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VOLUME II

IRREVERSIBILITY AND MOLECULAR DYNAMICS*. I.

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Abstract:

In this pair of papers I trace the development of Molecular Dynamics from its beginnings at Los Alamos to the present day. I emphasize the impact of recent developments on the problem of understanding irreversibility, as summarized in the Second Law of Thermodynamics.

I. Introduction.

Throughout Boltzmann's life-long atomistic study of irreversibility, he emphasized the one-body distribution function f_1, averaged over many particles, with the underlying dynamics taken to be a series of two-body collisions. His derivation of the H Theorem, linking dynamics and thermodynamics, remains *the* major accomplishment in understanding the Second Law of Thermodynamics. Today his analytic one-body approach has largely been superceded by using fast computers to simulate many-body "Molecular Dynamics".

Fermi originated Molecular Dynamics at Los Alamos in 1953. His few-body one-dimensional chains launched a generation of numerical studies of Lyapunov-unstable ordinary differential equations. By 1972 computers could simulate 1000-body gases, liquids, or solids, and a new nonequilibrium mechanics was developing to facilitate this work. In 1984, Nosé made a major contribution. He showed how to introduce macroscopic variables, such as temperature, pressure, and heat flux, directly into time-reversible microscopic equations of motion.

When Nosé's mechanics is applied to nonequilibrium systems zero-volume "strange attractors" form in the many-body phase space. The attractors provide a new explanation for the classical problem of irreversibility that fascinated Boltzmann. Here I trace the evolution of molecular dynamics from Fermi's work at Los Alamos to Nosé's recent work, and I speculate on the applicability of the new nonequilibrium ideas to quantum systems.

II. Boltzmann, the H Theorem, and Molecular Dynamics

It is fast computers that make molecular dynamics possible. The resulting dynamical simulations link the time-*reversible* fundamental viewpoint of microscopic mechanics to Boltzmann's microscopic, but approximate, kinetic theory, as well as to the phenomenological and time-*irreversible* macroscopic viewpoints of thermodynamics and hydrodynamics. These computer links among fundamentals, theory, and phenomenology change not just our point of view, but also our knowledge and our way of thinking about physics. In this review I describe these changes, beginning with Fermi's seminal calculations at Los Alamos, and ending on the presentday research frontier.

Both the underlying conceptual basis and the mathematical methods of molecular dynamics predate Boltzmann. Even today, the mechanical equations of Newton, Hamilton, and Gauss are solved with ancient algorithms based on Taylor's expansion. But before computers an algorithmic attack on molecular dynamics was premature. Maxwell and Boltzmann built kinetic theory from classical mechanics by averaging over space and time[1,2] in order to avoid a head-on attack on the many-body problem.

The most significant technical difference between today's computer calculations and Boltzmann's hand calculations is raw speed. This difference in speed is responsible for differences in attitude and in goals. Boltzmann didn't think seriously about calculating *all* the trajectories in a many-body system. It was impossibly complicated. As an alternative, Boltzmann introduced distribution functions in order to average over calculations too time-consuming to contemplate.
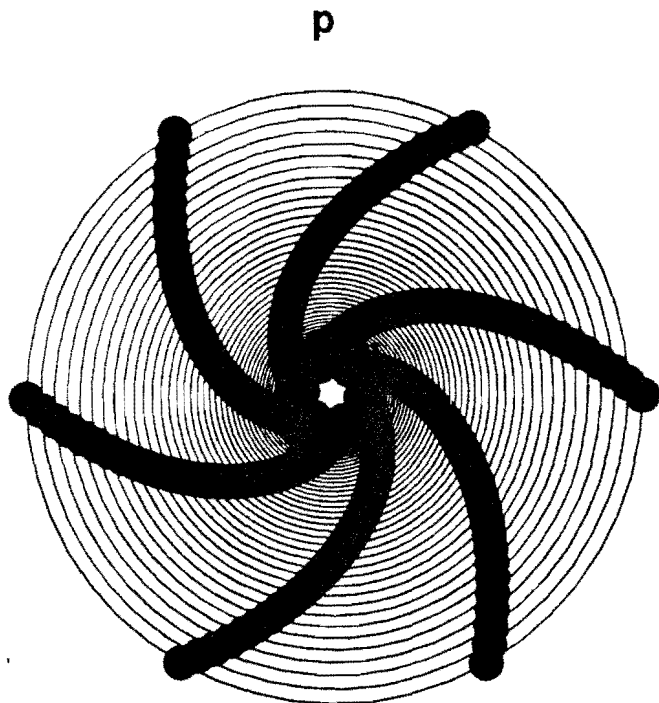
p

Figure 1. Harmonic-oscillator trajectory *via* the classic fourth-order Runge-Kutta method, using six steps per period to illustrate the approximate nature of the calculation. The exact trajectory is a periodic ellipse.

q

The situation is very different today. Historic textbook complaints bemoaning our inability to solve the equations of motion are obsolete. Right now the computers are about twelve orders of magnitude faster than humans. And parallel processing promises to increase the ratio much more. Now computers make it simpler to solve the original trajectory problem than to work out the average distribution functions. The trajectories are generated in discrete steps. The complicated molecular trajectories are divided up into simpler "timestep" sections, each of which can be worked out analytically. Linking these timesteps together generates an accurate trajectory. The accuracy is reduced as the timestep is increased. To illustrate, **Figure 1** displays an approximate harmonic-oscillator trajectory[3]. The exact trajectory is an ellipse. The approximation used in the Figure is typical for numerical work   It is the fourth-order Runge-Kutta algorithm. With the normal timestep choice, one-sixtieth of the oscillator period, the error in the Runge-Kutta approximation is much too small to see. In the Figure I use *six* steps per period rather than sixty, thereby increasing the energy error by a factor of one hundred thousand and making it possible to see two different errors associated with the numerical method. First, the *amplitude* gradually decreases. Second, the *phase* is shifted. Both errors are negligibly small for reasonable timestep choices.

