

# NONEQUILIBRIUM MOLECULAR DYNAMICS

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## INTRODUCTION

### *Microscopic vs Macroscopic Viewpoints*

From a fundamental point of view real materials are described by quantum mechanics. Because solving the time-dependent, quantum-mechanical, many-body problem is impractical, a detailed microscopic view of matter has to be restricted to the much simpler classical mechanics. In the classical description (1), the instantaneous "dynamical state" of a many-body system is given by the set of coordinates and momenta for all of the particles. This dynamical state and a rule for its time development reduces the classical problem to a well-posed initial value problem, the solution of a set of coupled ordinary differential equations. The accelerations that govern the time development can depend upon boundary conditions or other types of constraints.

As the particle trajectories develop from the initial dynamical state, subject to the imposed constraints, dynamical averages can be accumulated. Any thermodynamic or hydrodynamic state variables that depend upon coordinates and momenta can be averaged. If the problem is nonsteady or inhomogeneous, such averages can be tabulated as functions of time or space. Unacceptably large fluctuations in the averages can be reduced by generating several trajectories from similar initial dynamical states.

We call the ordinary classical Newtonian equations of motion,  $F = ma$ , or the equivalent Lagrangian or Hamiltonian equations of motion, without any special constraints, the "equilibrium equations of motion." These equations are reversible in time and, because external heat and work

sources are omitted, conserve energy. The particle trajectories they generate are said to be calculated by "equilibrium molecular dynamics." Many classical techniques have been developed for solving the equilibrium differential equations of motion (2-5). The simplest technique, replacing the Newtonian accelerations  $d^2r/dt^2$  with a centered second-difference approximation, is fully as cost-effective as more complicated schemes, unless very high accuracy is desired (6). In the Lagrangian or Hamiltonian formulations the coupled first-order equations can be solved conveniently by using classical Runge-Kutta or predictor-corrector methods. With any of these numerical schemes, conservation of momentum and energy are extremely useful checks of the numerical work.

In the event that two widely different time or distance scales contribute to the microscopic dynamics, it is logical to eliminate the shorter of these by averaging. In the resulting "stochastic" or "Brownian" dynamics (7), the interaction of the large, or heavy, solute molecules with the small, or light, solvent molecules can be approximated by using an effective diffusion coefficient. The solute dynamical trajectories then contain both the accelerations from the solute-solute interactions and a diffusive motion due to the numerous, but small, solvent-solute interactions. The energy conservation and reversibility of the Newtonian equations of motion are lost in the averaged stochastic approach.

The connection between the dynamical functions generated by any form of molecular dynamics and the corresponding thermodynamic or hydrodynamic macroscopic description is relatively straightforward. The two approaches correspond in conserving mass, momentum, and energy. But there is no such correspondence for entropy, because entropy is not a dynamical variable. Entropy is nevertheless important to many macroscopic approaches to nonequilibrium systems. Because entropy production characterizes irreversible flows and the equilibrium equations of motion are reversible, it is not surprising that for entropy the connection between the two points of view is incomplete. However, for mechanical variables depending only on coordinates and velocities, the connection is easily made. Both the potential and kinetic energies of the particles are pictured as localized at the particle sites, and make localized contributions to the flows of mass, momentum, and energy. Temperature is measured directly, as the fluctuation in the particle velocities. It is simple to formulate other dynamical variables, such as the stress tensor and heat flux vector, which depend only on these particles and momenta. Irving & Kirkwood (8) formalized this description in a way useful for most simulations. Modifications can be made if it is desirable to distribute the delta-function particle contributions over regions of the order of the particle volume to obtain smooth profiles for comparison with analogous continuum calcu-

lations (9). Shockwaves and liquid drops, with their rapid changes of thermodynamic properties in space, require care in averaging (10-14).

A "material," from this microscopic Newtonian viewpoint, is completely characterized by the forces between molecules, or parts of molecules, as functions of their relative location and velocity. The phase diagram and constitutive properties of the material follow as the complicated but straightforward consequences of the microscopic interactions among its constituent parts. The connections between interparticle forces and the macroscopic linear viscosities and thermal conductivity were established for gases by Boltzmann (15-16) and for general fluids by Green & Kubo (17). Thus the characterization of the constitutive equation of state is a well-posed mathematical puzzle with a unique solution that depends only on interparticle forces.

From the macroscopic continuum point of view, the time development of a material's behavior is described by the macroscopic differential equations describing the flow and conservation of mass, momentum, and energy. The macroscopic accelerations are produced by pressure-tensor gradients rather than microscopic interparticle forces. The pressure tensor, a function of energy, density, strain rate, etc, plays the same role in macroscopic dynamics as does the interparticle force, a function of distance, in microscopic dynamics. The characteristics of the macroscopic equations are limited in that they predict only the future, as they are irreversible in the time.

Because macroscopic behavior can be calculated from microscopic interactions, the microscopic description might appear to be simpler, or at least more "fundamental." The apparent simplicity is very misleading. At present it is at least as difficult to determine consistent microscopic flow behavior. The microscopic description is not likely to furnish quantitatively correct descriptions of real materials beyond the simplest metals, ionic melts, and rare gases. The main contributions of the microscopic point of view are understanding, semiquantitative estimates of experimental results, and the capability to interpolate or extrapolate experimental data into regions that are hard to reach in the laboratory.

These three possibilities—reproducing experimental data, predicting the unknown, and understanding the mysterious—together explain the persistence of interest in the mechanistic microscopic description of material behavior from the birth of kinetic theory up to today. The details available in the microscopic description do make it possible to understand simple hydrodynamic flows, but only when the proper questions are asked and the calculations are carried out correctly. The computational complications involved in studying hydrodynamic flows with Newton's equations have led to modified "nonequilibrium" forms described in the following sections.

### *Fluids at Equilibrium*

Eighty years ago, Gibbs formulated the microscopic basis of equilibrium thermodynamics. He stated that all dynamically accessible states should be weighted equally in calculating the equilibrium properties of isolated dynamical systems. At that time the partition functions Gibbs envisioned were mainly conceptual, as they were too difficult for practical calculation. Today, with fast computers, partition functions for simple materials can be estimated rapidly enough to be used as subroutines in numerical hydrodynamic calculations.

