Physica A 194 (1993) 450–461
North-Holland

PHYSICA A

Nonequilibrium molecular dynamics: the first 25 years

Wm. G. Hoover

Department of Applied Science, University of California at Davis/Livermore, Livermore, CA 94551, USA
and Department of Physics, Lawrence Livermore National Laboratory, P.O. Box 808, L-794, Livermore, CA 94551, USA

Equilibrium molecular dynamics has been generalized to simulate *non*equilibrium 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:

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

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, shock-wave 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.

1. Motivation/goals

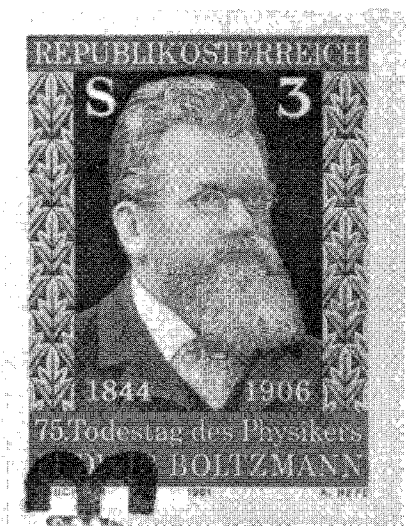
Three strong motivations led directly to nonequilibrium molecular dynamics: it furnished a welcome check for Green and Kubo's linear-response theory of transport; it promised success in treating *non*linear problems; it furnished a new tool for understanding real phenomena. These goals parallel Zwanzig's reviews [1] of the motivation underlying nonequilibrium statistical mechanics. In 1977, in a perceptive speech in Kyoto [2], 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 people [3]. It is natural that they had, and still have, similar ideas at about the same time.

2. 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, $\dot{\delta} \propto \delta$, 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, $\delta(t) \approx \delta(0) \exp(\lambda_1 t)$. The rate at which the *area* of an ellipse, defined by three neighboring trajectories, diverges defines the next exponent, and so on: $A(t) \approx A(0) \exp(\lambda_1 t + \lambda_2 t)$. 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. (See fig. 1 for portraits of Boltzmann and Lyapunov.) It was not until 1967 that Lorenz' analysis of weather forecasting popularized and underscored the importance of Lyapunov instability [4]. Now, the "butterfly effect", "chaos" and "Lyapunov



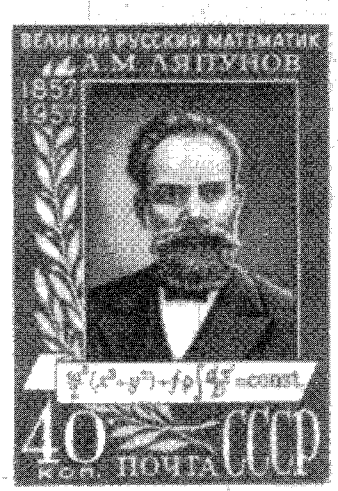


Fig. 1. Our founding fathers, Boltzmann and Lyapunov.

instability" are familiar parts of our physics vocabulary [5] 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 both deterministic and time-reversible. The simplest "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 constant (for a general background consult Hoover [6]). A more elegant alternative Gibbsian constraint force, producing the canonical distribution rather than the isokinetic one, was discovered by Nosé in 1984 [7], and was recently generalized by Bauer, Bulgac and Kusnezov (for references and the most general approach, see ref. [8]).

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 casualities 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 thermodynamics [9]. We will see that this understanding involves Mandelbrot's fractals and Lyapunov's instability spectrum. The irreversibility can occur in few-body systems. Even *one*-body Brownian motion can be treated in this way [8].

3. 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 equation [10].

At both weapons laboratories, high-explosive work spawned an active interest in shock waves. By 1967, the year of Lorenz' seminal work, hard spheres were passé. Vineyard, Rahman and Verlet were successfully extending

molecular dynamics to smooth pair potentials [11]. At Livermore I tried to use Rahman's ideas to make movies of shock-induced *soft*-sphere melting [12]. The movie project ultimately failed for lack of a reliable data storage device.

But times change. At Livermore we have 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 budget [13]. 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 is forecast in the near future [14].

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 forces [11]. 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:

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

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.