The approximate oscillator trajectory shown in the Figure captures the style of the approximate trajectories used in molecular dynamics studies. By the term "molecular dynamics" we simply mean such a numerical solution of the classical equations of motion, usually for many bodies. Given the forces, the only approximation is the use of a finite time step. Normally the effect of that approximation is demonstrably negligible relative to statistical errors. The many-body molecular dynamics trajectories can then replace, if they cover phase space well enough, the idealized continuous one-body distributions introduced and studied by Maxwell and Boltzmann. This reversal, from one-body distributions to many-body trajectories, occurred only because the time integration required by ordinary differential eq·   ns is simpler than the combined space-and-time integrations required to solve partial differential equations.

The origins of kinetic theory were European. In 1905 Mrs. Hearst persuaded Boltzmann to leave the pleasant sophistication of Vienna for a summer in California. His account of that summer is delightful reading [4]. He lectured at Berkeley on irreversible processes, his favorite research topic. He visited Livermore, Monterey, and the new Lick telescope at Mount Hamilton. While surviving the stress of California's rough roads, local prohibition, and western cuisine, Boltzmann clearly saw the future, especially in the potential of Mrs. Hearst's University of California.

A generation later, the United States set the pace in computation, and did so for another generation, using World War II's scientific immigrants to develop and implement differential equations on the world's most powerful computers. While the war was on, these were handcranked machines. But the bombs that ended the war demanded ever more complex calculations. By 1952 the Los Alamos "MANIAC" computer was about a million times faster than humans[5]. That amazing speed has now increased by another factor of a million. And the once-rural institution at which Boltzmann lectured the University of California, now controls more CRAYS and more scientific computing power than any other institution in the world.

III. Molecular Dynamics Begins at Los Alamos and Livermore.

Continually-growing computer power fosters ever more complex physics problems. And there is no limit to this growth. The most-interesting physics is nonlinear and "chaotic". In a chaotic problem small changes in initial conditions lead to big differences in the solutions[6-8]. Turbulence is such a problem. These problems are infinitely harder to solve by hand than are linear ones. But nonlinearity is no inherent problem for computers. With efficient algorithms computers can provide us with a highly-accurate approximate solution.

At Los Alamos, computers were vital to predicting and understanding short-time highly-nonequilibrium bomb experiments. Patriotism attracted many of the world's most talented and stimulating scientists to this work. They speculated on the applicability of growing computer power to other areas in mathematical physics. Computation moved from hand calculators to punched cards in 1943, under Feynman's supervision. The war ended and nearly ten years passed before Los Alamos' stored-program MANIAC computer was ready.
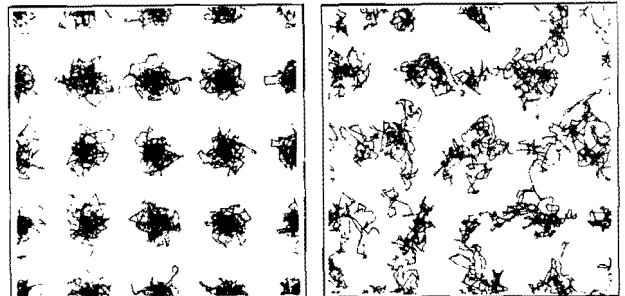
Fermi moved to Chicago after the war. He remarked that he would have stayed at Los Alamos had it been a University. But Fermi still returned in the summers, to work with Metropolis, Teller, Ulam, and other pioneers. Fermi had invented one useful many-body technique, the Monte-Carlo method, long before his Los Alamos days. The dynamic many-body problem, hard even for three bodies, remained a natural challenge in mechanics. After the war, as a summer commuter from Chicago, he introduced a primitive molecular dynamics at Los Alamos.

Fermi wanted to link molecular dynamics and thermodynamics, by watching the Second Law of Thermodynamics in action. To do this he simulated the motion of many-body chains of the type displayed in **Figure 2.** His idea was to watch many-body systems approach equilibrium [9], and to compare the results to the predictions following Boltzmann's one-body H-theorem route. Though short computer runs worked fine, one day an overlong computation seemed to reverse and back away from equilibrium.

Figure 3. Trajectory time exposures for three-dimensional hard spheres in the solid(left) and fluid(right) phases, from Reference [11]. Pictures such as these showed that purely-repulsive forces are sufficient to cause freezing.

There was no error. The backup was real. For studying the approach to equilibrium, Fermi's choice of system was unfortunate. He did not realize that one-dimensional chains do not equilibrate nearly as easily as do two- and three-dimensional systems. The failure of the chains to equilibrate surprised Fermi and helped awaken widespread interest in deterministic chaos in the next two decades.

