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Microscopic Simulations of Complex Hydrodynamic Phenomena

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NONEQUILIBRIUM MOLECULAR DYNAMICS AT LIVERMORE AND LOS ALAMOS

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Abstract: The early development, overall accomplishments, and near-term future of nonequilibrium molecular dynamics are described. The perspective here is personal and emphasizes developments in the western United States.

From Ann Arbor to Livermore *via* Durham

University courses taught by Stuart Rice, George Uhlenbeck, and my thesis advisor, Andy De Rocco, led me in the direction of statistical mechanics and computer simulation. Andy emphasized that the basis of statistical mechanics lies in the simple ideal-gas thermometer. I found that the basis of computer simulation was likewise relatively simple. At the University of Michigan FORTRAN was covered in a single three-hour evening lecture.

After graduate school and an interesting postdoctoral year, 1961-1962, with Jacques Poirier at Duke University, the attractions of working with Bill Wood, at Los Alamos, or with **Berni Alder**, at Livermore, balanced. I was impressed by Berni and Tom Wainwright's pictures of molecular trajectories in the October 1959 Scientific American and had likewise very much enjoyed my interview visit with Bill Wood at Los Alamos. But the "Rad Lab" offered more money, $1100/month, *versus* Los Alamos' $900, and the extra money made up my mind. I have never regretted coming to Livermore. One of the many benefits of that choice is the opportunity to help celebrate Berni's 65th birthday here in Sardinia. Starting out at Livermore with Berni's specialty, hard spheres, I spent the next ten years studying equilibrium properties, primarily the mechanical and thermal equations of state and the melting transition for a variety of "simple" systems. During this period free energy and phase diagrams[1] were my goals.

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The Beginning of Nonequilibrium Molecular Dynamics[2]

Despite considerable effort, 1967 was too early for nonequilibrium molecular dynamics[3]. Urged on by Russ Duff, I had tried to simulate strong shockwaves on the Livermore computers[3]. But the magnetic tapes used to store atomic coordinates for analysis were unreliable. About one tape in seven was unreadable. In 1967 **Nonequilibrium Molecular Dynamics** was not yet feasible.

By 1972 times had changed. For me, hard-sphere pressure studies and smooth-potential equilibrium studies were basically dead. A small army of workers[4] had developed an equilibrium perturbation theory so good that further equation-of-state work seemed uninteresting. The time was ripe for the challenge of nonequilibrium work and all the needed ingredients were at hand. By now we had learned to *generate* coordinates as they were needed rather than trying to *store* them for future analysis. Years before, Vineyard[5] and Rahman[6] had shown how to treat the motion of atoms interacting with continuous potentials. Rahman had even simulated an 864-atom Lennard-Jones fluid.

In 1972 I wanted to use fast computers to simulate *nonequilibrium* systems, and with continuous, rather than impulsive, potentials. A halftime teaching appointment in Edward Teller's Graduate Department of Applied Science made this possible. My first doctoral student, Bill Ashurst, shared my enthusiasm for nonequilibrium simulation. Bill had the necessary hundreds of hours of computer time available at the Sandia Livermore Laboratory. He began to develop nonequilibrium molecular dynamics in March of 1972 by seeking to match laboratory methods of measuring viscosity and heat conductivity. His work was certainly timely. Though we did not know it then, analogous independent work was being carried out in England by Lees and Edwards[7], as well as by Gosling, McDonald, and Singer[8]. In France, Levesque, Verlet, and Kürkijarvi[9] were pursuing Green and Kubo's more prosaic, and less physical, equilibrium-fluctuation approach to transport.

Basic Thermodynamic Concepts

The conceptual basis of the new nonequilibrium simulation methods is straightforward[2,10]. Mass, momentum, and energy are first divided up among the individual interacting particles, with each particle getting its share. Dividing up mass, momentum, and kinetic energy is unambiguous. Potential energy is more complicated. In the simplest treatment of the simplest case, pairwise-

additive forces, the potential energy of each pair is divided equally between the interacting particles. From this division of the basic conserved quantities the local values of mass, momentum, and energy can then be used to construct the fluxes: particle current, pressure tensor, and heat flux vector, respectively. These definitions, together with that of the temperature (local kinetic energy) are all purely mechanical, and so can be taken over unchanged from earlier equilibrium work. It is fortunate that neither Bill nor I had been infected by the strange and largely unproductive idea that temperature is most naturally *defined* in terms of entropy. Away from equilibrium, despite many attempts, entropy still has no useful definition, so that this path leads nowhere.

Walls and Thermostats

The Second Law of Thermodynamics implies that any steady nonequilibrium flow *must* necessarily include an energy source, and must also reject heat to its surroundings. Thus steady nonequilibrium flows *must* have heat sinks. The main computational problem is inventing appropriate boundary conditions governing those degrees of freedom which exchange heat and work between the system and its surroundings. We began with what appeared to us to be the *simplest* nonequilibrium problem, a fluid undergoing simple shear between two moving isothermal walls. Inventing a sufficiently smooth interaction between bulk particles and the walls was challenging. Figure 1 shows four of the many wall types we tried out. Bill evaluated various types of *rigid* walls: first, flat surfaces; then, orderly rigid rows of fixed particles; finally, a wall potential based on the liquid-phase pair distribution function. In every one of these cases we were dissatisfied by the resulting spatial ordering of adjacent particles. Bill invented *fluid walls* in June of 1972. These were fine. Within each fluid wall a relatively small number of particles, with constrained mean velocity and temperature, was confined by two reflecting boundaries.

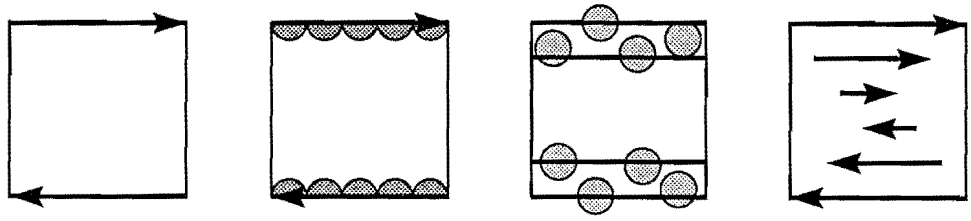


Figure 1. Rigid flat walls, rigid corrugated walls, fluid walls, homogeneous shear.

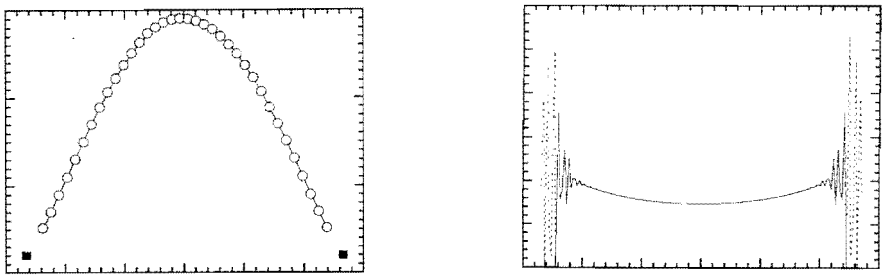


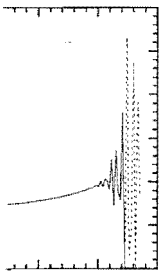
Figure 2. Temperature (left) and density (right) profiles in shear flow simulation. 37,500 bulk atoms are driven by the steady motion of 5610 boundary atoms.