4. 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 conductivity [15]. Gauss' isokinetic thermostat was formulated as a differential equation with $F_C \equiv -\zeta p \equiv \dot{\Phi} p/2K$. ($\Phi$ 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 others [19] 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" $H_Y = (q^2 + qp\,\mathrm{d}t + p^2)/2$. The trajectory approaches the harmonic oscillator one as $\mathrm{d}t$ is reduced. For finite $\mathrm{d}t$ 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 Störmer's:

$$q_{t+\mathrm{d}t} = q_t + p_t\,\mathrm{d}t\,, \qquad p_{t+\mathrm{d}t} = p_t - q_{t+\mathrm{d}t}\,\mathrm{d}t\,.$$

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 1985 [20]. 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 theory [15] 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: $3NkT \equiv \Sigma\, p^2/m$.

A family of one-body "Galton Board" problems that I began to study with Tony Ladd in 1983 and followed up with Bill Moran [21] 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. Two- and three-dimensional Poincaré cross-sections cutting through five typical three- and four-dimensional multifractal strange attractors are illustrated in fig. 2:

1. Isokinetic dissipative motion in the Galton Board (top left);
2. Field-driven conductivity in a sinusoidal potential (top right);
3. Two-body shear flow – a shearing Galton Board (bottom left);
4. One-dimensional, one-particle thermodynamic PV cycle (bottom middle);
5. Viscous dissipative motion in the Galton Board (bottom right).

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 fig. 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

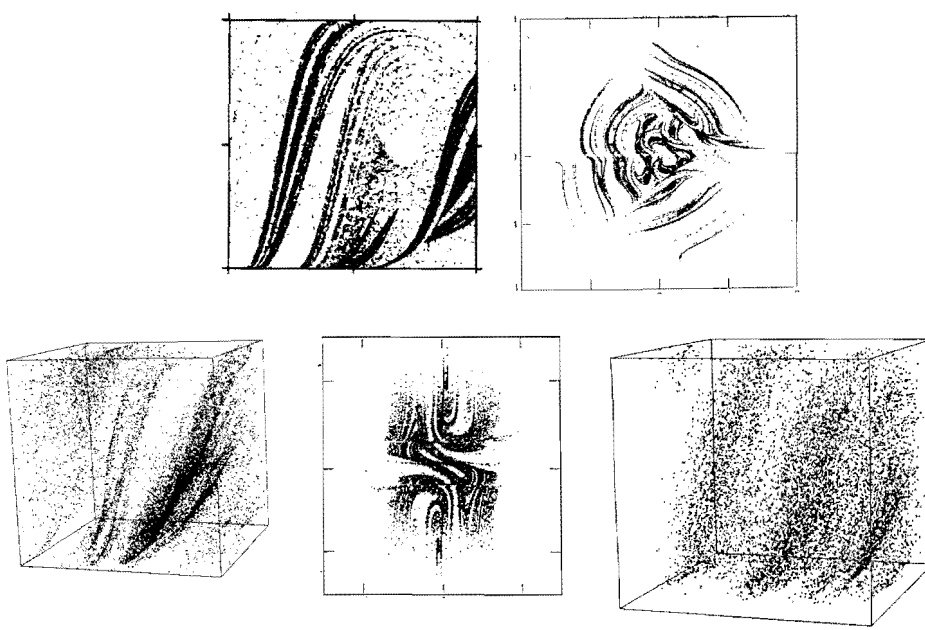


Fig. 2. Five deterministic time-reversible nonequilibrium strange attractors stabilized by Nosé–Hoover thermostats.

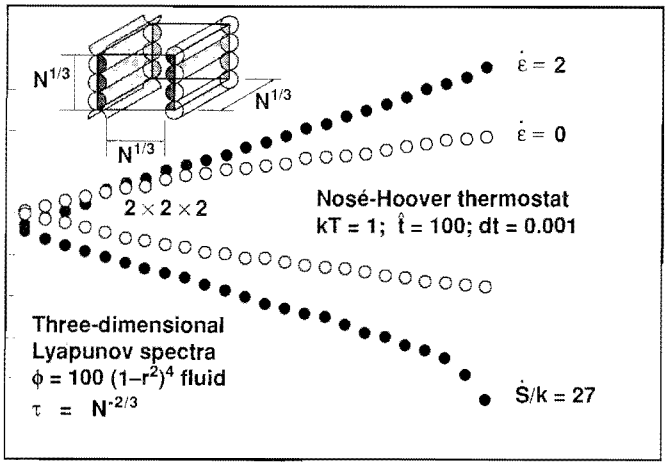


Fig. 3. Equilibrium and nonequilibrium Lyapunov spectra ($3N$ Lyapunov exponent pairs) for a boundary-driven eight-atom shear flow.

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 shift [23]. The general case is more complicated. Fig. 3 illustrates the shift of the spectrum for an inhomogeneous 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 values [24]. A more complete quantitative understanding of the large-system dimensionality drop awaits the teraflop and petaflop machines of the next decade [14].