About 100 years ago, van der Waals and Boltzmann calculated analytically the contribution of three- and four-body effects to hard-sphere thermodynamic properties. Today, this same approach can be pursued further, to seven-body or eight-body effects, by using fast computers. Alternatively, this systematic approach can be abandoned in favor of brute-force Monte Carlo or molecular dynamic simulation (18-21). With the brute-force techniques, problems involving thousands of strongly interacting particles can be solved. This capability is fortunate because, without the simulations, theory could not advance. The only reliable test of theories is confrontation with experiments, either traditional laboratory experiments or computer experiments. Computer experiments are unique in providing detailed information about systems in which the forces are known. Operational theories based on forces can then be tested against quantitative computer results.

Operational theories can be developed or discarded according to their success in matching machine results. The equilibrium perturbation theory of fluids, originating in the work of Canfield, Mansoori, Rasaiah, and Stell (22), is now a highly developed example of a numerical theory that has been modified to fit a large body of computer-generated data.

It is a measure of the difficulty of the many-body problem that *a priori* theoretical approaches to equilibrium properties have been relatively unsatisfactory. But a successful perturbation approach, in which some computer-generated numerical solutions are used as a base, is certainly better than no approach.

The success of equilibrium perturbation theory in reproducing the dependence of thermodynamic properties on interparticle forces has generated many attempts to construct corresponding nonequilibrium perturbation theories. Unfortunately, the highly nonlinear response of the classical equations of motion to small perturbations, leading to the rapid separation of similar phase-space trajectories, is responsible for the failure of all such theories so far proposed (23, 24).

In principle, the equilibrium theory can be thought of as containing the

nonequilibrium theory as an unlikely, but possible, fluctuation. In practice, interesting nonequilibrium states are such unlikely fluctuations that even the linear transport coefficients, which can be found numerically by Green-Kubo analysis of fluctuations (4), can be obtained more accurately by direct nonequilibrium methods.

Even today, the connection between the microscopic force-law point of view and laboratory experiments is tenuous. It is true that the properties of one simple spherical rare-gas molecule, argon, have been accurately described on the basis of reasonable two- and three-body forces. Krypton, an equally simple material, is still complicated enough that an analogous correlation of microscopic forces with macroscopic properties has not yet been worked out (25, 26).

### *Fluids Close to Equilibrium*

Our understanding of nonequilibrium problems is in a relatively more primitive state because an operational nonequilibrium theory, resembling Gibbs' equilibrium theory in generality, doesn't exist for nonequilibrium systems. One can see why: Equilibrium is one, unique state; non-equilibrium is everything else. There is one relatively simple class of nonequilibrium problem. Close enough to equilibrium, a macroscopic theory containing nonequilibrium fluxes linear in the gradients is sufficiently accurate, and local values of the pressure, energy, density, and temperature can still be usefully interrelated through the equilibrium equation of state. Farther from equilibrium, where nonlinear fluxes and changes in the constitutive relations are important, there is no theoretical approach like Gibbs' to use as a basis. We shall see that the numerical molecular dynamics methods provide a substitute for this missing theory.

The closest approach to a fundamental nonequilibrium theory is Maxwell & Boltzmann's binary-collision picture of gas transport (15). This Boltzmann-equation approach successfully expresses the dilute-gas transport coefficients and the approach to equilibrium in terms of a set of two-body problems. The Maxwell-Boltzmann approach is exact for linear problems, and is apparently a good starting point for nonlinear problems as well.

In "linear" problems close to equilibrium, where nonequilibrium fluxes varying with powers higher than the first can be ignored, Newton's viscous flow theory and Fourier's heat-flow theory are adequate. In such close-to-equilibrium cases there is abundant evidence that the Boltzmann equation correctly predicts the transport of mass, momentum, and energy for low-density gases.

For dense fluids the Maxwell-Boltzmann approach does not apply; the

only exact results known are formal, and hold only in the linear regime governed by Newton's and Fourier's viscosity and conductivity flow laws. In this case the transport coefficients have been related to the decay of equilibrium correlation functions by the "Green-Kubo" relations. Evaluating this decay involves solving the N-body problem and so is not nearly so easy as the two-body low-density Boltzmann solution. The high-density problem is further complicated because momentum and energy can both be transported directly, through intermolecular forces, rather than simply through the convective motion of particles. This potential transfer can even change the sign of the phenomenological Burnett coefficients describing the increase or decrease of the transport coefficients with increasing gradients. Enskog's 1926 theory was designed to treat this potential transport in a semiquantitative way, and does so remarkably well. Unfortunately, there is no known simple approach that begins with the Enskog theory and adds on a chain of successive improvements that lead ultimately to a correct theory.

Current attempts to extend our understanding of transport phenomena to higher density borrow from hydrodynamics and have been successful in describing flows at scales greater than a particle diameter, but seem to hold little promise for a quantitative understanding of small-scale, rapid nonequilibrium fluid behavior. The state of the art has been reviewed by Zwanzig (27).

Much of the theoretical work carried out on fluids has been directed toward (a) understanding the correlation functions that appear in equilibrium fluctuation theory and (b) understanding fundamental flows. The relatively slow decay of the low-density correlation functions with time has been successfully explained, from a semiquantitative point of view, by the mode-coupling theory. The quantitative agreement of this theory with the results of computer simulations of viscous flow is very poor at high density, with observed correlation functions two or three orders of magnitude greater than those predicted theoretically (28, 29).

Plane couette flow has received a great deal of attention because it is the simplest hydrodynamic flow and can be simulated computationally with relative ease. Corresponding extensions of thermodynamics to cover fluids and solids undergoing shear have been reasonably successful (30), but have shed no light on the significance of entropy far from equilibrium.

Zwanzig (31) has pointed out a promising connection between the rate dependence and the frequency dependence of the shear viscosity. Either effect modifies pressure fluctuation correlations, and it is possible that a quantitative understanding will relate the long-time decays of these correlations to the nonanalytic dependences of the pressure tensor and the energy on the strain rate.