The confined wall particles could interact *across* these reflecting boundaries with nearby bulk Newtonian particles. The generalization from shear flow to heat flow was easy. The two fluid walls, now stationary, were maintained at *different* temperatures. In all of these cases the velocity and temperature constraints were implemented by small velocity adjustments at the end of each time step.

The resulting thermostatted boundaries made it possible to simulate steady-state flows of momentum and energy in nonequilibrium liquids. Typically a few hundred bulk atoms were confined between two fluid-wall boundaries which served as heat and momentum reservoirs[11]. Just this year [1991] Liem, Brown, and Clarke[12] have carried out a set of wall-boundary simulations. They chose to follow Vineyard[5] by using solid, rather than fluid, walls. They applied this technique to shear flows with 37,500 bulk atoms driven by reservoirs containing 5610 boundary atoms constrained in planes by Hooke's-Law springs. The density and temperature profiles from their calculation are shown in Figure 2. Note the relatively long-ranged ordering effect of the solid walls on the fluid density.

Comparison with Green-Kubo Transport Coefficients

Shortly after we had perfected the measurement of shear viscosity and heat conductivity we got the news of Verlet, Levesque, and Kürkijarvi's determination of the triple-point transport coefficients from a relatively-long 40-hour equilibrium fluctuation simulation[9]. These French Green-Kubo liquid results were in *terrible* agreement with experimental data for liquid argon. First,



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the shear viscosity was much too high, for reasons which have never been explained[13]. Further, the wrong drawing was used in showing the shape of the pressure autocorrelation function used to calculate the bulk viscosity. Finally, a factor of two had been left out of the published thermal conductivity result. All told, these Green-Kubo results reinforced scepticism. On the other hand, our own shear viscosity and thermal conductivity calculations agreed nicely with experiment. Thus the three difficulties with the first Green-Kubo transport results strongly suggested, quite erroneously and, perhaps unfortunately, that the nonequilibrium and equilibrium methods might not agree.

Homogeneous Periodic Flows

Along with Lees and Edwards[7], and later Evans[14], we too had studied periodic *homogeneous* shear flows. The main goal underlying such homogeneous periodic methods was to reduce the considerable size-dependence stemming from the wall regions. See again Figure 2. A few years later we generalized our homogeneous shear method to the simulation of *bulk* viscosity. Our technique[15] for bulk deformation resulted in the same motion equations Andersen[16] was then developing independently for *isobaric* simulations.

Heat flow was more difficult to treat. We were unable to find a homogeneous and periodic algorithm for thermal conductivity. Mike Gillan[17] and Denis Evans[18] solved this mystery independently, discovering a direct technique, based on the Green-Kubo fluctuation formula, for measuring the thermal conductivity as the response to an artificial external field. All of these simultaneous and independent discoveries of the *same* numerical techniques showed that the time was ripe for nonequilibrium simulations.

Equations of Motion

Orwell's 1984 was a revolutionary and seminal year for both the style and the scope of atomistic simulation. Car and Parrinello were inventing new and fundamental equations of motion including the electronic degrees of freedom in fully dynamical simulations[19]. Farid Abraham[20] extended the size record for simulation, publishing a study of a big system, 161,604 atoms. In Canada Shuichi Nosé used integral feedback to exert frictional control on temperature in a novel way exactly consistent with Gibbs' statistical mechanics[21].

A dozen years earlier, when Bill Ashurst had been working on his dissertation, we had mainly been concerned with *difference* equations, and had not expressed our *"ad hoc"* boundary thermostat forces in terms of ordinary *differential* equations. It was not until 1982 that we[22], and apparently independently Evans[23], in 1983, expressed these thermostat forces in terms of time-reversible friction coefficients. For me, the so-called "Nosé-Hoover" formulation of these thermostat forces took shape in Paris in 1984, just before my stimulating visit with Philippe Choquard in Lausanne. Bad weather had changed my plane's landing site from Orly to De Gaulle. Soon afterward, I found myself riding a bus, and later, waiting for a train, with a lone co-passenger, a Japanese with the inscription "NOSE" on his suitcase. This was a real coincidence. Both of us were in Paris two days early for one of Carl Moser's CECAM workshops. When my inquiries showed that "Nose" was indeed "Nosé", we arranged for a productive and pleasant four hours spent on a bench in front of Notre Dame, sorting out the fine points of Nosé's 1984 papers. The reversible friction forces we were discussing in Paris had a form suggested by control theory:

$$\dot{p} = F - \zeta p \, .$$

The friction coefficient ζ can be chosen to impose the desired temperature relative to a specified stream velocity by using either differential ("Gauss") or integral ("Nosé-Hoover") control. Differential control can provide a canonical distribution in coordinate space[22] along with an isokinetic distribution in momentum space. Nosé proved[21] that integral control can reproduce Gibbs' canonical distribution in the full phase space. Either *differential* control--equivalent to resetting the velocities at each time step--or *integral* control, can be used to specify the friction coefficient ζ:

$$\zeta_D \equiv -\dot{\Phi}/2K \, ; \, \zeta_I \equiv \int [(K/\langle K \rangle) - 1] dt/\tau^2 \equiv \int [(T/\langle T \rangle) - 1] dt/\tau^2 \, .$$

Φ, K, and T are respectively potential energy, comoving kinetic energy, and temperature, while τ is an arbitrary reservoir relaxation time.

We will see that these same friction coefficients ζ are direct measures of the dimensionality loss associated with nonequilibrium phase-space flows. For example, in a dense-fluid nonequilibrium shear flow with strain rate $\dot{\varepsilon}$, the loss of phase-space dimensionality, relative to the total dimensionality D, is

$$\Delta D/D \approx (\sigma \dot{\varepsilon}/c)^2 \approx \zeta/\nu \, ,$$

where σ is the collision diameter, c is the sound velocity, and ν is the collision frequency. For a heat flow driven by a temperature gradient ∇T the result is similar:

$$\Delta D/D \approx (\sigma \nabla T/T)^2 \approx \zeta/\nu \, .$$

In a strong shockwave, where both velocity and temperature change on an atomic scale, the relative dimensionality loss $\Delta D/D$ approaches unity. In the more typical gentle macroscopic flows, where the two characteristic lengths $c/\dot{\varepsilon}$ and $T/\nabla T$ exceed the atomic scale by perhaps ten orders of magnitude, the corresponding loss of phase-space dimensionality is entirely negligible.