Teller wanted a laboratory to compete with Los Alamos. The new rival, the Lawrence Radiation Laboratory, at Livermore, took shape while Los Alamos' MANIAC computer was being developed. At Livermore, Alder and Wainwright soon tested Boltzmann's one-body H-Theorem analysis of the approach to equilibrium[10]. They studied the motion of 100 three-dimensional hard spheres. These many-body hard-sphere studies confirmed Boltzmann's equilibration analysis. Alder and Wainwright's further studies were conclusive in showing that the freezing transition, and the existence of the solid phase, depends only on repulsive forces. The time-exposure trajectories shown in **Figure 3** document this early work[11]. Also significant was the quantitative agreement of the molecular dynamics calculations with Wood and Parker's Monte-Carlo simulations of the same systems. The two numerical techniques were found to agree not just in the thermodynamic limit, but even for systems of just a few particles[12].

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16

Figure 2. 16-spring anharmonic oscillator chain studied by Fermi, Pasta, Ulam, Tuck, and Menzel at Los Alamos. The typical starting condition was the lowest-frequency "mode" shown in the Figure, with quadratic or cubic forces added to the Hooke's-Law linear forces.

These early demonstrations that thermodynamic phase equilibria, as well as the approach to equilibrium, could be modelled with just a few interacting particles, established the utility of molecular dynamics in linking microscopic and macroscopic behavior. At last Maxwell and Boltzmann's conceptual basis linking fundamental microscopic approaches, molecular dynamics, kinetic theory and statistical mechanics, to phenomenological macroscopic approaches, thermodynamics and hydrodynamics, was secure. There was no longer any real doubt that microscopic many-body dynamics could reproduce macroscopic behavior. It was simply a question of figuring out how to do it as quickly, easily, and efficiently as possible.

IIII. Applications to Real Solids and Liquids at Brookhaven, Argonne, and Orsay.

Across the country from Alder and Wainwright's California calculations with idealized hard spheres, Vineyard, at Brookhaven on Long Island, simulated the behavior of real irradiated copper crystals. Vineyard demonstrated the applicability of the many-body molecular-dynamics techniques to real atomic-scale problems involving the interaction of high-energy radiation with matter. His results appeared first on the cover of the Journal of Applied Physics, reproduced here as **Figure 4.**
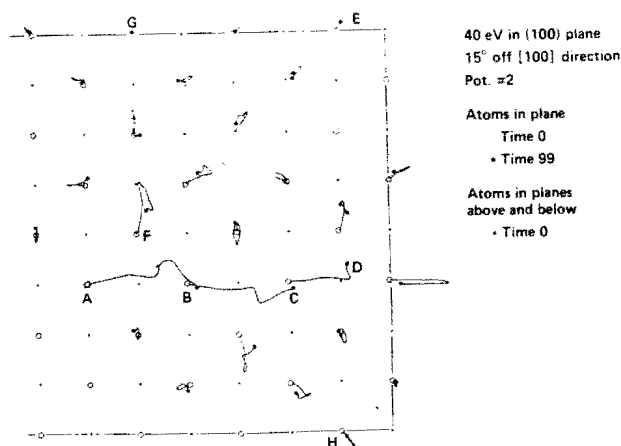

Figure 4. Cover of the August 1959 Journal of Applied Physics. The boundary particles obey irreversible viscoelastic equations of motion.

The conception, execution, and description of these early calculations were models of simplicity and clarity. Vineyard characterized nonequili energy storage following high-energy irradiation. He studied radiation damage by scattering energetic particles from crystals, following the individual collisions, with the viscoelastic boundaries draining off heat to reduce the effect of small system size. He established the importance of "focussing collisions", which transmit energy, coherently and through long distances[13].

Long before these early days of molecular dynamics, equilibrium gases and solids were fairly well understood. Gases could be treated as nearly-independent particles, while solids could be treated as nearly-independent phonons. Liquids were more mysterious. In principle, the known many-body equilibrium distribution function could be integrated over N-2 particle coordinates, to find the two-body distribution function needed to understand pressure and energy. But this averaging was too involved for practical calculations. A generation of physicists developed complicated distribution-function theories to discuss liquids[14], but little actually emerged before computer simulation. With fast computers this generation's theory became obsolete. After a period of testing, the old approaches, integral equations, cell models, and virial series, could be retired, replaced by perturbation theory.

In the early days of molecular dynamics, "solving" another many-body problem had mean. making another computer simulation. But by 1970, perturbation theory[15] made possible quantitative predictions of many-body thermodynamic properties in terms of *reference* computer data. The basic two-body "reference-system" properties were taken from computer experiments. A crude example is shown on the next page, in **Figure 5**, where the Lennard-Jones-pair-potential and argon phase diagrams are displayed together. The Lennard-Jones potential is not a specially faithful representation of argon, but is certainly a reasonable reference-system basis for perturbation calculations. And the perturbation theory worked well for "simple liquids", meaning monatomic fluids like argon.