Interest in extreme conditions, largely fostered by government projects designed to threaten or placate people with thermonuclear energy, has led to ever more detailed information and speculation about underlying flow mechanisms in systems far from equilibrium.

### *Fluids Far From Equilibrium*

Far from equilibrium the transport coefficients are modified. Why is fluid viscosity reduced at high deformation rates? How do shear flows produce "normal-stress" effects, such as the Weissenberg and die-swell effects? How thick is a strong shockwave in a dense liquid? Each of these rheological questions involves the nonlinear flow of fluids; that is, conditions are so far from equilibrium that the phenomenological transport coefficients describing the diffusion of mass, momentum, and energy are changed from the small-gradient values that can be obtained from equilibrium fluctuation theory. Answers to rheological questions involve descriptions on two scales: (a) the microscale description of atomistic flow mechanisms and (b) the macroscale description given by solutions of nonlinear fluid dynamical boundary value problems. "Nonequilibrium molecular dynamics" has grown in an effort to describe efficiently the microscopic flows necessary to a quantitative macroscopic description of nonlinear flow phenomena. This growth has been caused, on one hand, by more quantitative detailed experimental information, from neutrons, X rays, and lasers (32), and, on the other, by more quantitative detailed computer experiments that keep pace with increasing computer speeds. The computers make possible the simulation of nonequilibrium flows, using constraints or special boundaries to enforce the nonequilibrium character.

Nonequilibrium molecular dynamics began in America and England. By now, calculations have been reported in Belgium, France, Germany, Holland, Italy, Japan, and Russia. In Australia, Denis Evans' work has contributed greatly to the development of new techniques. Evans' papers (28, 33) on the rheological properties of fluids indicate the variety of behavior that occurs even in the simplest of mass-point central-force many-body systems. The spatial and velocity distribution functions are not the only characteristics measured. Shear thinning (reduction of the viscosity with strain rate), normal stress effects (changes in the diagonal components of the pressure tensor induced by an off-diagonal strain rate), viscoelasticity (high-frequency elastic response by a viscous fluid), and shear birefringence (shear-induced orientation of polyatomic molecules) have all been characterized quantitatively for simple microscopic models.

The amalgamation of the microscopic and macroscopic theories and simulations with experimental information has been proceeding for about 10 years, and was the subject of an international conference organized by

Howard Hanley, "Nonlinear Fluid Phenomena," sponsored by the National Bureau of Standards at Boulder in June of 1982. For a view of nonequilibrium problems wider than is possible here, the Boulder proceedings (32) should be consulted.

### *Scope of This Review*

I begin this review by briefly surveying the development of molecular dynamics from the early computers at Los Alamos, to the national laboratories at Brookhaven, Livermore, and Argonne, to the present day era of personal computers. The technical content of these early calculations has been reviewed here (18, 20) and elsewhere (19, 34) in comprehensive detail, so I emphasize problems of current, or recent, interest. Lack of time and space bias this emphasis toward my own special interests and approaches. I wish to stress the connection of these new approaches with the classical ideas of mechanics. Mechanics is currently enjoying increased study and use with the vastly improved opportunities to compute, and not just formulate.

The first calculations indicated some basic complexities in computer simulations. Boundary conditions have to be carefully chosen to reduce the influence of surfaces. Because surfaces of phase separation are present in first-order phase equilibria, the special difficulties associated with these studies led naturally to calculations in which the temperature and volume were controlled dynamically. Because Newton's (or Lagrange's or Hamilton's) equations do not explicitly contain these independent variables, new thermally varying and deformational equations of motion had to be developed. Such new equations are now available in profusion. Their application is what we call "nonequilibrium molecular dynamics." We shall see that "nonequilibrium molecular dynamics" simulations can be thought of as a generalization of Gibbs' statistical mechanics to the nonequilibrium case.

After reviewing the development of nonequilibrium molecular dynamics I summarize the results obtained so far. Nonlinear viscous flow has been characterized fairly well, both in two and in three dimensions. There has been some corresponding work on diffusion and conduction. The shock-wave problem, particularly simple because its boundaries are equilibrium ones, is evaluated next. I then consider the possibilities for simulating the flow of macroscopic granular materials and for calculating the properties of polymer melts and solutions (35). Solid state problems are then discussed (21), which are intrinsically more specialized due to the much greater range of defect structures present in solids than in fluids. Last of all I focus on rapidly developing areas that will soon require their own specialized reviews as their audiences expand in the next few years.

## HISTORICAL DEVELOPMENT OF EQUILIBRIUM AND NONEQUILIBRIUM MOLECULAR DYNAMICS

### *Molecular Dynamics at the National Laboratories*

Weapons and energy calculations involve the flows of ordinary matter, light, neutrons, and plasmas, often under "extreme conditions" of high temperature and pressure. Thus, the national laboratories pursuing these calculations invest heavily in the latest computers. As fringe benefits, other large-scale computations have been carried out there too.

As the laboratories and their computers grew, so did the scope of the molecular dynamics problems studied. At Los Alamos, the simulations begun by Fermi, Pasta, and Ulam, who studied the one-dimensional chain, were followed later by extensive Monte Carlo and molecular dynamics work. The failure of the Fermi-Pasta-Ulam chains to approach equilibrium generated considerable and continuing interest in ergodic theory. The later work, by Wood (36), Holian, and their co-workers, led to the development of equilibrium perturbation theory and to characterization of shockwave states far from equilibrium.

At Livermore (5), Alder, Wainwright, and their colleagues studied the dependence of hard-sphere and square well thermodynamic and linear transport properties on boundary conditions, number of particles, and the range of the attractive forces. They concentrated on determining how the classical approaches of Boltzmann, van der Waals, Kirkwood, and Eyring compared with modern simulations of dense fluid behavior. These early calculations set a high standard for later work on faster machines with more complicated forces.

At Brookhaven (2), Vineyard and his co-workers interpreted radiation damage in crystals caused by energetic elastic collisions. Rahman, at Argonne (3), studied the structure of model fluids, using continuous potentials like those of Vineyard. These early studies proceeded in a leisurely way, carried out over periods of years, and were published in occasional comprehensive reports and journal articles. Parallel pioneering work was carried out in France (4) by Verlet and his co-workers, and, on a scale more limited by computational power, in Russia (37-39).

