of fluids under shear. Conventional rheological theory is cognizant of normal-stress *differences* in non-Newtonian fluids but fails to recognize that the *trace* of the pressure tensor is also dependent upon strain rate.

Even for planar Couette flow, a complete explanation of the nonlinear

effects revealed in the computer simulations is still lacking. Simulation results suggest that the effective nonlinear viscosity of atomic fluids varies as the square root of the strain rate. Although this functional dependence is predicted by mode-coupling theory, the observed amplitudes are orders of magnitude larger than conventional theory predicts. These "enhanced long-time tail effects" have been observed in a wide variety of related phenomena (Hanley 1983). They seem to be related to the divergence of shear viscosity at the glass transition. Kirkpatrick (1984), Das et al. (1985), Leutheuser (1984), Keyes (1984), and Tokuyama (1984) have each suggested different mode-coupling approaches to the shear-thinning phenomena seen in computer simulations, but these various suggestions have not yet been elaborated in a generally accessible or accepted form.

Shear-flow simulations have been carried out on solids as well as fluids (Evans 1982a, Hoover et al. 1982, Tanaka 1983). The results so far available are consistent with the power-law variation of stress with strain rate used by metallurgists. The dependence becomes stronger at high temperature.

Work on granular materials, in which the "particles" are extended bodies rather than mass points, is underway (Walton 1982), but little quantitative information is available. The particles' interactions include elastic, inelastic, and frictional components.

### 6.3 *Steady Heat Flow*

The flow of heat between reservoirs was treated by Ashurst (1973). Related smaller-scale studies have also been carried out recently (Tenenbaum et al. 1982, Ciccotti et al. 1979). This work demonstrates that the thermal conductivity

$$\kappa = -Q/\nabla T \quad (18)$$

can either increase or decrease with  $|\nabla T|$ , depending upon the thermodynamic state.

Evans and Gillan discovered a way to simulate heat flow in a homogeneous periodic system, which thus makes the reservoirs at physical boundaries unnecessary (Evans 1982b, Gillan & Dixon 1983). In this method an external driving force coupled to the particle energies and the potential part of the pressure-tensor contributions,

$$F_d = \lambda(\Delta E + \Delta P_{xx}^\Phi V, \Delta P_{xy}^\Phi V, \Delta P_{xz}^\Phi V), \quad (19)$$

produces a heat current  $Q_x$  fully consistent with the Green-Kubo linear-response theory. It is interesting to note that the Evans-Gillan method succeeds in calculating the thermal conductivity in the absence of a temperature gradient. We should point out here that there are slight differences between the Evans and the Gillan schemes. Gillan measures the

energy and pressure differences (19) relative to the ensemble average. This means that the Gillan equations are not momentum preserving. Momentum in the Gillan scheme is only conserved on a time-average basis. This in turn leads to further difficulties, in that the so-called "adiabatic incompressibility of phase space" (Evans & Morriss 1984a,b) is not satisfied. These errors are not present in the Evans method, which is rigorously momentum preserving and which satisfies the "adiabatic incompressibility" condition (Evans 1982b, Evans and Morriss 1984a).

The same method can be applied to solids (Hoover et al. 1984). In such an application, the driving force can be simplified slightly to include only pressure-tensor contributions.

The conductivities obtained with the new homogeneous and periodic simulations are consistent with the earlier direct-simulation results. All the conductivities can be correlated through a corresponding-states relation linking conductivity to entropy (Grover et al. 1985). This connection can be understood by noting that both properties depend upon the frequency at which particles collide—a frequency of the order of the solid-phase Einstein frequency. The correlation provides conductivity predictions correct to within about 10% over a wide range of fluid densities and represents an improvement over D. Enskog's model. Rosenfeld's (1977) correlation of viscosity with entropy can be motivated in exactly the same way: Neighboring particles exchange momentum at the Einstein frequency. This correlation provides viscosities accurate to within about 30%. It is most interesting that nonlinear-response theory (Evans & Holian 1985, Morriss & Evans 1985) predicts a simple form for the nonequilibrium steady-state distribution function obtained with Nosé's constraint force (thermostat)

$$F_c = -\zeta p, \quad d\zeta/dt \propto K - K_0 \quad (20)$$

and the Evans-Gillan driving force

$$F_d = \lambda(\Delta E + \Delta P_{xx}^\Phi V, \Delta P_{xy}^\Phi V, \Delta P_{xz}^\Phi V). \quad (21)$$