5. Some conclusions

From the pedagogical standpoint the main conceptual point revealed by analyzing 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 neces-

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

sarily involve feedback. For a recent illustration of the feedback concept, see fig. 4.

6. 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 boundaries [25]. Their profiles, reproduced in fig. 5, indicate the finite extent of boundary influences and the eventual convergence to a smooth hydrodynamic profile. Despite the relatively large gradients no significant nonlinear effects were detected. Nonlinearity does occur with higher gradients. Shear-induced spatial ordering and low-density nonlinear transport coefficients in shear and heat flows have been carefully simulated and analyzed by Hess and Loose [26]. They have found good

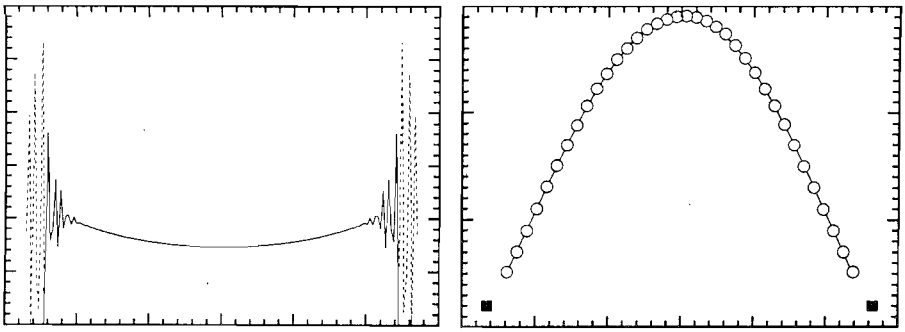


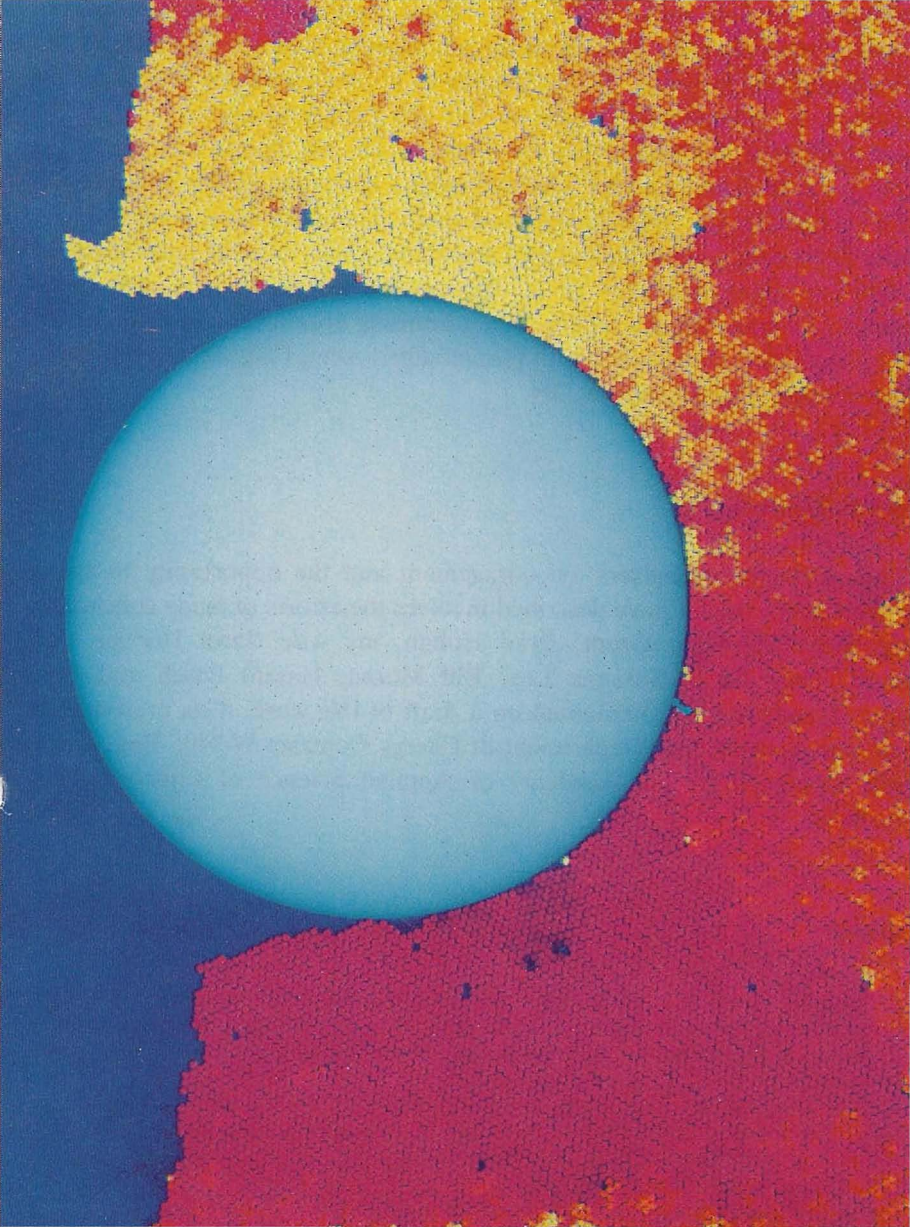
Fig. 5. Density (left) and temperature (right) profiles for plane Couette flow.