With reference-system properties for hard spheres established at Los Alamos and at Livermore, the idea of describing liquids, using the more-realistic continuous-potential case, was acted on by Rahman. Rahman, working alone at the Argonne Laboratory near Chicago, took on an outstanding hard-but-tractable problem in equilibrium statistical mechanics, the modelling of an equilibrium monatomic liquid. Rahman[16] was the first to study a realistic liquid with molecular dynamics and to compare the results with experimental data. The structures that he found with 864 atoms were in agreement with laboratory experiments and inspir further molecular-dynamics studies of equilibriun liquids.
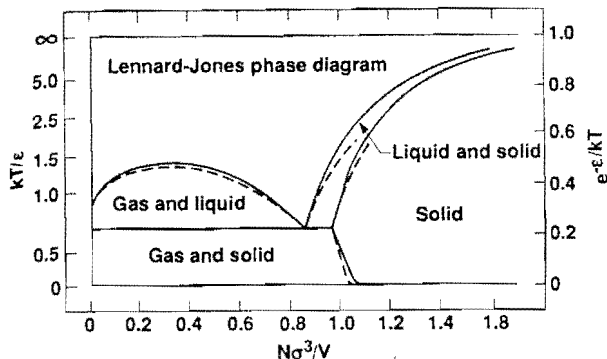
Figure 5. **Three-phase temperature-density phase diagrams for the Lennard-Jones pair potential, from molecular dynamics and Monte-Carlo simulations(solid), and for Argon, from experiment(dashed).**

Rahman also measured the equilibrium time-correlation functions needed to generate the linear transport coefficients. Soon after, Verlet, Levesque, and Kürkijarvi, in France, took up molecular dynamics and carried out definitive studies of both thermodynamic and transport properties of the prototypical Lennard-Jones liquid[17]. Since then, with spreading computer power and interest, molecular dynamics has become a truly international enterprise[18].

To illustrate this idea, but without any attempt at completeness, I mention as examples Evans in Australia, Posch in Austria, Bellemans in Belgium, Klein in Canada, Singer in England, Hansen in France, Hess in Germany, Berendsen in Holland, Rapaport in Israel, Iacucci in Italy, Nosé in Japan, Barojas in Mexico, Dremin in Russia, and Toxvaerd in Sweden.

Most liquids are polyatomic, not monatomic and "simple", and the classical treatment of polyatomic molecules has remained a subject of theoretical speculation. Many successful numerical simulations have appeared[18,19]. The viscosity for butane, for instance, has been investigated by two completely independent methods[20] and both simulated results lie within about 25% of the experimental viscosity. The simulation of large biological molecules followed naturally[21], as did also solid-phase applications in materials science[22], but with remaining major uncertainties with respect to the forces and the effect of quantum mechanics on the dynamics. The main motivation for undertaking large-molecule studies is the rapidly-improving resolution of experimental techniques. See **Figure 6** for a recent detailed scanning-tunneling-microscope snapshot of DNA[23].
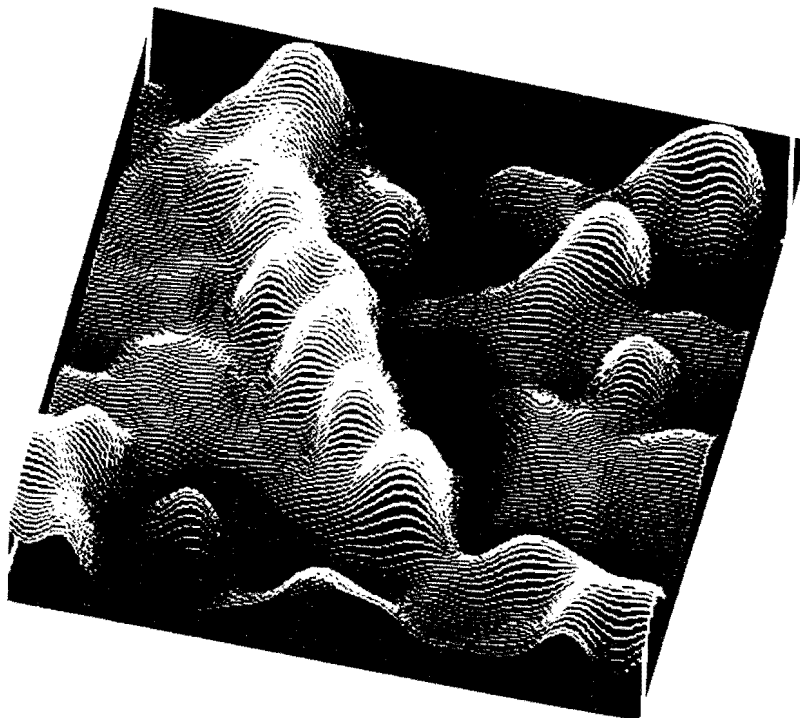