The resulting distribution function,

$$\ln [f/f_{\text{canonical}}] = (\lambda V/kT) \int_0^t Q_x(-s) ds, \quad (22)$$

and the analogous result for shear flow,

$$\ln [f/f_{\text{canonical}}] = -(\gamma V/kT) \int_0^t P_{xy}(-s) ds, \quad (23)$$

are equally simple (Evans & Holian 1985, Evans & Morriss 1984b, Morriss & Evans 1985). Although both of these expressions are fully consistent

with linear-response theory and also with Kubo's original power-series representation of the nonlinear response (Kubo 1957), they are relatively difficult to evaluate, test, and understand far from equilibrium.

#### 6.4 *Rotating Flows and Tests of Material Frame Indifference*

An often-invoked approximation (Lumley 1970, Söderholm 1976, Ryskin & Rallison 1980) in continuum mechanics is that the constitutive properties of a material are unchanged by rotation (after taking into account, of course, the density increase resulting from centrifugal forces). Both the centrifugal and the Coriolis forces are responsible for the breakdown of this "principle." This has been clearly illustrated in one dynamical simulation, and it can be clearly seen by considering a thought experiment.

Consider the rotation of a cylinder of material about its axis. Assume that appropriate heat reservoirs are applied, ensuring a purely radial temperature distribution. If the system is at rest, or is undergoing uniform translation, then the heat-flux vector will also be in the radial direction. The principle of material frame indifference asserts that the direction and the magnitude of the heat-flux vector remain unaltered if the system is rotating, say, about its own axis. Because such a rotating system is a noninertial coordinate frame, Newtonian mechanics is in conflict with this "principle." Einstein showed that the equations of motion satisfied locally, in an accelerating frame of reference, are identical to the equations one would derive in an inertial frame subject to an equivalent gravitational field. There is no way of distinguishing inertial forces, such as the Coriolis force, from gravitational forces. Such forces inevitably give rise to an angular heat-flux vector component in the problem described above. In a straightforward simulation (Hoover et al. 1981) of this problem, an angular heat current that was close to the predictions of kinetic theory was found.

Centrifugal forces also frustrate the usefulness of the "principle of material frame indifference." In our rotating cylinder, the centrifugal potential's nonlinear character  $[-(mr^2\omega^2)/2]$  causes, for instance, homonuclear diatomic molecules to orient preferentially in a radial direction. This means that such a fluid would be birefringent, requiring a generalization of the usual Navier-Stokes constitutive relations for fluids. The rotation rate required to achieve a 1% alignment is of order 1 THz. For macromolecules, the effect is much larger and should be observable at modest rotation rates.

The Reynolds number for neutrally buoyant particles of radius  $r$ , rotating at frequency  $\omega$  in a medium of kinematic viscosity  $\eta/\rho$ , is  $\rho\omega r^2/\eta$ . Thus, the viscous and Coriolis forces for millimeter particles in water are

comparable at frequencies of order 1 Hz. Small molecules, on the other hand, would again require terahertz frequencies.

The fact that the "principle of material frame indifference" has survived so long indicates that nonlinear transport coefficients are small and that their measurement from experiment is often highly model dependent and therefore ambiguous.

## 7. THE FUTURE

Atomistic simulations have gradually been applied to larger systems, bigger molecules, and more complicated boundary conditions, in keeping with the growing capabilities of computers. This work involves difficulties in the formulation of thermodynamic quantities (Ladd 1984, Marechal & Ryckaert 1983, Evans 1981b), in the integration of the equations of motion (Evans 1977, Evans & Murad 1977), with both fast and slow time scales, and in the enhanced dependence of the results on boundary conditions (Ryckaert et al. 1977) as the size of the molecule approaches the size of the computational cell. The challenging nature of these problems, coupled with the rewarding nature of medicine and drug design, is contributing to the extensive developmental effort in this field. Protein dynamics has been reviewed by McCammon (1984). The protein models, liquid fragmentation simulations (Blink & Hoover 1985), and simulations of aerodynamic flows all show that molecular dynamics can play a role in fluid mechanics complementary to the finite-difference and finite-element methods. The free competition among the proponents of various techniques can be relied upon to lead to the best use of available computing capacity.