Finite-Difference Forms for the Equations of Motion

The simplest form of the simplest algorithm for solving the equations of motion, Störmer's, as used by Verlet[9] and *many* others, is:

$$\ddot{r} = (F/m) \Rightarrow (r_{t+dt} - 2r_t + r_{t-dt})/dt^2 \equiv (F_t/m) \, .$$

This patently time-reversible algorithm describes isolated systems with constant volume and energy. This same algorithm can be generalized to equilibrium simulations based on known Gibbs' ensembles at constant temperature or constant stress or to nonequilibrium simulations[24] for which no workable ensemble approach yet exists. In the isothermal case, for instance, the Störmer analog of the Nosé-Hoover equations of motion becomes:

$$\ddot{r} \equiv (F/m) - \zeta \dot{r} \Rightarrow (r_{t+dt} - 2r_t + r_{t-dt})/dt^2 \equiv (F_t/m) - \zeta_t (r_{t+dt} - r_{t-dt})/(2dt) \, ;$$

$$K \equiv \Sigma (m/2)\dot{r}^2 \Rightarrow K_t \equiv \Sigma m (r_{t+dt} - r_{t-dt})^2/(8dt^2) \, ; \, \Delta K_t \equiv K_t - \langle K \rangle \, ;$$

$$\dot{\zeta} \equiv \Delta K_t/\langle K \rangle \tau^2 \Rightarrow (\zeta_{t+dt} - \zeta_{t-dt})/(2dt) \equiv \Delta K_t/\langle K \rangle \tau^2 \equiv \Delta T_t/\langle T \rangle \tau^2 \, .$$

The first of the three difference equations can be solved for the set of new coordinates $\{r_{t+dt}\}$. These new coordinates appear again in the next equation, which provides a centered-difference expression for the kinetic energy K_t at time t. The new friction coefficient ζ_{t+dt} can then be computed from the kinetic energy difference ΔK_t.

Like Verlet's original approach to molecular dynamics this generalization shares the same desirable time-reversibility and stability properties. The reason for the exceptional stability of the Störmer-Verlet schemes has recently been clarified by H. Yoshida[25]. He showed that the discrete points $\{r_{ndt}\} \equiv \{r_t\}$ generated by the Störmer difference equations lie upon a continuous trajectory generated by a perturbed Hamiltonian. This perturbed Hamiltonian is "close to" the original one, differing from it by a term of order dt.

Higher-Order Generalizations of the Störmer Algorithm

Yoshida also generalized this idea, showing how to generate a family of higher-order algorithms which, like Störmer's, preserve phase-space volume. Thus the Störmer algorithm, and its more modern generalizations[24] to nonequilibrium flows, owe their deterministic time-reversible nature to an underlying Hamiltonian foundation. At the expense of additional storage and reduced stability relative to the Störmer method, another algorithm, simpler, and considerably more accurate than Yoshida's scheme, can be derived[2]. It uses coordinates from five successive time steps and forces from three. In the microcanonical constant-energy case this higher-order scheme is:

$$r_{t+2dt} - r_{t+dt} - r_{t-dt} + r_{t-2dt} \equiv (dt^2/4m)[5F_{t+dt} + 2F_t + 5F_{t-dt}] .$$

Velocities can be estimated from these coordinates and forces. For instance,

$$v_t \equiv (1/60dt)[7r_{t+2dt} + 16r_{t+dt} - 16r_{t-dt} - 7r_{t-2dt}] - (dt/5m)(F_{t+dt} - F_{t-dt}) .$$

These ideas also apply to Nosé-Hoover canonical or isobaric equations of motion.

From Linearity to Nonlinearity

Within a few years the new nonequilibrium simulations quickly reproduced not just the diffusion coefficients, but also the bulk and shear viscosities, yield stresses, and heat conductivities for simple fluids and solids. The accumulated fluid results turned out to obey a modern corresponding-states version of Enskog's theory, emphasized by Rosenfeld[26], in which the excess collisional part of the transport can be related to an effective hard-sphere size through the (equilibrium) entropy. Because Francis Ree and I had devoted several years of

effort to the measurement and interpretation of the entropy for hard spheres[27], we were pleased to find this application.

After the linear transport coefficients were under control intrinsically *nonlinear* processes were next to be simulated[28]. At Los Alamos, Brad Holian followed Klimenko and Dremin[29] in simulating strong shock waves[3,30]. At Livermore and Davis, we studied plastic flow in solids[22]. Our molecular and mesoscopic simulations followed studies of dislocation dynamics which my son and I carried out during my sabbatical leave in Australia, 1977-1978. The dislocation and plasticity work was then encouraged and supported by the Army

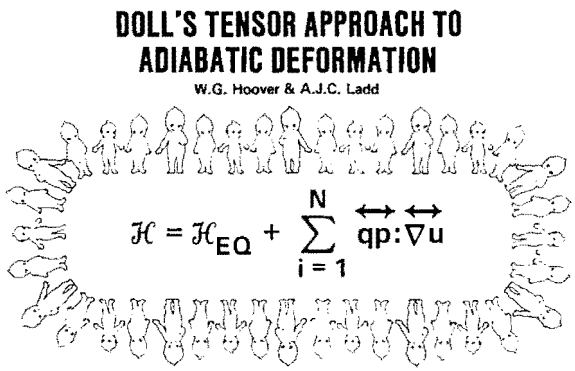

Figure 3. 1980 IUPAP Edmonton Poster describing "Doll's Tensor" Σqp . This approach provides a Hamiltonian description of viscous and plastic deformation.

Research Office, mainly through the kind efforts of Ed Saibel. Howard Hanley's excellent 1982 meeting at Boulder[28] also provided a strong stimulus for this work, as did several conversations at the otherwise relatively sterile meetings of the International Union of Pure and Applied Physics [Edmonton (1980) and Edinburgh (1983)]. My attempts to give talks describing my work with Tony Ladd on the nonlinear transport of shear momentum at these IUPAP meetings failed completely, resulting in the Doll's Tensor and Lorentz' Gas poster-session contributions shown in Figures 3 and 4.

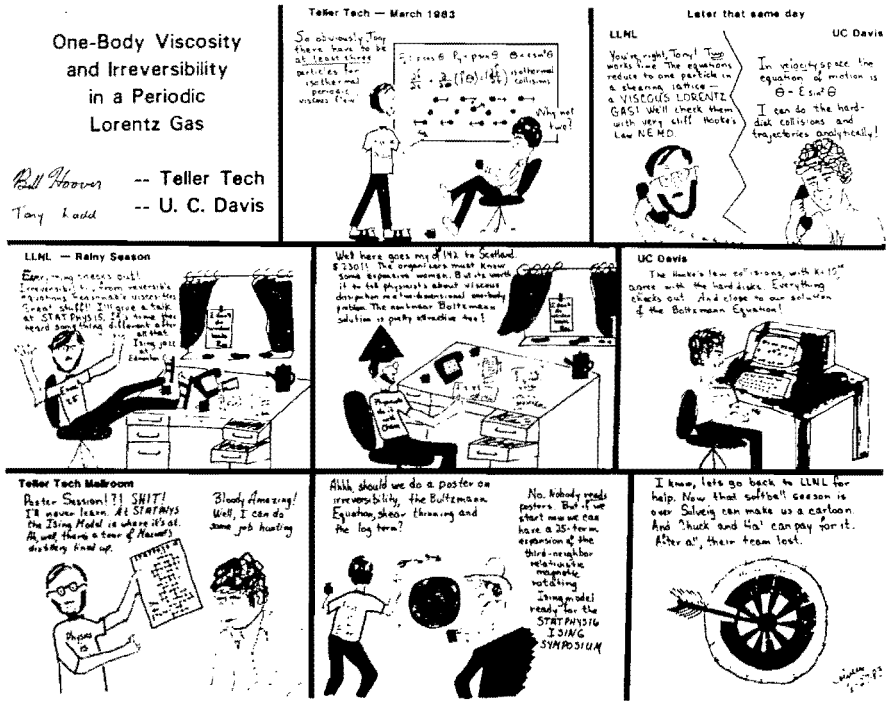

Figure 4. 1983 IUPAP Edinburgh Poster, drawn by Solveig Shearer, describing two-body shear-flow work supported by The Army Research Office's Ed Saibel.