Figure 6. **DNA, as seen using a scanning tunneling microscope, as described in Reference [23].**
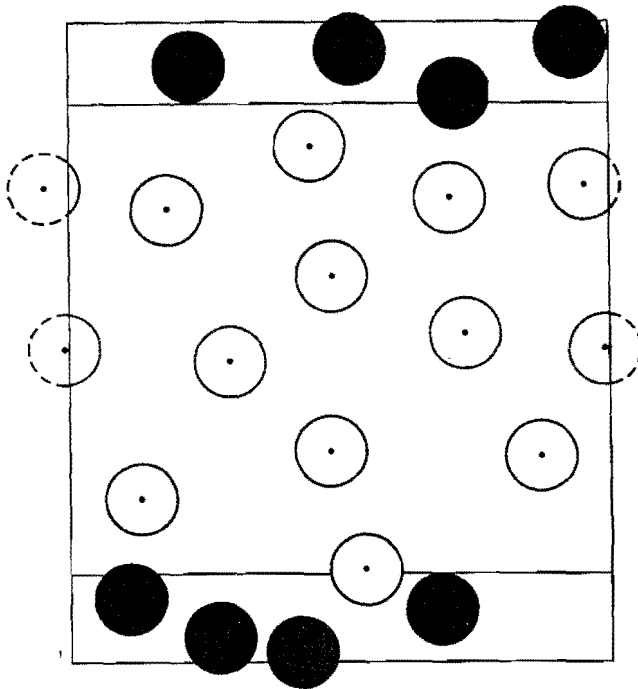
Figure 7. Eight shaded fluid-wall particles interact with twelve Newtonian Particles following time-reversible thermostatted equations of motion.

V. Molecular Dynamics Far From Equilibrium.

Equilibrium Newtonian molecular dynamics was expected to give accurate transport coefficients-- diffusion, viscosity, and thermal conductivity--through Green and Kubo's fluctuation theory, but the agreement with experiment turned out to be poor. The early many-body simulations of liquid transport properties contained errors. The calculated triple-point viscosity of liquid argon, assuming a pairwise-additive Lennard-Jones potential for the interatomic forces, was considerably too high. The thermal conductivity was worse, different from experiment by a factor of two, much too much to explain on the basis of force-law uncertainty. Thus, resolving disagreements between the equilibrium fluctuation theory[17] and experiment was one of the main motivations for the early nonequilibrium simulations[24]. Ashurst and Hoover set out to measure liquid transport properties by direct nonequilibrium methods. They simulated laboratory flows with what they called "Nonequilibrium Molecular Dynamics". Independent related work, but on a smaller scale, was then being carried in England by Gosling, McDonald, and Singer[25], and by Lees and Edwards[26].

Transport properties are mainly of interest not for checking fluctuation theory, but for use in hydrodynamic simulations of nonequilibrium flows. Of course sufficiently simple flows can be used to find the transport coefficients themselves. Nonlinear simulations of *driven* systems, in nonequilibrium steady states were studied at length by Ashurst in his Ph. D. thesis work at Livermore[24]. He developed time-reversible momentum and heat reservoirs which could be used to drive shear flows and heat flows while maintaining steady boundary temperatures. The boundaries he used, after trying out many less-satisfactory alternatives, are shown in **Figure 7.**

Ashurst had no vested interest in the use of the traditional classic time-irreversible Langevin and Fokker Planck stochastic equations. Instead, his instincts led toward time-reversible methods. The time-reversal-invariance of his nonequilibrium equations of motion is essential to the understanding of irreversibility discussed in Section VI. His boundary-driven work led to the steady-state generalization of homogeneous-deformation dynamics developed independently by Lees and Edwards[26]. Ashurst devoted serious attention to boundary conditions, exploring a variety of rigid and periodic boundaries, both fixed and in motion. This work led directly to shear and bulk deformation methods used to study viscosity and plasticity, identical to those formalized independently by Andersen[27] and Parrinello and Rahman[28] to describe the equilibrium constant-pressure and constant-stress ensembles.

To offset thermal fluctuations, molecular dynamics was typically applied to highly-nonequilibrium problems. These were indeed *very* far from equilibrium, although not *so* far away as conditions in a strong shockwave. In the dynamical shockwave simulations temperature changed by thousands of degrees, and pressure by half a million atmosopheres, in a shockwidth of a few atomic diameters. The nonequilibrium simulations showed, in qualitative agreement with experiment, a small but definite decrease in viscosity with strain rate. The change of conductivity with increasing temperature *gradient* could be either an increase or a decrease, depending on the temperature.

With non-Newtonian boundary conditions incorporating mass, momentum, and energy reservoirs, a variety of new simulation types became possible. Nonequilibrium simulations could include moving perio boundaries. Volume and shape changes could be imposed homogeneously or through displacements induced by fields or localized at physical boundaries. These possibilities are illustrated in **Figure 8.**

Figure 8. Four types of boundary conditions for simulating fluid or solid deformation. The motions are driven by (I) external fluid-wall particles, (II) homogeneous periodic deformation, (III) inhomogeneous external fields, and (IIII) moving corrugated boundaries.
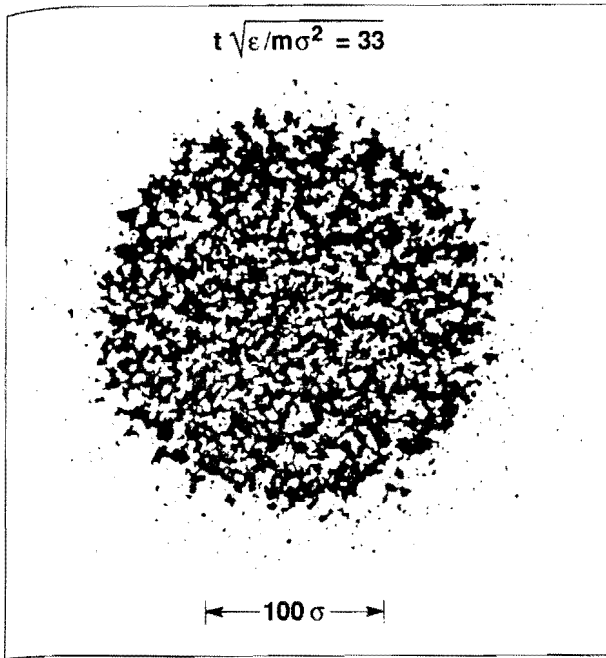
$$t\sqrt{\epsilon/m\sigma^2} = 33$$