agreement among three different approaches to nonlinear transport: the Boltzmann equation, hydrodynamic stability theory, and simulations.

Larger gradients can occur in shockwaves. Density can double, with temperature and pressure increasing by many orders of magnitude, all in a distance of one or two atomic diameters. The corresponding strain rates exceed 10^{12} hertz. 25 years of nonequilibrium shock-wave studies have shown that linear transport theory is a surprisingly good first approximation to this highly nonlinear problem. Klimenko and Dremin's seminal shock-wave simulations were brought up to date in 1980 [27]; these have now been followed by Robertson, Brenner and White's dense-fluid simulations of the shock-induced dissociation of chlorine [28]. Salomons and Mareschal have shown that Burnett-level heat-flux contributions improve the hydrodynamic predictions of dilute-gas shock-wave structure [29].

The Rayleigh–Bénard problem, discussed by Lorenz [4], 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 convection [30]. I first saw the details of such patterns in Sitges, in 1980, where Gollub [31] showed pictures of some laboratory rolls which had not yet stabilized on a time scale 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 symmetry [13] shown in fig. 6. Grain growth studies, based on Holian's ideas [13] for generating polycrystalline initial conditions, and Abraham's seminal work on spinodal decomposition [32] also suggest the generality of symmetry breaking. Just as in the breaking of time symmetry, the fundamental mechanism is deterministic chaos, Lyapunov instability.



7. Extending nonequilibrium molecular dynamics

Applications demand more practical work in the direction of simulating metals and covalent materials. For a recent simulation of recording-head lubrication see ref. [33]. 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 Parrinello [34].

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 zones [13]. Another is to use smooth-particle hydrodynamics [35].

Acknowledgements

I appreciate the organizers' encouragement and the opportunity to speak here. The work which I have described involves the efforts of many colleagues, among them Tony De Groot, Brad Holian, my wife Carol Hoover, Jeff Kallman, Tony Ladd, Susanne Lee, Bill Moran, Harald Posch and Fred Wooten. Harald kindly commented on a draft of this work. This presentation was in part supported by Department of Energy Contract W-7405-Eng-48 and in part supported by the Academy of Applied Science of Concord, New Hampshire.

References

[1] R. Zwanzig, Annu. Rev. Phys. Chem. 16 (1965) 67; Where do we go from here?, in: Perspectives in Statistical Physics, H.J. Raveché, ed. (North-Holland, Amsterdam, 1981).
[2] R. Kubo, in: Oji Seminar on Nonlinear Nonequilibrium Statistical Mechanics, Prog. Theor. Phys. Suppl. 64 (1978) 1, opening address.
[3] A.W. Lees and S.F. Edwards, J. Phys. C 5 (1972) 1921; E.M. Gosling, I.R. McDonald and K. Singer, Mol. Phys. 26 (1973) 1475; L.V. Woodcock, Chem. Phys. Lett. 10 (1971) 257; W.T. Ashurst and W.G. Hoover, Phys. Rev. Lett. 31 (1973) 206.
[4] E.H. Lorenz, Nature 353 (1991) 241.
[5] J. Gleick, Chaos (Viking, New York, 1987).
[6] W.G. Hoover, Computational Statistical Mechanics (Elsevier, Amsterdam, 1991).
[7] S. Nosé, J. Chem. Phys. 81 (1984) 511.
[8] D. Kusnezov, Phys. Lett. A 166 (1992) 315.