The new methods make it possible to design more flexible fluid-flow models. So far, little has been tried along the lines of local definitions of thermodynamic and hydrodynamic variables. But this is necessary for the treatment of flows containing vortices and other localized inhomogeneous fluid features.

The discovery of qualitatively new rheological effects, producing ordered phases at high strain rates, is reminiscent of the equilibrium nematic and smectic phases (Erpenbeck 1984, Heyes et al. 1985). These new observations should stimulate interaction between rheologists and computational physicists. Theoretical advances will be required in order to understand the dimensionless flow parameters at which these new dynamic phase transitions occur (see Figure 3).

Two-dimensional fluids exhibit an apparent instability at low strain rates, where the mode-coupling approaches predict an obviously unstable *negative* shear dilatancy and diverging viscosity (Evans & Morriss 1983). Hydrodynamic analyses of these instabilities, coupled with computer

simulations designed to measure the macroscopic currents and vortices generated in two dimensions, may prove useful in stimulating an experimental search for these phenomena.

The mechanical simulations, which preceded molecular dynamics, are advancing too. This work began with J. Hildebrand's gelatin-ball study of the pair-distribution function of hard spheres and with the bubble-raft studies of crystals carried out by L. Bragg and J. F. Nye (Feynman et al. 1964). Pierański's recent, highly evolved study of melting, dislocations, and vacancy motion (Pierański et al. 1978) sets a high standard. This latter work makes possible quantitative comparisons with (computer) experiments. The resemblance of the data collected to those reported by Alder & Wainwright (1962) is striking. The density interval found for ball-bearing melting agrees well with the computer-experiment hard-disk analog. For some problems, these simulations, as well as analogous nonequilibrium simulations using plastic spheres (Clark & Ackerson 1980, Ackerson & Clark 1983) may well prove cheaper than computer simulations. Their main drawback at present is the lack of a quantitative stress measurement.

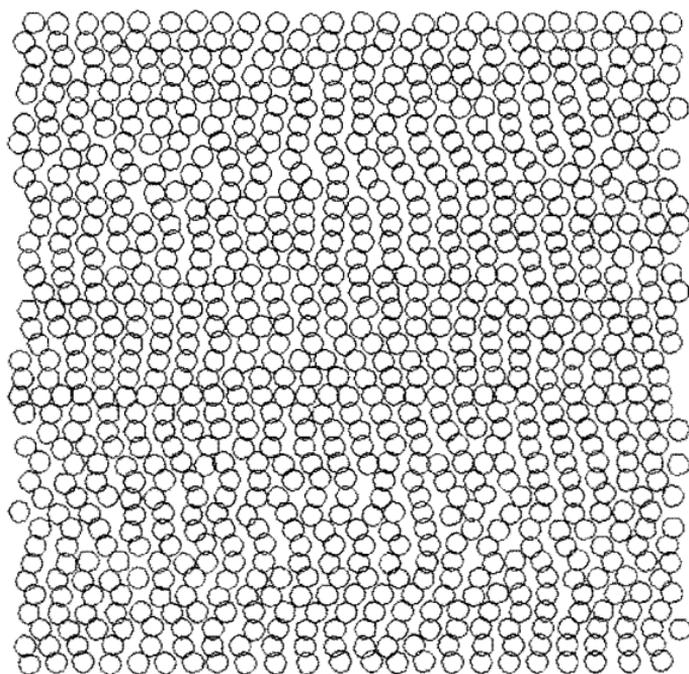


Figure 3 Instantaneous picture of the two-dimensional soft-disk fluid under high shear [ $\gamma\sigma\sqrt{(m/\epsilon)} = 10$ ]. The fluid particles order parallel to the streamlines. There is essentially no lateral diffusion perpendicular to the streamlines. The undulating vertical strings of highly overlapping particles are not understood (Heyes et al. 1985).

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