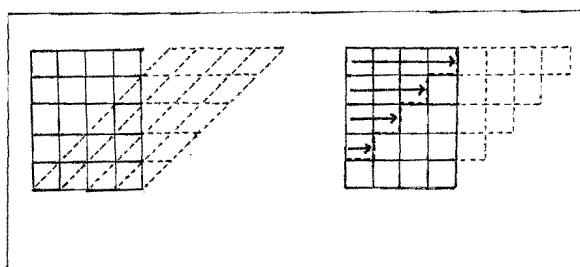
These early calculations can presently be duplicated on home computers, so the ability to publish molecular dynamics calculations is correspondingly widespread (40). With this expansion has come a more hectic pace in which untried ideas or faulty formulations are sometimes published. Despite the minor frustrations caused by this quality control problem, the vastly increased participation in the computer-simulation enterprise has been extremely beneficial in stimulating new ideas. Even more rapid expansion and proliferation is likely in the years ahead.

### *The Impact of Phase Metastability on Equations of Motion*

The main dramatic feature of equilibrium thermodynamics is the singular behavior associated with phase changes. At the gas-liquid and solid-liquid coexistence curves, material properties change discontinuously. Near the gas-liquid critical point, fluctuations that are ordinarily negligibly small become macroscopic as the compressibility and heat capacity diverge. An early challenge to microscopic simulation was to reproduce these qualitative features of real materials on a molecular scale. The Livermore and Los Alamos hard-sphere and square-well calculations established that the phase equilibria could be reproduced, and that periodic boundaries, illustrated in Figure 1, substantially reduced the number dependence of pure-phase thermodynamic properties. At the same time these boundaries inhibited surface formation and stabilized metastable phases, so that van der Waals loops could be observed.

These metastable phases were soon studied for their own intrinsic interest. Kinetic and mechanistic studies of both supercooled fluids and superheated solids have been carried out. Considerable effort has been devoted to the artificial stabilization of glassy phases (36, 41, 42). Hard-sphere glassy phases had been generated, at Los Alamos and Livermore, by "compressor" experiments in which the hard-sphere diameter was gradually increased with time. Other fluids could be forced to form glasses by rapid cooling. These volume and temperature controls were the first instances of deliberate alteration of the equilibrium equations of motion to satisfy desirable macroscopic constraints: the first "nonequilibrium molecular dynamics."

Recently the relatively long persistence of these metastable states in computer simulations has led to some interesting speculations on the



*Figure 1* Periodic boundaries for a two-dimensional system undergoing plane shear deformation. The basic cell can be visualized as a square (with squares above and below it) or as a parallelogram in which the cell shape changes with time. In either case the characteristic velocity of each cell exceeds that of the one just below it by the product of the cell length and the strain rate.

existence of first-order melting in two-dimensional systems. This speculation was abetted by the existence of a "theory" for melting based on the presence of dislocation pairs. Abraham has studied this question comprehensively and, in two very readable papers (43, 44), describes the evidence that melting in two dimensions is just like melting in three dimensions.

Another approach to phase equilibria, taken by Woodcock, Ladd, and Cape, is to examine systems large enough for two or even three phases to coexist (45, 46). These calculations are complicated by the extremely long times required for thermal equilibration between phases. Mechanical equilibration proceeds at the speed of sound, but thermal equilibration proceeds more slowly, by diffusion of heat.

### *Calculations at Constant Temperature, Pressure, Energy, Heat Flux, and Strain Rate*

The first dense-fluid simulations in which temperature was constrained, as a boundary condition, were described in Ashurst's thesis (47). He rescaled the momenta in his "reservoirs" or "fluid walls" to maintain the center-of-mass velocity and temperature constant. The differential equation of motion describing this velocity rescaling contains, in addition to the usual equilibrium forces  $F$ , constraint forces  $-a - bp$ :

$$dp/dt = F - a - bp, \quad 1.$$

where the functions of coordinates and momenta,  $a$  and  $b$ , vary with time so as to satisfy the collective N-body constraints:

$$\sum p = 0; \quad \sum p^2/m = 3NkT. \quad 2.$$

$a$  and  $b$  can be determined by substituting Eq. 1 into the time-derivatives of the two constraint equations (Eq. 2) with the results:

$$a = \langle F \rangle; \quad b = \langle Fp/m \rangle / \langle p^2/m \rangle, \quad 3.$$

where the angular brackets  $\langle \rangle$  indicate instantaneous averages over the N bodies included in the sums (2). It is easy to verify that these choices identically satisfy the constraints of fixed momentum and temperature. It should be observed that the new nonequilibrium equations, like Newton's, are still fully deterministic and formally reversible in time. Under most conditions  $a$  and  $b$  decrease as the number of terms in the sums (2) increases.

It is interesting that the above differential equations describing the velocity-scaling process were not written down until about ten years after Ashurst's calculations (48, 49). During this ten-year period dozens of isothermal calculations were carried out, so that temperature was often treated as an independent variable, like volume and energy.

The metastable glassy-state extension of the fluid equation of state had been generated by gradually compressing hard-sphere systems. Similar glassy-phase calculations could be carried out in either of two ways for soft spheres: by lowering the temperature or increasing the density. Both the soft-sphere equilibrium and nonequilibrium properties depend only on a combination of density and temperature,  $(N\sigma^3/V)(\epsilon/kT)^{3/n}$ , where pairs of particles interact with a repulsive potential  $\epsilon(\sigma/r)^n$ . So in this case there is no real distinction between isochoric velocity scaling and isothermal volume scaling.

Calculations at constant pressure tensor, energy, enthalpy, strain rate, and heat-flux vector are likewise possible but were not developed until 1980–1982. These more recent developments began with a simulation of bulk viscosity (50, 51) and the formulation of a “constant-pressure” molecular dynamics (52).