Nonlinear Flows and Steady-State Information Theory

Nonlinear flows are more easily treated in small systems than in large systems and at low density rather than high. The *simplest* case, the two-body low-density problem can be solved *exactly* by using a special form of Boltzmann's gas theory. In such a case molecular dynamics can be avoided entirely. For two low-density hard spheres undergoing homogeneous periodic nonequilibrium mass or momentum flows the exact one-particle phase-space probability density can be expressed as a solution of the Krook-Boltzmann equation[31]:

$$\dot{f} = [f_{eq} - f]/\tau ,$$

where τ is the time between collisions.

Solutions of such few-body low-density transport problems deepened my understanding of Jaynes' and Shannon's and Zubarev's "information theory". That theory seeks the distribution function which *maximizes* Gibbs'

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(equilibrium) entropy by *minimizing* the corresponding phase-space integral $\iint f \ln f dp dq \equiv \langle \ln f \rangle \equiv -S/k$. It is sometimes claimed that this same theory can be applied generally, even far from equilibrium. If it were true then Gibbs' entropy would likewise be very useful far from equilibrium. I tested this idea. In the low-density, spatially-homogeneous Galton Board case, for fixed density, temperature, and current, this variational approach seeks the momentum probability density f(p) which maximizes the entropy integral $S/Nk \equiv -\int f \ln f dp$. For me it was interesting to see that the solution of this problem, the information-theory f_{IT}, was very different from the f_{KB} from the (exact) Krook-Boltzmann equation and the f_{MD} measured in the corresponding direct molecular-dynamics simulation[31,32]. Unlike the latter two exact distributions the maximum-entropy information-theory distribution is *not* a *steady* solution. Unless the current is maintained steady, by forcing not only the *average* current $\langle I \rangle$, but also all of its time derivatives, $\langle dI/dt \rangle$, $\langle d^2I/dt^2 \rangle$, $\langle d^3I/dt^3 \rangle$, ... to vanish, the current will simply decay to zero. *All* the time derivatives of the current would have to be set equal to zero in order to reproduce the simpler results from the Boltzmann equation or from computer simulation. The collective effect of these many constraints is responsible for the loss of phase-space dimensionality seen in nonequilibrium strange attractors. With this collapse Gibbs' equilibrium form for the entropy, $-k\langle \ln f \rangle$, *diverges* to minus infinity. Thus information theory is *not* a useful approach far from equilibrium.

Fractal Attractors from Nonequilibrium Molecular Dynamics[2]

The diffusion, viscosity, and heat conductivity coefficients produced by nonequilibrium molecular dynamics simulations are roughly consistent with predictions based on Enskog's hard-sphere model. But systematic improvements of this crude 1926 model are hard to make and present day theory has bogged down. This lack of progress is perhaps not surprising in view of the underlying chaotic dynamics which generates more information than can be contained in *any* theory. There is no convenient nonequilibrium analog to Gibbs' equilibrium distributions. The corresponding nonequilibrium kinetic equations, investigated by Yamada and Kawasaki[33], Visscher[34], as well as Evans, Holian, and Morriss[35,36], suggested that the phase-space distribution functions diverge for nonequilibrium steady states. In 1986, it turned out that the nonequilibrium phase-space distribution functions actually are divergent, with the probability density collapsing onto a fractal strange attractor of reduced dimensionality.

In a fractal object the number of points neighboring a typical attractor point and lying within a distance r varies as r^D where D is nonintegral and, in typical "multifractal" attractors, also varies from place to place. This fractal nature became clear to me when another doctoral student, Bill Moran, generated phase-space plots for a simple two-body nonequilibrium steady-state system, the Galton Board[37], which I had investigated earlier with Tony Ladd[32]. See Figure 5. Because later investigations of similar systems[38,39] showed that the behavior of this simple system is typical, I will discuss simple few-body systems here.

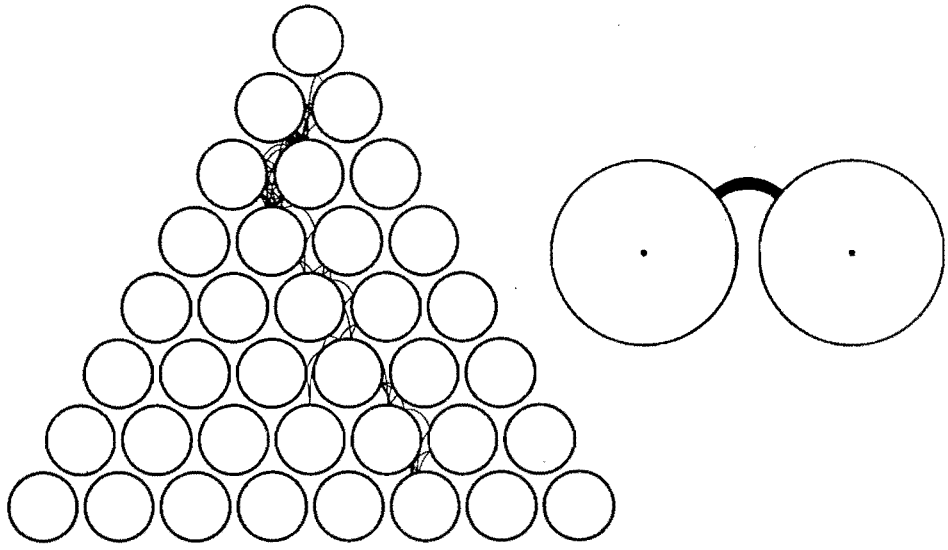

Figure 5. Galton Board with typical 99-collision chaotic trajectory sequence (left). Extraordinary periodic trajectories can be stabilized at special field values (right).

Fractal Few-Body Systems

We begin by describing the simplest models which generate phase-space fractals. Figures 6 and 7 show two of the corresponding (multifractal) objects, those corresponding to nonequilibrium mass currents and shear momentum currents. With relatively strong nonequilibrium driving, the corresponding phase-space dimensionality loss can typically be on the order of ten percent of the total dimensionality. Similar losses characterize the phase-space attractors of macroscopic many-body systems too, with the maximum dimensionality loss corresponding to the extreme conditions present in a strong shockwave, where velocity and temperature and energy all change qualitatively in distances of the order of the interatomic spacing.