$$\longmapsto 100\,\sigma \longrightarrow$$
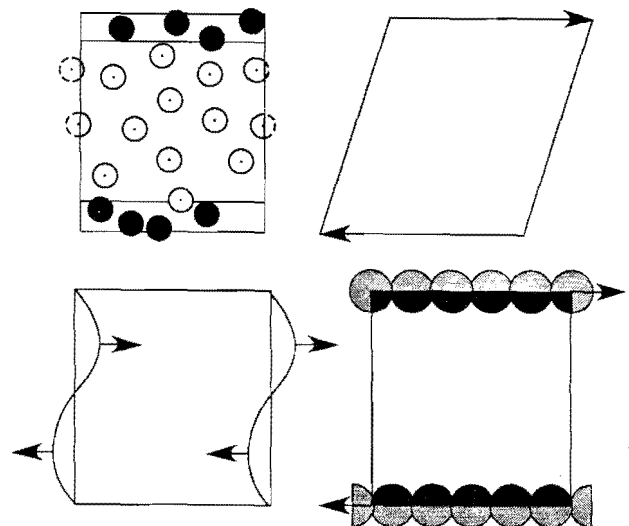
Figure 9. Fragmentation simulation showing over 14,000 two-dimensional Lennard-Jones atoms in free.expansion from a hot compressed state.

The first calculations confirmed that the various approaches gave consistent results[24]. At Los Alamos, strong shockwaves[29] were simulated by contracting boundaries. The results were not very different from the linear-transport Navier-Stokes predictions, despite gradients much larger than those typically used in nonequilibrium simulations. Thus the nonlinear behavior of the transport coefficients in shockwaves is very different from that found in the gentler homogeneous deformations. Despite the very large gradients shockwave transport coefficients are close to the zero-gradient linear-transport values. This insensitivity to nonlinearity is still largely unexplained, though some fundamental low-density kinetic-theory studies have been carried out[30]. Years later the reversed case, expansion, was used to study fragmentation[31,32] and fracture[33], as shown in **Figures 9 and 10**.
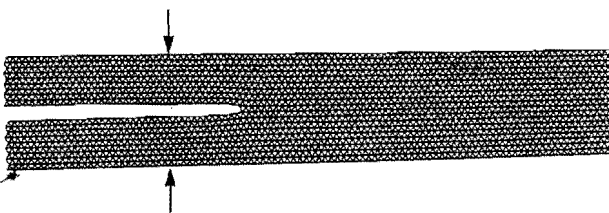

Figure 10. Fracture simulation showing an arrested crack in a crystal with a tapered boundary under tension. The imposed tensile stress caused the crack to proceed past the stopping point, indicated by arrows, predicted by static fracture mechanics.

Eckart Meiburg, in Gœttingen, was the first to carry out large-scale hydrodynamic simulations with molecular dynamics[34]. Besides the shockwave work, earlier less-extensive smaller-scale studies[35,36] had likewise suggested that molecular dynamics and hydrodynamics match closely. Computers were becoming powerful enough to consider again averaging to measure distribution functions. A typical averaged flow field taken from Meiburg's work is shown in **Figure 11**. In that Figure Meiburg's arrows represent stream lines of the fluid flow. Like Vineyard's, Meiburg's work is a model of clarity. He studied the motion of tens of thousands of hard spheres flowing past an obstruction and observed an average flow field looking very much like the initiation of a von-Karman vortex street.

Figure 11. Hard-sphere simulation of flow past a splitter plate. Arrows represent stream lines. The beginnings of a "vortex street" can be seen.
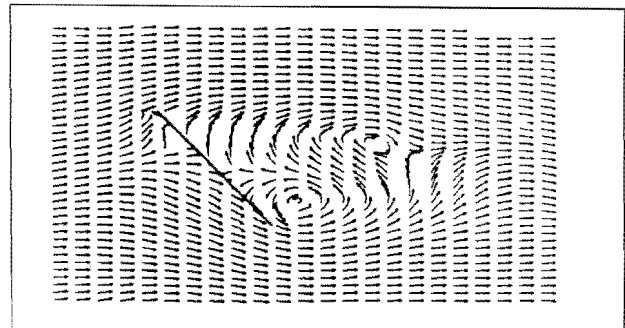
More recently, Mareschal, Kestemont, Mansour, and Puhl[37] have studied Rayleigh-Bénard instability, in which a fluid heated from below, in a gravitational field, develops cylindrical convection currents. A typical averaged flow field distribution in shown in **Figure 12**. They made a careful comparison of molecular-dynamics results with hydrodynamic solutions of the Navier-Stokes equations. The Rayleigh-Bénard model is of special historic interest through its link to the computational study of chaos introduced in Lorenz'[38] classic paper on atmospheric turbulence which appeared in 1963.