Bulk viscosity describes the extra nonequilibrium stress present when a fluid is compressed or expanded at a finite rate of strain. If the compression and expansion is carried out cyclically, then the irreversible heating per cycle is proportional to the bulk viscosity coefficient. The cyclic process complicates computer simulation. It was necessary to develop equations of motion for the periodic expansion and contraction of a fluid. The expansion had to be periodic in space, to eliminate surface effects, and periodic in time, to allow averaging of many cycles. If we denote the time-varying strain by  $\epsilon$  and if the momentum  $p$  at  $r$  measures velocity relative to the comoving hydrodynamic velocity, then the coordinate equation of motion is

$$\dot{r} = (p/m) + \dot{\epsilon}r. \quad 4.$$

In order to force the deformation (Eq. 4) to describe an adiabatic process, with  $\dot{E} = -P\dot{V}$ , it is necessary (50) that the momenta also respond to strain rate:

$$\dot{p} = F - \dot{\epsilon}p. \quad 5.$$

The complete set of equations of motion, Eqs 4 and 5, is deterministic, and formally reversible in the time, like Hamilton's equations of motion. But, through dynamic instability, it produces the irreversible macroscopic dissipation described by the hydrodynamic bulk viscosity coefficient.

Andersen simultaneously incorporated adiabatic deformation Eqs. 4 and 5 into the equations of motion to force the pressure to relax toward a preassigned value. The title of Andersen's paper (52), “Molecular Dynamics Simulations at Constant Pressure and/or Temperature,” suggests that the dynamical phase functions, whose average values are temperature and pressure, are held constant. Both dynamical phase functions actually oscillate about the specified values with relaxation times that are free

parameters in Andersen's description. In this way his scheme is different from the isothermal scheme, Eqs. 1 and 3, which produces a constant dynamic temperature. Evans & Morriss have recently shown (53) that constant pressure calculations can likewise be carried out (54) in a stable way, without Andersen's relaxation time.

Bellemans has pointed out that these relaxation calculations are examples of "control theory" in which feedback mechanisms, based on values of a function and some of its time derivatives, are used to govern future behavior. Temperature-tensor components and pressure-tensor components are obvious choices to which control theory can be applied, but by no means the only ones. Calculations at fixed angular velocity have likewise been carried out. The extent to which the constrained phase functions influence the observed hydrodynamics has not been analyzed theoretically, but could and should be. Simulations of shear flow at constant temperature and at constant energy are so closely alike (32) that even long calculations show no systematic difference.

From the standpoint of statistical mechanics, the new "nonequilibrium molecular dynamics" calculations should be viewed as an extension of Gibbs' approach to nonequilibrium systems in the spirit envisioned by Jaynes. In the equilibrium case all accessible states have the same energy. The relative weights of these states are given by Gibbs' theory. Away from equilibrium it has been difficult to generate a properly weighted set of nonequilibrium states. Nonequilibrium molecular dynamics does this. In the nonequilibrium simulations, a many-body system explores, with reversible microscopic equations, a more restricted part of phase space in which additional macroscopic constraints are specified. To the extent that the specified constraints correspond to the restrictions of laboratory experiments, or approach these as the size of the system is increased, we expect that macroscopic constitutive properties of the nonequilibrium system will faithfully describe macroscopic behavior.

### *Occam & Gauss*

The *ad hoc*, case-by-case nature of these early constrained nonequilibrium molecular dynamics calculations disguised the possibility of a general approach to constrained molecular dynamics, in which the constraints control macroscopic thermodynamic functions rather than the more usual holonomic control of microscopic geometric variables.

The Occam-Thoreau admonition to keep models as simple as possible is familiar, even to nonscientists. Gauss' principle of least constraint is less familiar, but a close relative. Gauss' principle implies, and is more general than, Newton's equations of motion. Gauss stated that the trajectory followed by a constrained many-body system lies as close as possible to the

unconstrained trajectory. It is perhaps surprising that many (55) constrained trajectories are possible. Even for such a small system as three Hooke's-Law particles (56), there are infinitely many trajectories passing through a given point in the phase space, which simultaneously conserve mass, momentum, and kinetic—not total—energy. These trajectories all have different effective masses, through different initial values of a Lagrange multiplier chosen to fix the kinetic energy.

To illustrate Gauss' principle we derive the equations of motion that constrain the kinetic energy (temperature) to a constant value. Gauss' principle is equivalent (1) to the minimization of the sum

$$\sum \frac{1}{2} m [\ddot{r} - (F/m)]^2 \equiv \sum \frac{1}{2} m (\Delta \ddot{r})^2. \quad 6.$$

Here this minimization must satisfy the constraint that

$$\sum \frac{1}{2} m \dot{r}^2 = \frac{3}{2} N k T \quad 7.$$

is a constant. If we consider a change  $\delta \ddot{r}$  in the extra accelerations  $\Delta \ddot{r}$  satisfying the constraint, Eqs. 6 and 7 give, respectively,

$$\sum m \Delta \ddot{r} \delta \ddot{r} = 0 = \sum (m \ddot{r} - F) \delta \ddot{r}, \quad 8.$$

and

$$\sum m \dot{r} \delta \ddot{r} = 0. \quad 9.$$

The Lagrange multiplier solution of Eqs. 8 and 9 is then

$$m \ddot{r} = F - \lambda m \dot{r}, \quad 10.$$

and the constraint condition, Eq. 7, is satisfied for the choice

$$\lambda = \sum F \dot{r} / \sum m \dot{r}^2, \quad 11.$$

giving equations of motion identical to those of Ashurst's velocity-scaling Eqs. 1-3.

This example suggests that we could apply Gauss' principle to constrain any dynamical variable that can be expressed as a phase function. The resulting accelerations would involve contributions proportional to derivatives of the constraint equations with respect to the particle coordinates and velocities. Not only does this procedure lead to Ashurst's velocity-scaling isothermal molecular dynamics, but it has also provided workable schemes for determining the diffusion and heat-conduction coefficients (56).