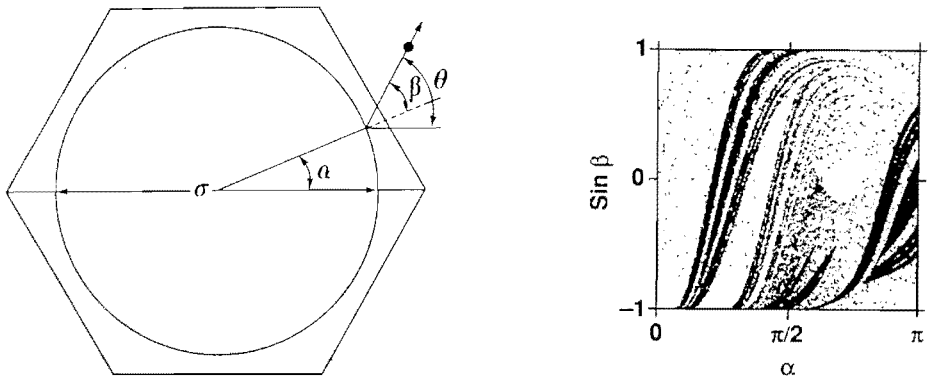

Figure 6. Unit cell for the Galton Board (left) showing the angles α and β defining collisions. Corresponding fractal collision sequence (right) in (α,sinβ) space.

The Galton Board problem[37] can be viewed as a periodic two-body system, or, equivalently, by switching to a coordinate system fixed on one of the particles, as a one-body scattering problem. In the one-body picture a particle falls, under the influence of an accelerating field, through a periodic array of scatterers. The kinetic temperature of the falling particle is kept constant by using a frictional force $-\zeta p$, where p is the momentum and ζ varies with time. In the two-body problem both bodies are accelerated symmetrically, one "up" (say) and the other "down". Two collision sequences, one chaotic and one periodic, are shown in the one-body Figure 5.

The nonequilibrium accelerating field (of strength E) generates *curved* trajectories, rather than straight lines, with the direction of the velocity varying with time according to the nonlinear equation:

$$\dot{\theta} = -(E/p)\sin\theta \ .$$

Here the angle θ describes the orientation of the velocity vector relative to the field direction. At high density a sequence of collisions can be generated numerically at the rate of millions of collisions per hour of computer time. Figure 6 shows the distribution of collisions for two hard disks in a moderately strong field. The distribution is multifractal, with a singular probability density distribution which diverges as the mesh is refined.

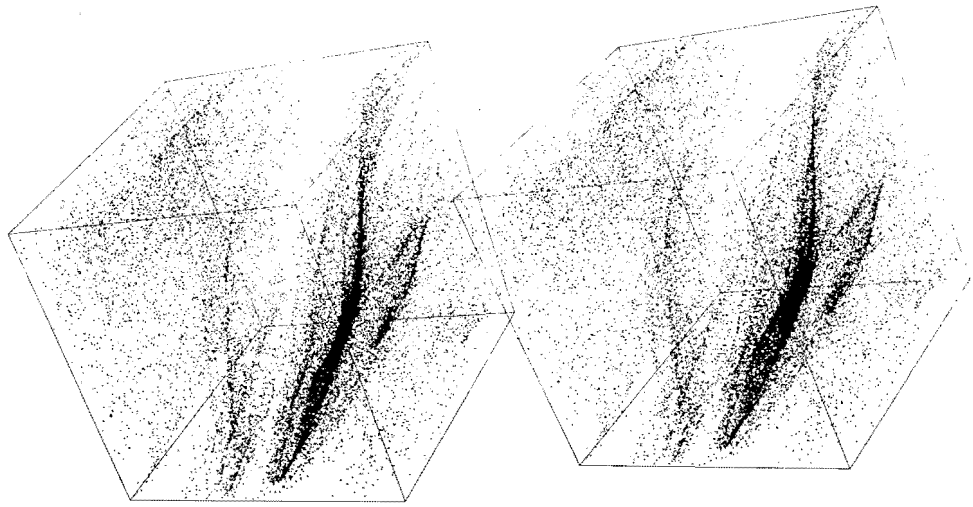

Figure 7. Stereo attractor for the periodic two-body hard-disk shear flow. The angles α and β are defined as in Figure 6. The third dimension represents time.

This divergent fractal behavior is not at all special to the Galton Board. An analogous problem involves the periodic shear of two disks[32,40] as suggested by Figure 4. Choose the simple flow $u_x \equiv \dot{\varepsilon} y$. In that case the equation of motion is:

$$\dot{\theta} = \dot{\varepsilon} \sin^2\theta \, ,$$

where θ gives the direction of the velocity relative to the flow direction, x. Because the shape of the system repeats periodically, in a time equal to the inverse of the strain rate $\dot{\varepsilon}$, the phase space for the shear flow problem is four-dimensional rather than three. The distribution of collisions occurs within the three-dimensional subspace shown in the stereo Figure 7. Once again the distribution is a fractal attractor, diverging as the mesh is refined.

Heat flow is still more complicated, requiring three particles, not just two, for heat flux without mass flux. In two space dimensions such a flow, with center of mass, center-of-mass velocity, kinetic energy, and heat flux vector fixed (seven constraints all told), takes place within a five-dimensional subspace of the 12-dimensional phase space. Here pairs of collisions occur within a simple four-dimensional collision subspace analogous to the usual Poincaré section. By using *color* and/or *animation*, energy and momentum of colliding particle pairs can also be shown, making it possible to analyze four-or-even-five-dimensional problems geometrically. Unfortunately the constraint forces required to generate

the underlying fixed-flux dynamics are relatively intricate, and I have not yet been successful in generating even the corresponding four-dimensional fractal subspace distributions. The further complexity of flows coupling the mass and heat currents, illustrating the Soret and Dufour effects, requires *six*-dimensional phase spaces with five-dimensional Poincaré-section analogs.

Fractal Many-Body Systems

The fractal nature of the two simple systems illustrated in Figures 6 and 7 is *typical* of *all* steady or time-periodic nonequilibrium flows, and has interesting topological and philosophical consequences. For *all* such nonequilibrium simulations which use Nosé-Hoover thermostatting forces it is possible to resolve Loschmidt's paradoxical question: "How can time-reversible equations of motion have irreversible solutions?" The nonequilibrium simulations all show that a phase-space collapse to a fractal strange attractor occurs with a collapse rate given by the summed spectrum of Lyapunov exponents[40-42]. The Nosé-Hoover equations of motion establish that the time-reversed motion is confined to a zero-measure unstable repellor (geometrically similar to the attractor, but with mirror-image momenta). Thus the time-reversed motion is unobservable on two counts. First, its phase-space measure vanishes. Second, flow in the vicinity of the repellor is unstable, expanding rather than contracting.

