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Nonequilibrium Molecular Dynamics: The First 25 Years

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Running Title: 25 Years of Nonequilibrium Behavior

Nonequilibrium Molecular Dynamics: The First 25 Years

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Abstract:

Equilibrium Molecular Dynamics has been generalized to simulate Nonequilibrium systems by adding sources of thermodynamic heat and work. This generalization incorporates *microscopic* mechanical definitions of *macroscopic* thermodynamic and hydrodynamic variables, such as temperature and stress, and augments Atomistic forces with special Boundary, Constraint, and Driving forces capable of doing work on, and exchanging heat with, an otherwise Newtonian system:

$$\{ \dot{p} \equiv F_A(q) + F_B(q) + F_C(q,p) + F_D(q,p) \} \equiv m[q_{t+dt} - q_t + q_{t-dt}]/dt^2 \}.$$

The underlying Lyapunov instability of these nonequilibrium equations of motion links microscopic time-reversible deterministic trajectories to macroscopic time-irreversible hydrodynamic behavior as described by the Second Law of Thermodynamics.

Green-Kubo linear-response theory has been checked. Nonlinear plastic deformation, intense heat conduction, shockwave propagation, and nonequilibrium phase transformation have all been simulated. The nonequilibrium techniques, coupled with qualitative improvements in parallel computer hardware, are enabling simulations to approximate real-world microscale and nanoscale experiments.

Motivation/Goals:

Three strong motivations led directly to nonequilibrium molecular dynamics: it furnished a welcome check for Green and Kubo's linear-response theory of transport; it promised success in treating *nonlinear* problems; it furnished a new tool for understanding real phenomena. These goals parallel Zwanzig's reviews¹ of the motivation underlying nonequilibrium statistical mechanics. In 1977, in a perceptive speech in Kyoto², Kubo likewise discussed the prospects for theoretical physics. Pointing out that physicists are not afraid to shun formalism and to face facts, Kubo emphasized that nonlinear problems were the *only* problems left. To solve these problems, once computers became available, nonequilibrium molecular dynamics *had* to be developed. The development was carried out by many people³. It is natural that they had, and still have, similar ideas at about the same time.

Relation to Thermodynamics and Hydrodynamics:

A century ago, Lyapunov analyzed the dynamic stability of differential equations. *Linear* analysis of the growth of a trajectory perturbation, $\delta \sim \delta$, gives just three possibilities: decay, oscillation, and divergence. The last case—divergence and exponential “sensitivity to initial conditions”—defines *Lyapunov instability*. The biggest Lyapunov exponent λ_1 gives the average rate at which two neighboring trajectories diverge, $\delta(t) \sim \delta(0)\exp(\lambda_1 t)$. The rate at which the *area* of an ellipse, defined by three neighboring trajectories, diverges defines the next exponent, and so on: $A(t) \sim A(0)\exp(\lambda_1 t + \lambda_2 t)$. Lyapunov's “*instability* chaos” is the fundamental link between reversible microscopic nonequilibrium dynamics and irreversible macroscopic physics.

Lyapunov's ubiquitous exponential divergence underlies Boltzmann's 1872 concept of "molecular chaos", the random orientation of collision partners in a low-density gas. Boltzmann's equation in turn links microscopic *molecular* chaos to macroscopic irreversibility and transport properties. It was not until 1967 that Lorenz' analysis of weather forecasting popularized and underscored the importance of Lyapunov instability⁴. Now, the "Butterfly Effect", "chaos" and "Lyapunov instability" are familiar parts of our physics vocabulary⁵ and key ingredients in our understanding of nonequilibrium molecular dynamics.

Both temperature and thermostats are missing in Newtonian mechanics. Both are required to simulate the energy flows described by the thermodynamics and hydrodynamics of nonequilibrium systems. Kinetic theory furnishes the operational definition of temperature through the ideal-gas thermometer. In nonequilibrium molecular dynamics temperature is always measured by kinetic energy.