## FLUID PHENOMENA

### *Simulation of Viscous Flows*

The simplest fluid flow problem is plane couette flow, in which the hydrodynamic  $x$  velocity component varies linearly with  $y$ , as is shown in

Figure 1. Because such a homogeneous shear flow, or a corresponding dilatational flow, could conceivably arise as an equilibrium fluctuation, it is possible to treat such problems with linear response theory. The theory predicts (17) that the Newtonian viscosities are given by the large system decay of shear or bulk pressure fluctuations:

$$\eta_{s/b} = (V/kT) \int_0^\infty \langle \delta P_{s/b}(0)\delta P_{s/b}(t) \rangle_{eq} dt, \quad 12.$$

where  $\delta P_s$  is the fluctuation in any off-diagonal pressure-tensor component and  $\delta P_b$  is the fluctuation in the mean pressure. Because the derivation of this relation and its analog for conductivity is not entirely convincing (57), and because early calculations of heat conduction based on an analogous approach failed to agree with experiment, other approaches to transport properties were developed. For plane couette flow, there are six approaches in all. These are indicated in Figure 2.

The physical idea underlying Green-Kubo linear response theory (A) can be taken literally (B), by applying a small external field that creates a shear flow infinitesimally different from the unperturbed one. This approach was

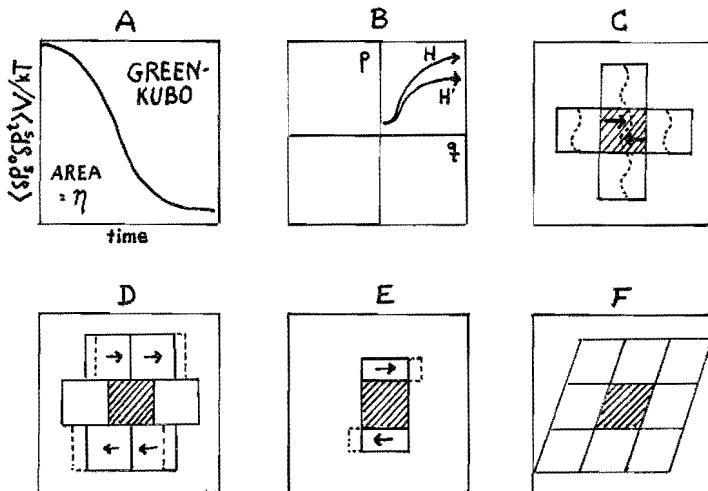


Figure 2 Six methods for determining the shear viscosity coefficient using molecular dynamics. Equilibrium method (A) is based on Green-Kubo analysis of equilibrium pressure fluctuations. In method (B) a perturbing force generates an infinitesimal strain rate. In method (C) a sinusoidal horizontal force generates a sinusoidal response. In method (D) the shear flow is maintained by periodic moving images of the basic cell (see Figure 1). In method (E) the flow is driven by reservoir regions maintained at fixed velocities and temperature. In method (F), also periodic in the sense of Figure 1, the deformation is driven by external forces affecting both the coordinates and the momenta. Methods (B-F) are examples of nonequilibrium molecular dynamics.

pioneered by Ciccotti and co-workers (58, 59). Gosling, McDonald & Singer (60) used an external force to drive a sinusoidal shear flow (C). Lees & Edwards (61) used periodic images of the system to shear it at constant strain rate (D). Ashurst & Hoover (62) used reservoir regions, with constrained average velocities and temperatures, as described above, to drive the shear flow from the boundaries (E). Finally, Ashurst & Hoover and Evans (63, 64) developed periodic deformation schemes, similar to those of Lees & Edwards, but constrained to constant temperature or energy (F).

Each of these methods has objections associated with it: the Green-Kubo integrand (A) has been studied numerically, using the Lennard-Jones potential near the triple point (D. Levesque, E. L. Pollock, private communication). The number dependence of the integrand is evidently large and unpredictable. The time during which the perturbed and unperturbed trajectories (B) remain well correlated is less than the decay time of the crucial correlations (32, 66). Transport coefficients for sinusoidal fields (C) are very different from the infinite-wavelength limit (67). The systems heated by moving boundaries (D) change temperature rapidly, on a picosecond timescale. Finally, the systems cooled at the boundaries (E) develop large temperature gradients. We believe that nonequilibrium molecular dynamics simulations with periodic boundaries—homogeneous and isothermal (F), or isoenergetic—are by far best for viscous flow simulation. Number dependence is evidently small, and convergence is rapid. Holian & Evans (68) have recently arrived at this conclusion by comparing Green-Kubo calculations with Evans' nearly homogeneous scheme.

A number of couette-flow simulations have been carried out. Hard spheres (69, 70), soft spheres, Lennard-Jones particles (71), soft-sphere mixtures (72), and polyatomic models of methane (64) and chlorine (73) have all been studied. What are the results from these simulations? Four separate physical effects have been characterized: the nonlinear, frequency-dependent decrease of viscosity with strain rate, the development of normal stresses with increasing strain rate, the change of the structure, measured by the pair distribution function, with strain rate, and the shift in the phase diagram with strain rate. Calculations detailing these effects have all been summarized by Evans & Hanley (28, 30). Although they use a nearly homogeneous isothermal algorithm, driven with boundaries of the Lees-Edwards type, there is little doubt that the same hydrodynamic (small strain rate, amplitude, and frequency) viscosity would result from the systematic application of any of the six methods. The viscosities are useful information because the best operational theory, Enskog's, is in error by about a factor of two near the freezing line.

The nonlinear viscosity depends upon strain rate and frequency in a complicated way. This dependence can be determined relatively well only at densities in the vicinity of the freezing line. At low and intermediate densities the nonlinearities are too small for accurate determination. In the high-density region there is good numerical evidence (73) that the viscosity varies with strain rate, with frequency, and with wave number:

$$\Delta\eta \sim \dot{\varepsilon}^{1/2}, \omega^{1/2}, k^{3/2}. \quad 13.$$

Viscosity no doubt also depends upon strain amplitude, but this dependence is harder to investigate numerically. Each of these effects has been predicted by mode-coupling theory, but with a much smaller coefficient. Zwanzig has pointed out that if the shear stress relaxation, Eq. 12, is measured in the corotating frame, the extra decay induced by rotation has the same form as the reduction due to frequency dependence (31).

Similar calculations in two dimensions are singular in the sense that the viscosity diverges (as  $\ln\dot{\varepsilon}$ ) at zero strain rate. Evans carried out isothermal calculations that clearly established a logarithmic dependence of viscosity on strain rate in two dimensions (74). In early reservoir calculations (34) this effect was disguised by large fluctuations—a persuasive indication of the superiority of the homogeneous methods for quantitative work.