The time-averaged evolution of steady phase-space flows can be described by the flow's Lyapunov exponents. These exponents, one for each dimension in the phase space, describe the orthogonal growth (or decay) rates of a comoving phase space hypersphere, or "ball", centered on a phase-space trajectory. In nonequilibrium steady states any comoving element of occupied phase-space volume, such as this ball, which I denote with the symbol ⊗, must decrease *exponentially* with time:

$$\otimes(t)/\otimes(0) \equiv \exp(\Sigma\lambda t) \equiv \exp(\Sigma - \langle\zeta\rangle t) \equiv \exp[-\Delta S(t)/k] \equiv \exp[-\langle\dot{S}\rangle t/k] \; .$$

The link to the external entropy production $\Delta S \propto t$ then follows directly from the Nosé-Hoover equations of motion, as shown in detail below. It is to be emphasized that the older Langevin random-force description of thermostats precludes such a quantitative link.

The fundamental cause of irreversible behavior, with $\Delta S > 0$, is the Lyapunov instability that forces nearby phase-space solutions to separate exponentially in time, as $\exp(\lambda_1 t)$, where λ_1 is the largest of the Lyapunov exponents. *Close* to equilibrium the resulting dissipation is small and quadratic, with $\dot{S}/k$ varying as the square of the deviation from equilibrium, $\dot{\varepsilon}^2$ or ∇T^2. The dissipation corresponds to phase-space shrinkage to a strange attractor, with a phase-space dimensionality loss quadratic in the nonequilibrium gradient. *Far* from equilibrium the dimensionality of the occupied phase space can shrink further and approach zero.

The spectrum of Lyapunov exponents $\{\lambda\}$ which describes this exponentially diverging instability can then be related to the Nosé-Hoover friction coefficients $\{\zeta\}$ and also to the entropy production ΔS associated with the system's interactions with external heat reservoirs. To demonstrate this result it is necessary first to show that fluctuations in the friction coefficients $\{\zeta\}$, and the corresponding temperatures are uncorrelated. This follows easily from the Nosé-Hoover motion equation for each friction coefficient ζ coupled with the observation that the time-averaged value of ζ^2 has zero time derivative:

$$[\ \dot{\zeta} \equiv [(p^2/mkT) - 1]/\tau^2 \Rightarrow \langle \zeta \dot{\zeta} \rangle \equiv 0\ ] \Rightarrow \langle \zeta p^2 \rangle = \langle \zeta \rangle mkT\ .$$

The lack of correlation between ζ and p^2 allows the summed reservoir heat exchanges to be expressed in terms of the friction coefficients themselves:

$$\dot{S}/k\ = \langle \Sigma \zeta p^2/mkT \rangle \equiv \langle \Sigma \zeta \rangle \equiv -\langle \Sigma \lambda \rangle \geq 0\ .$$

This result, that the entropy of the surroundings of any nonequilibrium steady or time-periodic state must increase, is surely the most interesting lesson from the nonequilibrium simulations.

The exponential divergence of nearby trajectories always results in the bending and folding associated with a phase-space feature called a Smale horseshoe[41]. Repeated bending and folding, required by exponential separation within a bounded space, is the microscopic geometric mechanism underlying macroscopic irreversibility. It is the intricate information embedded in the phase space by this chaotic folding mechanism which overwhelms the information content of any theory. Exactly the same folding mechanism, resulting in

qualitatively similar [which is to say, relatively featureless] Lyapunov-exponent spectra, underlies continuum simulations of hydrodynamic shear flows.

Nonlinear Nonequilibrium Theory

A *theory* for the Lyapunov exponents, fractal dimensionality, and nonlinear transport coefficients would be most welcome. So far, despite considerable effort, only a few results, directly related to the nonequilibrium thermostats, have been derived[35]. The most interesting of these is this: in *steady* flows the nonlinear transport coefficients follow from the same formula as do the near-equilibrium fluctuation-theory coefficients. Let us illustrate this point in the case of an isoenergetic field-driven mass flux. Because the nonequilibrium phase-space distribution function f must obey the generalized Liouville Theorem,

$$\dot{f} = -f[\partial \dot{p}/\partial p] \equiv \zeta f \, ,$$

where the friction coefficient which stabilizes the internal energy $\Sigma\phi_{ij} + \Sigma p^2/(2m)$ is determined by the field E:

$$\dot{p}_x = E + F_x - \zeta p_x \, ; \, \dot{p}_y = F_y - \zeta p_y \, ; \Rightarrow \zeta \equiv (Ep_x/mkT) \, ,$$

the exact nonequilibrium current at time t, $\langle p_x \rangle_t$ can be related to the work done between the initial time 0 and time t through the exact chain of relations:

$$\langle p_x \rangle_t = \int d\Gamma f_t p_x = \int d\Gamma \int ds \dot{f}_s p_x \equiv \langle E \int (p_x/m)_s (p_x)_t ds \rangle \, .$$

It is extremely interesting to find that the nonlinear current is given by the *same* autocorrelation integral as is found in the Green-Kubo linear perturbation theory. The trick to showing this is to write f_t, the distribution function at time t, as the time integral of $\dot{f}_s$ from time 0 to time t. Unfortunately nonequilibrium correlation functions are no more easily generated than nonequilibrium fluxes, so that the present "theory", while "exact", appears barren.

It might be thought that the trajectories associated with thermostatted degrees of freedom are completely artificial. It is amusing that the trajectories which result from the isokinetic constraint are really not so strange. Exactly the same trajectories follow from Hamiltonian mechanics if the coordinate dependence of the potential function is taken to be exponential, rather than linear in the

coordinate parallel to the field[43]. Thus the trapped trajectory shown in Figure 5, which is, like *all* periodic orbits, *unstable* without the accelerating field, is a fully-stable consequence of ordinary Hamiltonian mechanics in the presence of an exponential nonlinear field.

Unstable periodic orbits in phase space can be used to describe time averages on chaotic attractors[44,45]. Evidently chaotic phase-space orbits must eventually, and repeatedly, come arbitrarily close to their initial conditions. Thus *long* unstable periodic orbits can be used to approximate chaotic orbits. This approach can be made systematic by considering periodic orbits of increasing length. Orbits of equal duration τ are weighted according to the sum of their *positive* Lyapunov exponents:

$$W_+ = \exp(-\Sigma_+\lambda_i\tau)/\Sigma\exp(-\Sigma_+\lambda_i\tau) \, .$$

Provided that the equations of motion are time-reversible the forward and time-reversed orbits can be combined in pairs. The individual time-reversed weights,

$$W_- = \exp(+\Sigma_-\lambda_i\tau)/\Sigma\exp(+\Sigma_-\lambda_i\tau) \, ,$$

make a smaller contribution, smaller by a factor proportional to the quotient, $\exp(-\Sigma_+\lambda_i\tau)/\exp(+\Sigma_-\lambda_i\tau) \equiv \exp(-\Sigma\lambda_j\tau) \equiv \exp(+\Sigma\zeta_j\tau)$, where the final Lyapunov-exponent sum includes all the exponents. This approach[45] leads to several exact nonlinear relations linking the Lyapunov exponents, transport coefficients, and the multifractal spectrum $f(\alpha)$. Vance has recently explored the convergence of his new approach for the Galton Board problem[45].