[9] B.L. Holian, W.G. Hoover and H.A. Posch, Phys. Rev. Lett. 59 (1987) 10.
[10] B.J. Alder and T. Wainwright, Molecular dynamics by electronic computers, in: Transport Processes in Statistical Mechanics, Proc. IUPAP Symp., Brussels, 1956 (Interscience, New York, 1958) p. 97.
[11] J.B. Gibson, A.N. Goland, M. Milgram and G.H. Vineyard, Phys. Rev. 120 (1960) 1229; A. Rahman, Phys. Rev. A 136 (1964) 405; L. Verlet, Phys. Rev. 159 (1967) 98.
[12] R.E. Duff, W.H. Gust, E.B. Royce, A.C. Mitchell, R.N. Keeler and W.G. Hoover, Shock-wave studies in condensed media, in: Proc. IUTAM Symp. on Behavior of Dense Media under High Dynamic Pressures, Paris, 1967 (Gordon and Breach, New York, 1968) p. 404.
[13] W.G. Hoover, A.J. De Groot and C.G. Hoover, Comput. Phys. 6 (1992) 155 and cover.
[14] R. Preston, The mountains of Pi, The New Yorker, 2 March 1992, p. 36.
[15] D.J. Evans and G.P. Morriss, Nonequilibrium Liquids (Academic Press, New York, 1990).
[16] Proc. 1982 Boulder, Colorado Conf. on Nonlinear Fluid Behavior, Physica A 118 (1983).
[17] G. Ciccotti, D. Frenkel and I.R. McDonald, eds., Simulation of Liquids and Solids (North-Holland, Amsterdam, 1987).
[18] M. Mareschal, ed., Microscopic Simulations of Complex Flows (Plenum, New York, 1990).
[19] C. Grebogi, S.M. Hammel, J.A. Yorke and T. Sauer, Phys. Rev. Lett. 65 (1990) 1527; H. Yoshida, Phys. Lett. A 150 (1990) 262.
[20] Proc. 1985 Enrico Fermi Summer School at Varenna, Molecular Dynamics Simulation of Statistical Mechanical Systems, G. Ciccotti and W.G. Hoover, eds. (North-Holland, Amsterdam, 1986).
[21] W.G. Hoover and B. Moran, Viscous attractor for the Galton Board, Chaos, in press; W.G. Hoover, H.A. Posch, B.L. Holian, M.J. Gillan, M. Mareschal and C. Massobrio, Mol. Simul. 1 (1987) 79.
[22] W.G. Hoover, C.G. Hoover, W.J. Evans, B. Moran, J.A. Levatin and E.A. Craig, Irreversible processes from reversible mechanics, in: Microscopic Simulations of Complex Flows, M. Mareschal, ed. (Plenum, New York, 1990) p. 199.
[23] S. Sarman, D.J. Evans and G.P. Morriss, Phys. Rev. A 45 (1992) 2233.
[24] H.A. Posch and W.G. Hoover, Nonequilibrium molecular dynamics of classical fluids, in: Molecular Liquids: New Perspectives in Physics and Chemistry, J.J.C. Teixeira-Dias, ed. (Kluwer, Dordrecht, 1992) p. 527.
[25] S.Y. Liem, D. Brown and J.H.R. Clarke, Phys. Rev. A 45 (1992) 3706.
[26] W. Loose and S. Hess, Physica A 174 (1991) 47 and references therein; Shear-induced ordering revisited, in: Microscopic Simulations of Complex Flows, M. Mareschal, ed. (Plenum, New York, 1990) p. 267.
[27] B.L. Holian, W.G. Hoover, B. Moran and G.K. Straub, Phys. Rev. A 22 (1980) 2798.
[28] D.H. Robertson, D.W. Brenner and C.T. White, Phys. Rev. Lett. 67 (1991) 3132.
[29] E. Salomons and M. Mareschal, Phys. Rev. Lett. 69 (1992) 269.
[30] D.C. Rapaport, Phys. Rev. Lett. 60 (1988) 2480; M. Mareschal, ed., Microscopic simulations of instabilities, in: Microscopic Simulations of Complex Flows, M. Mareschal, ed. (Plenum, New York, 1990) p. 141.
[31] J.P. Gollub, The onset of turbulence: convection, surface waves, and oscillators, in: Systems Far From Equilibrium, Lecture Notes in Physics, vol. 132, L. Garrido, ed. (Springer, Berlin, 1980) p. 162.
[32] F.F. Abraham, Adv. Phys. 35 (1986) 1.
[33] J. Raloff, Science News 141 (1992) 260.
[34] D.K. Remler and P.A. Madden, Mol. Phys. 70 (1990) 921.
[35] H.E. Trease, M.J. Fritts and W.P. Crowley, eds. Advances in the Free-Lagrange Method, Lecture Notes in Physics, vol. 395 (Springer, Berlin, 1991).