Theoretical analysis is greatly simplified if the generalized constraint and driving forces of nonequilibrium molecular dynamics are deterministic and time-reversible. The simplest such thermostat can be based on Gauss' Principle of Least Constraint. The corresponding constraint forces keep the kinetic energy of a selected set of degrees of freedom constant⁶. A more elegant alternative Gibbsian constraint force, producing the canonical distribution rather than the isokinetic one, was discovered by Nosé in 1984⁷, and was recently generalized by Bauer, Bulgac, and Kusnezov⁸.

We will see that Gibbs' definition of entropy, $S_{eq} \equiv -k\langle \ln f \rangle$, and the corresponding equilibrium definition of temperature, $T \equiv (\partial E / \partial S)_V$, are twin casualties of these thermostat definitions. None of the reversible

deterministic thermostats provides a nonequilibrium analog for the equilibrium Gibbs entropy. The nonequilibrium Gibbs entropy diverges! Despite this lack of a nonequilibrium entropy the incorporation of heat flow through the time-reversible thermostat forces leads to a microscopic understanding of the macroscopic Second Law of Thermodynamics⁹. We will see that this understanding involves Mandelbrot's fractals and ~~the~~ Lyapunov's instability spectrum. The irreversibility can occur in few-body systems. Even *one*-body Brownian motion can be treated in this way⁸.

Computational Advances:

In the 1950's Alder, Wainwright, and Wood used the computers at Livermore and Los Alamos to show that a few dozen hard spheres could characterize both solid and fluid phases. Alder and Wainwright also showed that, apart from fluctuations, the evolution of unusual initial states is described by the Boltzmann Equation¹⁰.

At both weapons laboratories, high-explosive work spawned an active interest in shockwaves. By 1967, the year of Lorenz' seminal work, hard spheres were passé. Vineyard, Rahman, and Verlet were successfully extending molecular dynamics to smooth pair potentials¹¹. At Livermore I tried to use Rahman's ideas to make movies of shock-induced *soft*-sphere melting¹². The movie project ultimately failed for lack of a reliable data storage device.

But times change. At Livermore we progressed through seven successive incarnations of CDC and CRAY computers, each more powerful than its predecessors. Now these once-remarkable supercomputers are dinosaurs, giving way to machines like Tony De Groot's SPRINT, which is 100 times more cost-effective. Now we can

follow and display the motion of *millions* of atoms on a university budget¹³. The size and time scales of such simulations are approaching those of real microscale and nanoscale experiments. Another four or five orders of magnitude improvement ¹³ are forecast in the near future¹⁴.

Simulation algorithms are changing too. In the 1950's solving Newton's equations of motion for a few dozen hard spheres was a challenge. In 1960 Vineyard was the first to formulate interesting nonequilibrium boundary conditions for particles with continuous forces¹¹. Today, we can treat far from equilibrium flows with a million atoms using realistic interatomic forces. Boundary, constraint, and driving forces, added to the usual atomistic forces, furnish the sources of mass, momentum, and energy crucial to most nonequilibrium flows:

$$\dot{p} \equiv F_A(q) + F_B(q) + F_C(q,p) + F_D(q,p) \equiv m[q_{t+dt} - q_t + q_{t-dt}]/dt^2.$$

These new motion equations are still deterministic and still time-reversible. But they are not symplectic, so that phase volume can vary with time and exhibit irreversible behavior. Nevertheless the solution algorithms are based on Störmer's ideas from nearly a century ago. As computer capacity continues to expand, calculations incorporating electronic, as well as atomic, coordinates will become commonplace.

Nonequilibrium Molecular Dynamics Develops:

During the ten years leading up to Howard Hanley's 1982 Boulder conference on Nonlinear Fluid Behavior efficient algorithms consistent with the Green-Kubo relations were discovered for diffusion, shear and bulk viscosity, and heat conductivity¹⁵. Gauss' isokinetic thermostat was

formulated as a differential equation with $F_C \equiv -\zeta p \equiv \dot{\Phi}p/2K$. [Φ and K are the potential and kinetic energies of the thermostatted degrees of freedom.] In 1982 it was not clear to outsiders that Green-Kubo linear-response theory was an exact limiting case of the nonequilibrium simulations. Only specialists knew.