Figure 12. Averaged fluid flow velocity vectors in a two-dimensional simulation of compressible Rayleigh-Bénard heat flow in a vertical gravitational field. The two vortices found with molecular dynamics match the predictions of continuum mechanics, as described in Reference [37].
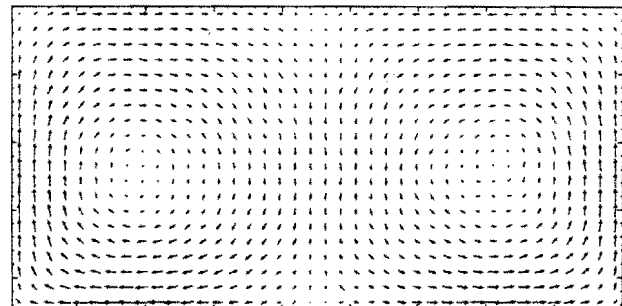
VI. Irreversibility and Instability from Time-Reversible Two-Body Mechanics

Both Newton's and Schrœdinger's equations of motion are "time-reversible". This means that any movie illustrating a Newton or Schrœdinger solution can be run either backward or forward through the movie projector. Both versions satisfy the same equations of motion. In the reversed direction, the Newtonian velocities would change sign, as would the corresponding imaginary component of Schrœdinger's wave function, but the time-reversed classical trajectory, or quantum probability density, is as good a solution of the equations of motion as the forward one.

The conflict between these fundamental time-reversible descriptions of motion and the even-more-fundamental irreversible behavior of the "real" world has attracted continuing interest since Boltzmann's time. Boltzmann focussed attention on the time evolution of the averaged one-body probability density, $f_1(q,p,t)$.

The gas-phase Boltzmann equation for the time-development of f_1, as well as the linearized Krook-Boltzmann approximation, and the Fokker-Planck plasma equation, all evolved from analytic attempts to express and understand patently-irreversible many-body phenomena in terms of the one-body distribution function. These simplifications are less necessary today. We can follow the details of phase-space deformation, as given by the the time history of the N-body distribution function, f_N, for 32-body systems. Today we can generate accurate trajectories for a million particles. And particle mechanics has itself been modified to treat the problems addressed by Boltzmann, Fokker, and Planck. A 1984 modification of Hamiltonian mechanics, discovered by Shuichi Nosé and described in Paper II, is the key to these modern n trajectory investigations of irreversible behavior.

Boltzmann studied the one-particle distribution function in dilute nonequilibrium gases. His time-*irreversible* Boltzmann equation

$$df_1/dt = (\partial f_1/\partial t)_{\text{collisions}} ,$$

provided a plausible description averaged over a large number of particles. By ignoring fluctuations and correlations, Boltzmann estimated the time-dependence of the one-body-phase-space probability density. His most famous result, derived from the Boltzmann equation, was the H Theorem. That theorem shows that isolated systems irreversibly approach equilibrium. Thus, Boltzmann's equation already lacked the time-reversibility of Newtonian mechanics and provided an approximate entropy function which could not decrease with time.
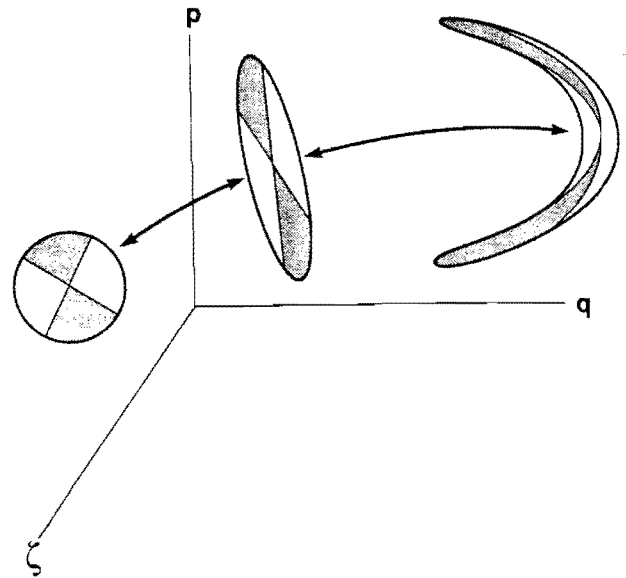

Figure 13. Schematic time-development of a phase-space hypersphere into a short-time hyperellipsoid, and a longer-time Smale horseshoe.

The fundamental mechanism underlying the approach to equilibrium is now known to be "Lyapunov instability"[39-43]. This instability, and its many-body generalization to the "Lyapunov spectrum", describes the exponential spreading apart of initially-neighboring many-body-phase-space trajectories, as well as the exponential growth, or decay, of many-dimensional phase-space hypervolumes. See **Figure 13**. The trajectory spreading has to be simultaneously accompanied by an orthogonal compression because *any* Hamiltonian flow, when averaged over all directions in the phase space, is incompressible. The orthogonal rates of growth and decay of phase-space separation are given by "Smale Pairs" of Lyapunov exponents, equal in magnitude but opposite in sign. The idea of measuring distance between points in phase space might seem bizarre, because coordinates, momenta, and friction coefficients all have different physical units. But because the growth and decay rates are *exponential*, the muliplicative choice of scales of the axes are irrelevant. Exactly the same exponents would result for any other choice of generalized coordinates and momenta.