The structure of a fluid is modified in a shear flow. To a first approximation the structure simply undergoes an infinite-frequency shear, with an amplitude that can be estimated from the Maxwell relaxation time multiplied by the imposed strain rate. Quantitative studies, for both pure fluids and mixtures, have been carried out by Hanley, Evans & Hess (75–77).

The structural changes must correspond to shifts in energy and other thermodynamic properties, to the extent that these can be defined for nonequilibrium systems. Hanley & Evans (30) measured the strain-rate dependence of the free energy for the Lennard-Jones fluid, assuming that generalized thermodynamic relations hold for a fluid under shear, but with strain rate as a new state variable. They show that there are measurable shifts in the phase diagram, similar to those found, at lower rates, in polymer melts and solutions.

Strain rate is the independent variable in the Doll's-Tensor nonequilibrium equations of motion. Parrinello & Rahman (78) used Andersen's version of the equations, in which the pressure tensor is fixed (52), to study analogous solid-phase equilibria.

The Couette flow problem is a useful prototype for testing new ideas for nonequilibrium simulations. In this way it has been shown that velocity-dependent forces, present in a rotating frame, must be included in the microscopic equations of motion. Otherwise the kinetic part of the shear stress, and both the kinetic and potential parts of the normal stresses, are in

error. More recently, several different isothermal schemes have been evaluated in this way (J. Dufty, private communication, 1982; W. G. Hoover and A. J. C. Ladd, private communication, 1982). It is possible to constrain any combination of the  $x$ ,  $y$ , and  $z$  temperatures during couette flow. The choice made influences the nonlinear flow properties. If these same choices are analyzed through the relaxation-time approximation to the Boltzmann equation (81), it is found (J. Dufty, private communication, 1982; W. G. Hoover and A. J. C. Ladd, private communication, 1982) that application of the isothermal constraint to all three components of the temperature gives results agreeing with the Chapman-Cowling solution for Maxwell molecules. This same approach can also be used to calculate the dependence of Boltzmann's entropy on the strain rate. The result,

$$\Delta S/Nk = -(\dot{\epsilon}\tau)^2/2 + (\dot{\epsilon}\tau)^4/4 - \dots, \quad 14.$$

where  $\tau$  is the collisional relaxation time, could be compared with simulations or with theoretical predictions, if the latter could be carried out to fourth order in the strain rate.

Two other kinds of viscous-flow simulations have been performed using nonequilibrium molecular dynamics. The periodic and homogeneous bulk viscosity simulations show that, for dense fluids, the errors in Enskog-theory predictions increase as the repulsion becomes softer (65). No quantitative theory explaining these bulk-viscosity results has yet been constructed. There have also been simulations of the vortex viscosity, which measures the coupling of molecular rotation to the vorticity. These calculations (82) can be carried out either by measuring the decay of molecular rotations or by measuring the entropy production associated with maintaining molecular rotations with external forces. These simulations are precursors of polyatomic and polymer flow simulations.

### *Heat Flow, Rotation, and the Boltzmann Equation*

The diffusion of heat can be studied through analogs of four of the six methods developed for shear flow. Ciccotti, Jacucci & McDonald (59) suggested an external-field method derived from the Green-Kubo fluctuation calculation. Ashurst (47) simulated the flow of heat between reservoirs maintained at constant temperatures. Later, Ciccotti & Tenenbaum developed a similar, somewhat less useful, reservoir technique (83). Evans & Gillan proposed driving a heat current with an energy-dependent external force. Evans has shown (84) that not only are the results of this method consistent with the Green-Kubo and reservoir results, but fluctuations are substantially reduced, allowing much more accurate estimates of the hydrodynamic conductivity. Gauss' principle of least constraint can be

applied to the heat-current case too, by constraining the heat flux vector. The dissipation associated with this constraint determines the heat conductivity.

Heat conductivity behaves differently from viscosity in that it may either increase or decrease with increasing current, whereas the viscosity of simple fluids has never been observed to increase with increasing strain rate. The conductivity has been studied (85) in a constrained rotating system, in order to demonstrate that the angular Coriolis accelerations impart an angular heat current in response to a purely radial temperature gradient. This nonlinear effect, observed in a dense-fluid computer experiment, was originally predicted by the Boltzmann equation, and illustrates the failure of the "principle of material frame indifference" of continuum mechanics.

### *Fluid Shockwaves*

The simplest hydrodynamic problem beyond plane couette flow and one-dimensional heat flow is a planar one-dimensional shockwave. Such a shockwave is a steady adiabatic compression wave, linking together two equilibrium states. For this reason, together with the technical importance of shockwaves in aerodynamics, warfare, mining, explosive metal-working, and chemical synthesis, considerable interest in their properties exists.

Gas-phase shock waves are only a few mean free paths thick. Laboratory and computer experiments agree fairly well with predictions from the Boltzmann equation. Until recently (86) analogous measurements for liquids and solids could not be carried out because the length scale is too small. Computer experiments (10–12, 87) are ideally suited to these small-scale dissipative waves. A pair of these structures can be generated by modifying the Lees-Edwards scheme of Figure 2D so that the periodic images compress, rather than shear, the basic fluid cell. The shockwaves found agree fairly well in structure with the predictions of the Navier-Stokes equations. The main difference is that the shockwave thickness exceeds the Navier-Stokes prediction by as much as 30%. The velocity distributions within the shockwave are quite unlike either the Maxwell-Boltzmann or the Mott-Smith bimodal predictions (11). The importance of these nonequilibrium distribution functions to chemical reactivity has been forcefully argued by Klimenko & Dremin (13, 88).