As Taylor's series would suggest, not too far from equilibrium the viscosity and conductivity show nonlinear variations which are quadratic in the deviation from equilibrium. Unfortunately such quadratic terms can depend upon the thermodynamic boundary conditions so that a definitive determination of nonlinear material properties is not easy. It is for instance evident that the direction of the heat flux, the orientation of the angular momentum, and the time rate of change of temperature can all influence the anisotropicity of the normal stresses in a shear flow. Articulating and solving the well-posed problems needed to unravel this complexity remains a stimulating and challenging task. It seems likely that a numerical approach to solving the Boltzmann equation, described at this School in Professor Bird's lecture, would be helpful, particularly in two-dimensional problems.

Nonlinearity and Shock Waves

A nonlinear problem which is free of these boundary difficulties is a steady shock wave. The shock wave boundary conditions are purely equilibrium ones, and lead to a strongly nonequilibrium steady state which can be very far from equilibrium, with pressure gradients on the order of trillions of atmospheres per centimeter. I have enjoyed working on shock wave problems with Brad Holian, first at Livermore, and later at Los Alamos, for about 25 years. We were first influenced by Russ Duff's enthusiasm[3] and Klimenko and Dremin's success in simulating fluid shockwaves with molecular dynamics[29]. The results, for weak shocks, were not very different from the predictions of the continuum Navier-Stokes equations[29]. Brad improved on the earlier Russian work by carrying out careful simulations of much stronger dense-fluid shockwaves[30] and found true nonlinear increases within the shock wave, about 30%, for both the viscosity and the heat conductivity.

Nonlinearity and Material Frame Indifference

At Livermore I had read about the so-called "Principle of Material Frame Indifference" with considerable scepticism. An idea embodied in the "Principle", that rotation would have no essential effect on material properties, seemed to me wrong [mine is a widespread, but sometimes controversial, view]. I therefore carried out simulations of heat flow[46] in a rapidly-rotating system in order to demonstrate that a truly nonlinear coupling, that linking the heat flux vector and the Coriolis force, can violate that "Principle". Although the relatively-large two-dimensional fluctuations limited the precision of these results Enskog's vintage-1926 theory of nonlinear transport was vindicated. Both the shockwave and rotating conduction simulations showed that Chapman and Cowling[47] were correct in predicting that the Burnett and Super-Burnett coefficients are relatively small, even "far from equilibrium". Thus nonequilibrium systems are not hard to "understand". The simple linear laws of Fick, Newton, and Fourier, are generally enough. Investigations designed to find significant exceptions to Navier-Stokes hydrodynamics have been largely unproductive.

Bigger Systems and the Future of Simulation

Massively-parallel computation is today's scientific revolution. The parallelism is achieved by dividing the problem, atomistic, continuum, or

hybrid, into contiguous parts, one part for each individual processor. Each processor's contents is in turn divided up into a number of spatial zones. Million-atom simulations[48,49] are revolutionizing atomistic computer simulation. *Billion*-atom simulations should follow soon.

I have listened to Carl Moser preach this gospel of parallel computers for about a decade. Tony De Groot made me a true believer when it took him only a few days to convert our CRAY molecular dynamics program for the SPRINT[50], a transputer-based computer Tony built in 1988 at a cost of $30,000. The cost-effectiveness of the SPRINT, computation per dollar, exceeds that of the CRAYs by a factor of several hundred. Figure 8 shows close-ups of a pair of two-dimensional million-atom simulations performed on the SPRINT as a prelude to our recent more-realistic three-dimensional simulations of indentation and cutting. At least in two dimensions, *coloring* can be used very effectively to indicate the orientation of each atom's neighbors. The coloring and generation method for amorphous grains were both suggested to us by Brad Holian and follow algorithms which he, Art Voter, and Terry Dontje developed at Los Alamos. The indentation of a granular crystal, one stage of which is shown at the right in Figure 8, can be followed very effectively using color videotape. The force law used in these simulations is an embedded-atom potential typical of simple metals like nickel and copper. The relatively small size-dependence of the two-dimensional work[49] suggested that three-dimensional million-atom systems are big enough to provide an adequate description of material failure.

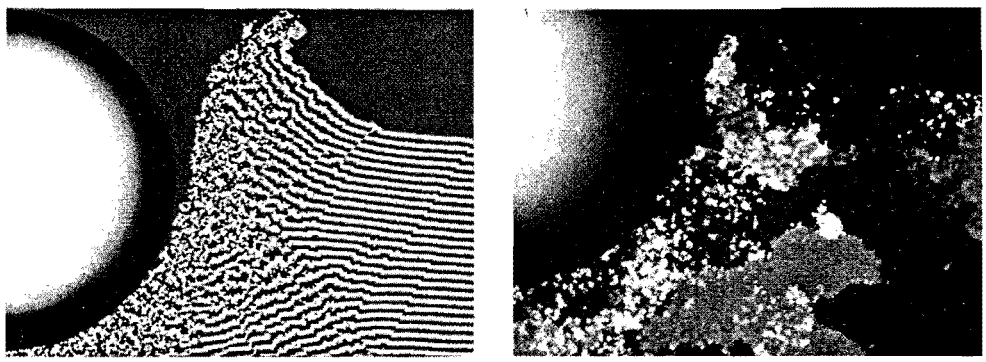

Figure 8. Closeups showing indentation of a perfect crystal (left) and a granular crystal (right). Granular atoms are shaded to indicate their neighbors' mean orientation. Figures 8 and 9 were created with the very welcome help of Mike Allison, Tony De Groot, and Carol Hoover, all at LLNL (Livermore).

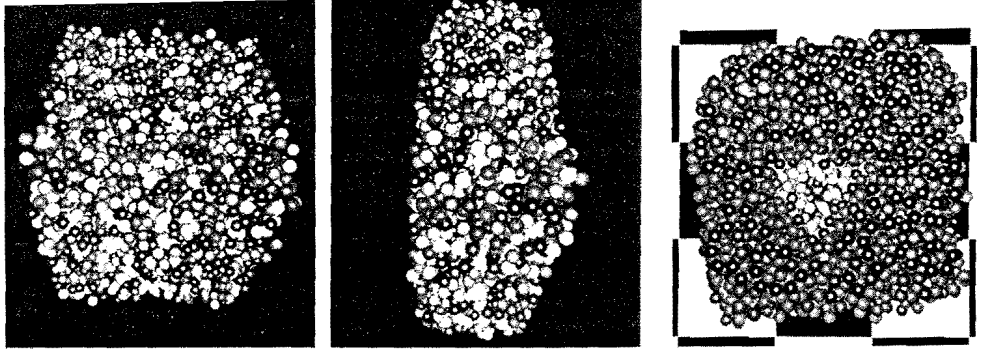

Figure 9. At the left, the longitudinal isothermal compression of an *amorphous* silicon solid at half the melting point. Here the solid is compressed between two frictionless plates. At the right, the isothermal indentation of a silicon single crystal at half the melting point using an indentor with an equilateral-triangle cross section. The indentor (not shown) moves as a rigid body made up of an equilateral tetrahedron of atoms. Indentor atoms interact with crystal atoms through the repulsive part of the Lennard-Jones pair potential.