Nonequilibrium molecular dynamics was exposed to the scrutiny of the experts attending Howard Hanley's 1982 Boulder Conference, **Nonlinear Fluid Behavior**¹⁶. Discussion centered on the validity and reversibility of the motion equations, nonlinear response theory, the proper boundary conditions, and on the relation of calculations to properties of real molecules. By now these questions have been substantially resolved. For useful summaries see the reprint volume **Simulation of Liquids and Solids**¹⁷ and the Proceedings of Michel Mareschal's Brussels meeting, **Microscopic Simulations of Complex Flows**¹⁸.

It has been confirmed that the finite-word-length accuracy of the simulations does not limit the validity of the results. Yorke, Yoshida, and others¹⁹ have established the existence of "shadow trajectories" which lie close to computed ones. Yoshida's "shadow trajectories" are the most interesting. As a simple illustration of his general result, consider the smooth (q,p) trajectory generated by the "Yoshida Hamiltonian" $H_Y = qpdt + (q + p)^2/2$. The trajectory approaches the harmonic oscillator one as dt is reduced. For finite dt the [Hamiltonian] trajectory is of course symplectic, conserving phase volume. But it also [surprisingly!] traces out the phase-space points generated by an algorithm equivalent to Stormer's:

$$q_{t+dt} = q_t + p_t dt; p_{t+dt} = p_t - q_{t+dt} dt.$$

Partly in response to discussions at Boulder I became convinced that the study of small systems was necessary to an understanding of nonequilibrium systems. Gary Morriss and I reported on some of these results at the Enrico Fermi Summer School at Lake Como in 1985²⁰. The small-system and time-reversibility studies both showed that Gibbs' entropy diverges for nonequilibrium steady states!

I continued working on small systems while on sabbatical in Vienna, working with Karl Kratky and Harald Posch while corresponding with Denis Evans, Brad Holian, and Gary Morriss. I became convinced that the Kawasaki-Visscher-Evans-Holian-Morriss exact but formal response theory¹⁵ had conceptual problems when applied to nonequilibrium steady states. The equations for the phase-space distribution function diverged. A key consequence of the divergence was that Gibbs' statistical definition of temperature in terms of the phase-space entropy $S \equiv -k\langle \ln f \rangle$, $T \equiv (\partial E / \partial S)_V$, had to be abandoned. When the phase-space density $f(q, p, t)$ collapses onto a strange attractor Gibbs' entropy diverges. Thus temperature *must* be defined according to kinetic theory: $3NkT \equiv \sum p^2/m$.

A family of one-body "Galton Board" problems that I began to study with Tony Ladd in 1983 and followed up with Bill Moran²¹ showed that the fractals popularized by Mandelbrot generally underlie nonequilibrium systems and even some equilibrium ones.

We have studied several such few-body strange-attractor examples^{21,22}. In every case the equations of motion were deterministic and time-reversible, and in every case Lyapunov instability broke the symmetry to provide irreversible behavior. Poincaré cross-sections cutting through five typical multifractal strange attractors are illustrated in Figure 2:

1. Isokinetic Dissipative Motion in the Galton Board;
2. Field-Driven Conductivity in a Sinusoidal Potential;
3. Two-Body Shear Flow—a Shearing Galton Board;
4. One-dimensional, One-particle Thermodynamic PV Cycle;
5. Viscous Dissipative Motion in the Galton Board.

By 1987 the realization that time-reversible deterministic nonequilibrium molecular dynamics *always* produces fractal structures led us to understand the Second Law of Thermodynamics as a time-symmetry breaking of Lyapunov-unstable thermostatted flows^{6,9}. The examples in Figure 2 illustrate the general rule that, *despite time reversibility of the motion equations*, the Lyapunov exponents, which give the averaged rate of expansion and contraction in phase space, *always* have a negative sum in steady nonequilibrium flows. For homogeneously thermostatted systems Sarman, Evans, and Morriss, have shown in addition that each such pair of exponents undergoes an equal negative shift²³. The general case is more complicated. Figure 3 illustrates the shift of the spectra for an inhomogenous eight-body system, a shear flow thermostatted at the boundaries.