### *Flows of Granular, Polyatomic, and Polymeric Materials*

Molecules with structure—ranging from diatomics, through polymer melts containing hundreds of atomic units, even up to soil, seeds, and oranges—can be simulated with nonequilibrium molecular dynamics. There are two apparent difficulties. First, there is a disparity between the high-frequency

vibrations within one structure and the somewhat lower frequency of collisions between structures. The highest frequency controls the molecular dynamics timestep. This problem has been avoided by using either constrained bonds, which don't vibrate at all (89), or artificially soft bonds (90), which vibrate at a low frequency. Fixman pointed out (91) that constrained bonds affect the dynamical bond-angle distribution. It is unlikely that this would have any qualitative impact on polymer behavior, but the constraint effect is serious for realistic simulations of small molecules, like butane (92). Second, there is a force-law problem for the larger granular materials. These inelastic particles absorb energy internally, as heat. The wealth of measured granular-flow phenomena is stimulating the development of inelastic force models capable of describing these energy flows. The energy can be supplied by boundary agitation or by a gravitational field. The experimental data for granular flows, velocity, and depth profiles in chutes, as functions of solid-phase fraction and velocity (93, 94) invite simulation.

There are some qualitatively interesting effects in polymer chain flows too (35). It appears that the functional dependence of viscosity on chain length undergoes a transition-like change at chain lengths of about 300 monomer units. A practical way of simulating such long chains has yet to be developed.

In addition to the challenge of finding reasonable force laws for polymeric and granular materials, there may be some interesting physics involved in carrying out and interpreting molecular dynamics simulations. There are symmetric and nonsymmetric versions of the pressure tensor for molecules with structure (95), and there are several ways in which large molecules could be accelerated to produce a shear flow. It seems likely that any of these choices will reproduce the linear transport properties of the flowing material, but that the nonlinear terms will be influenced by the details of the calculation.

One particularly simple structure is the rough-sphere model, in which particles exchange angular momentum as well as linear momentum on collision. An attempt was made (96) to generalize this transfer process to the soft-potential case, but the resulting interaction was physically unrealistic. At present it is not clear whether or not a simple prototype model for granular materials can be built on existing central-force models.

### *Conductivity and Dielectric Phenomena*

Electrical conductivity can be determined as perhaps the simplest application of linear response theory. By applying a small electric field, and comparing two neighboring trajectories, Ciccotti & Jacucci (97) measured the conductivity of a charged Lennard-Jones particle. Sundheim (98) has

used a larger field (up to seven orders of magnitude greater than laboratory fields) to determine the conductivity for a model of molten KCl. His 1728-particle conductivity was about 20% less than the experimental conductivity and showed that current remains linear with the field up to the high level just mentioned. Pollock & Alder (99) and Watts (100) have determined the dielectric constant for dipolar Lennard-Jones particles by nonequilibrium simulations, including frequency dependence in Watts' case.

## SOLID PHENOMENA

Two characteristics complicate bonding in real solids: (*a*) in most cases the forces are not central, and (*b*) the forces are readily changed near defects. In the solid phase, defects of various kinds are the main interesting objects for study using nonequilibrium molecular dynamics. The defect-generating simulations started by Vineyard continue to employ collisions of reasonably perfect crystals with incoming high-energy particles. Crystals containing as many as 54,000 atoms have been studied (101). A recent paper on laser annealing uses nonequilibrium velocity scaling to describe the absorption of energy by a crystal surface (102). Successive nonequilibrium quenches have been applied to crystals and to glasses. Analysis of the temperature recovery yields quantitative estimates for the vibrational frequency distribution (103).

Voids in crystals, leading to stress concentration and fracture, have been the object of several, mostly two-dimensional, investigations (21, 104). These investigations allow determination of the gross properties of brittle cracks, such as dependence of the velocity on temperature and stress. But it is abundantly clear that the plasticity present in ductile fracture is extremely hard to simulate on a microscopic level. Even so, the equation of state for solids at very high rates of strain, above  $10^5$  hertz, is relatively simple, and can be characterized by nonequilibrium simulations (48).

Considerable progress has been made in characterizing the motion of edge dislocations through crystals, but even in the idealized two-dimensional case, knowing all of the properties of the dislocations, it has not been possible to make a quantitative estimate of the plastic flow stress, except through simulation.

Shockwaves in solids are another extremely difficult problem. It has been shown (12, 105) that the rise times for these waves are extremely short and that the scale of the underlying plastic flow is size dependent. For this reason it is highly unlikely that a quantitative estimate of solid-phase shock structure can be generated with molecular dynamics.

There is considerable Russian literature on idealized, two-dimensional, solid-phase problems. Strength reduction, by absorption of impurity atoms

at defects, the influence of stress on diffusion, and the sintering and failure of stress-concentrating solids are described in a recent comprehensive review by Shchukin & Yushchenko (21).

## FUTURE DEVELOPMENTS

Additional simulation work is needed to evaluate the usefulness of generalized hydrodynamics in transport problems far from equilibrium. The considerable effort expended in determining the wavelength and frequency-dependent decreases of the transport coefficients (W. E. Alley, B. J. Alder, in preparation) still leaves unexplained the apparent increases seen in shockwaves.

Solid-state transport problems will continue to be studied. These calculations are complicated by more serious number dependences and long equilibration times. Nevertheless, the simple results found at high rates of strain suggest that more detailed mechanistic studies of nonequilibrium solid flows would produce new theoretical approaches.

The surge of interest in rheological problems (107) suggests that polymer melt and solution problems will attract increasing attention. One of the most challenging of these problems, a dramatic change in the dependence of viscosity on molecular weight, occurring at a polymer length of about 300 monomer units, lies outside the range of straightforward simulation (108). Nevertheless, a model that takes into account several contiguous monomer units through a renormalized interaction could possibly be developed to deal with this transition. An analytical characterization of the snakelike reptation movement of the long chains, thought to be responsible for the transition, is likewise desirable. A simpler but equally fascinating topic for future research is the alignment of shorter-chain polyatomic molecules by shear flows, heat flows, and shockwaves.

The stochastic-dynamics approach of the Langevin equation has been used to describe conformational relaxation and diffusion of large molecules (109). It seems likely that such stochastic calculations could be adapted to flow problems as well, to determine approximate viscosities and conductivities for large molecules.

Finally, chemical applications of nonequilibrium molecular dynamics are appearing. The work that Klimenko & Dremin have carried out on the sensitivity of aromatic and aliphatic hydrocarbons to shockwave compression (13) is particularly provocative. They combined semiempirical potentials with classical trajectory analysis to predict reaction pathways. Whether or not this approach will prove useful in designing energetic materials remains to be seen.

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