In our very recent *three*-dimensional work we have concentrated on the simple three-body force model of Stillinger and Weber[51] for silicon. This brittle material has both crystalline and amorphous phases of commercial importance. There are recent laboratory-indentation experiments on both and we are carrying out parallel simulations. So far we have studied solid-phase plastic deformation and indentation flows of 4096-atom amorphous[52] and crystalline[53] samples of silicon, as shown in Figure 9. The basic amorphous structure was provided by Fred Wooten. The Figure illustrates relatively-slow isothermal compressions of the two sample types at half the melting temperature.

In preparation for the day when computer-center administrators are forced to accept the reality of massively-parallel processing we are presently devoting ourselves to the combining of atomistic and continuum mechanics, using molecular dynamics in some zones and Lagrangian continuum mechanics in others. At present the Car-Parrinello method for the dynamic simulation of ground-state quantum mechanics is slow, 400 hours on the CRAY for a picosecond history of 60 carbon atoms. But the thousand-fold cost improvement possible with parallelism together with the possibility of *hybrid* programs promises a new horizon, at which Schrödinger's equation, for the electrons, underlies thermostatted nonequilibrium nuclear trajectories.

Continuum Mechanics

In addition to its generalization to other Gibbs' ensembles and to higher-order algorithms, the same centered-difference Störmer scheme that is so useful in molecular simulations can just as easily be applied to continuum simulations. In "Lagrangian" continuum mechanics the system of interest is divided up into zones which obey finite-difference versions of the equations for conservation of mass, momentum, and energy:

$$d\ln\rho/dt = -\nabla\cdot u \; ; \; \rho\dot{u} = -\nabla\cdot P \; ; \; \rho\dot{e} = -\nabla\cdot Q - P:\nabla u \; .$$

These Lagrangian Equations of Motion can also be solved numerically by dividing the mass into quadrilateral (in two space dimensions) or parallelepiped (in three dimensions) "zones" and using a two-step generalization of Störmer's Algorithm, advancing the coordinates {r} and strains {ε} from time $_t$ to time $_{t+dt}$:

1. Advance the coordinates defining the zone vertices to time $_{t+dt}$ using the pressure tensor following from the strain at time $_t$:

$$(r_{t+dt} - 2r_t + r_{t-dt})/dt^2 = [-\nabla\cdot P(\varepsilon_t)/\rho_t] \Rightarrow r_{t+dt} \; .$$

2. Use the time $_t$ strain rates $\{\dot{\varepsilon}\}$ that result to calculate the time $_{t+dt}$ strains (which lead to the pressure tensor and new strain rates):

$$(\varepsilon_{t+dt} - \varepsilon_{t-dt})/(2dt) \equiv \dot{\varepsilon}_t \Rightarrow \varepsilon_{t+dt} \Rightarrow \dot{\varepsilon}_{t+dt.}$$

It is interesting that the bilinear-displacement triangular zones which are ideally suited to problems in continuum elasticity fail miserably for plastic flow and have to be replaced by quadrilateral zones[54]. This is because the number of constant-volume constraints and number of degrees of freedom are equal (to twice the number of vertices) for triangular zones. The constraints prevent convergence of the numerical solution to the physical one(s) as the mesh is refined.

Quadrilateral zones have their own difficulties. If the shear stresses are averaged over the zones then the "hourglass" deformation shown in Figure 10 has no restoring force, leading to "hourglass instability". This instability can be avoided by introducing a special "artificial viscosity" to damp the hourglass mode of deformation, or by defining local shear strain tensors in the four

quadrants of each zone. In the latter approach, which we have followed, an additional eight variables per zone are required. These are the two independent shear strains for each of the four cell quadrants, $\{\epsilon_{xx}-\epsilon_{yy},\epsilon_{xy}\}_4$. These, together with the cell volume make it possible to calculate all the pressure-tensor components, the mean pressure $P = (1/2)(P_{xx}+P_{yy})$, and the independent shear components, $\{P_{xx}-P_{yy},P_{xy}\}_4$. With this approach continuum simulations with as many as a million Lagrangian zones are feasible today.

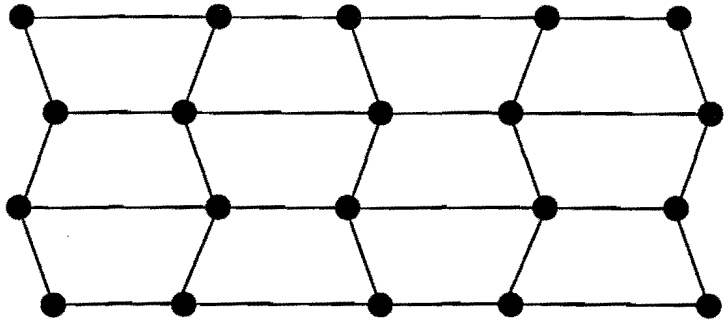

Figure 10. The "Hourglass" instability to which quadrilateral zones are prone.

General Remarks for Students

Scepticism, particularly where obsolete ideas are involved, is healthy[55]. The stochastic Langevin approach has recently been superceded by the more-flexible time-reversible deterministic methods[56] which generalize Nosé's approach to simulation. Monte Carlo methods have likewise been replaced with deterministic dynamical simulations. Dynamic simulations have likewise pointed out the shortcomings of approximate approaches based on the idea of a nonequilibrium entropy. All these relics of the past are being replaced.

But novelty is not always desirable. Simulations need to be founded on sound quantitative principles which allow for checking, intercomparisons, and systematic improvement. Otherwise what poses as "work" is little more than an animated cartoon. Those who read and write research papers in physics are naturally annoyed when others insist on doing things their own way, just for novelty's sake. George Stell invented the apocryphal journal Setbacks in Physics, restricted to erroneous work on problems which had already been solved correctly by others. All the veterans here could cite many papers which could fit such a journal.

We found a different example of excessive novelty in an otherwise excellent Computer Science Department in Japan. The doctoral students were required to publish *five* papers in the course of their graduate studies. There the resulting required novelty was often infinitesimal. But novelty *can* be good and should not be routinely discouraged. Had I heeded the sometimes discouraging words of the grand old men of computer simulation, the idols of my University days, both the equilibrium free-energy methods which Francis Ree and I developed and the nonequilibrium friction-coefficient methods which have kept me occupied since about 1980 would have had to have been discovered and explored by someone else. Had I substituted the judgment of some laboratory administrators for my own, many of the most interesting problems which we have worked out over the past 30 years would still be unsolved. Even the judgment of the editors of our best journals can at times veer off course[57]. The most interesting and stimulating work, because it overlaps boundaries and does not follow a well-worn path, is typically the most difficult to publish. But it does have lasting value and will eventually prevail. This meeting, at which a wide variety of techniques has been skillfully displayed, marks an extremely useful step toward the massively-parallel hybrid methods which, through an articulation of significant problems, will lead us to a more basic understanding of fluid turbulence, solid plasticity, and other such delights.

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