In phase space, the spreading instability progresses from small scales, with hyperspheres elongating into hyperellipsoids, to large scales, at which the deforming hyperellipsoids must bend to follow the macroscopic phase-space motion. On the infinitesimal microscale the Lyapunov instability can be seen as sensitive dependence on initial conditions, as revealed by a linear stability analysis of the equations of motion.

Figure 14 shows a simple example, the Newtonian Lyapunov-unstable bouncing of two balls in a constant vertical gravitational field. The lower of the balls is held fixed. For clarity, the upper, moving ball is shown as a mass point. In cartesian laboratory coordinates the bounces become more widely separated with each bounce. In semilogarithmic coordinates the exponential instability of the motion is clearly apparent.

In many-body phase space the generalized exponential Lyapunov instability is described by the Lyapunov spectrum[41-43]. **Figure 15** shows typical many-body spectra for both two- and three-dimensional fluids and solids. The Smale-pair symmetry of these equilibrium spectra follows from the equivalence of forward and backward solutions of the equations of motion. In nonequilibrium steady states, this symmetry is broken, and the sum of the Lyapunov exponents is negative.
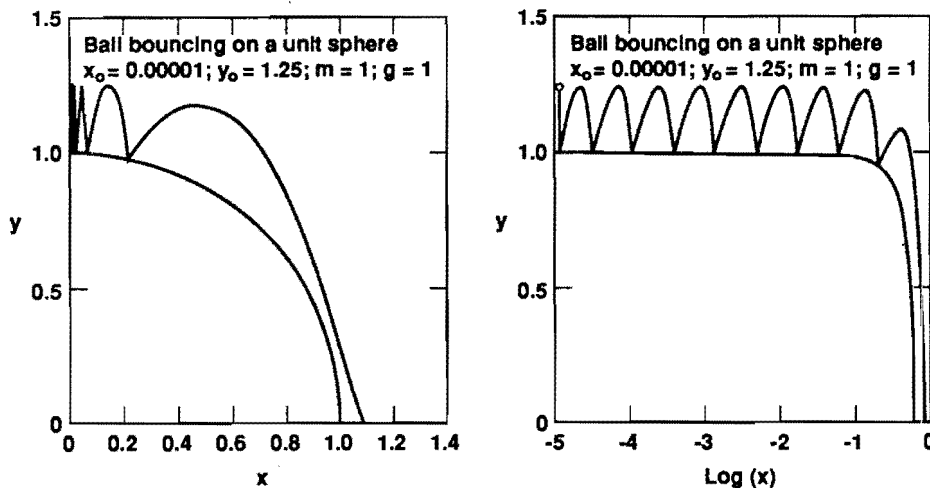
Figure 14. Bouncing of a mass point on an infinitely-massive elastic ball of unit radius. The maximum height of the bouncing point is 1.25. Plotting the *same* trajectory on a semilogarithmic scale (at right) shows the characteristic Lyapunov instability responsible for macroscopic irreversibility.
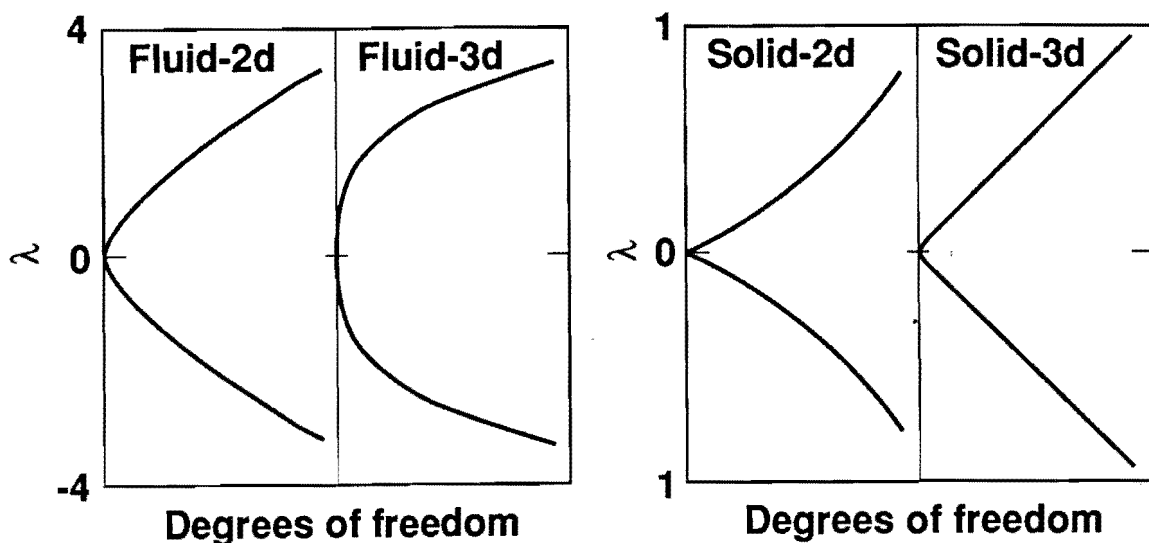
Figure 15. Typical Lyapunov-exponent spectra for two- and three-dimensional fluids and solids. The phase-space stretching rates (positive Lyapunov exponents) and compression rates (negative Lyapunov exponents) are shown as symmetric Smale pairs. This equilibrium symmetry is broken in the nonequilibrium states discussed in Section VI and in Paper II.

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