The predominantly negative Lyapunov exponents shrink the occupied phase-space, not only in volume, but also in *dimensionality*, well below the equilibrium value²⁴. A more complete quantitative understanding of the large-system dimensionality drop awaits the teraflop and petaflop machines of the next decade¹⁴.

Some Conclusions:

From the pedagogical standpoint the main conceptual point revealed by analysing computer simulations is clear: Lyapunov's *mechanical* instability underlies Boltzmann's *thermodynamic* stability. Thus the microscopic sensitivity to initial conditions provides the averaging required for the inexorable work-to-heat dissipation associated with the Second Law of Thermodynamics. The macroscopic Second Law of Thermodynamics can be derived from the microscopic mechanical equations describing time-reversible deterministic thermostats. The Nosé-Hoover thermostats fundamental to this derivation necessarily involve feedback. For a recent illustration of the Feedback concept, see Figure 4.

Recent and Future Applications of Nonequilibrium Molecular Dynamics:

Let us highlight a few recent examples of nonequilibrium flows and cite recent books for more^{6,15-18,20}. Liem, Brown, and Clarke recently published very detailed density and temperature profiles for a nonequilibrium shear flow driven by isothermal boundaries²⁵. Their profiles, reproduced in Figure 5, indicate the finite extent of boundary influences and the eventual convergence to a smooth hydrodynamic profile despite the huge gradients. The ordering and the low-density nonlinear transport coefficients in such flows have been simulated and analyzed by Hess and Loose²⁶. Shockwave studies have continued, and show that linear transport theory is a good first approximation to this highly nonlinear problem. Klimenko and Dremin's shockwave simulations were brought up to date in 1980²⁷; these have now been followed by Robertson, Brenner, and White's simulations of the shock-induced dissociation of chlorine²⁸.

The Rayleigh-Bénard problem, discussed by Lorenz⁴, has been the object of many simulations. Rapaport, Mareschal, and others have used molecular dynamics to generate intricate roll patterns which transfer heat between two reservoirs through convection²⁹. I first saw the details of such patterns in Sitges, in 1980, where Gollub³⁰ showed pictures of some laboratory rolls which had not yet stabilized on a timescale of 400 hours. These long times emphasize the limits of simulation and experiments.

The breaking of spatial symmetry in the Rayleigh-Bénard problem has solid-state analogs. Our indentation simulations, starting out with a perfectly symmetric single crystal, show the interesting loss of space symmetry¹³ shown in Figure 6. Grain growth studies, based on Holian's ideas¹³ for generating polycrystalline initial conditions, and Abraham's seminal work on spinodal decomposition³¹ also suggest the generality of symmetry breaking. Just as in the breaking of time symmetry, the fundamental mechanism is deterministic chaos, Lyapunov instability.

Extending Nonequilibrium Molecular Dynamics:

Applications demand more practical work in the direction of simulating metals and covalent materials. Landman's pictures of recording head lubrication are a recent example³² directly related to practical applications. This practical emphasis will grow. For realism the electrons must be included. There is much to be done with the new ideas for electronic motion simulation begun by Car and Parrinello³³.

Nonequilibrium simulation has its limits. From an atomic perspective, a micron is a long distance and a microsecond is a long time. There is a pressing need for extending the scope in time and space. There are many ways to try to do this. They need to be tried out and evaluated.

Unfortunately these methods are fully as time-consuming as is the solution of the partial differential equations of continuum mechanics. One promising approach is to consider the interaction of continuum zones with particle-filled zones¹³. Another is to use smooth-particle hydrodynamics³⁴.

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Figure Captions

Figure 1. Our founding fathers, Boltzmann and Lyapunov.

Figure 2. Five deterministic time-reversible nonequilibrium strange attractors stabilized by Nosé-Hoover thermostats.

Figure 3. Equilibrium and Nonequilibrium Lyapunov spectra for a boundary-driven eight-atom shear flow.

Figure 4. Lee Lorenz' 25 May 1992 New Yorker drawing.

Figure 5. Density and temperature profiles for plane Couette flow.

Figure 6. Spatial symmetry loss during plane-strain indentation

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