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NONEQUILIBRIUM MOLECULAR DYNAMICS--PAST, PRESENT, & FUTURE

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THE PAST:

Until 1973 nonequilibrium statistical mechanics was based on Green-Kubo linear perturbation theory. Nonequilibrium Molecular Dynamics opened up an alternative approach, not only to fluid viscosity and heat conductivity but also to dynamic plasticity, shockwaves, and nonlinear transport. Nonequilibrium molecular dynamics was developed to simulate steady-state laboratory methods for determining transport coefficients. Irreversible heating was combatted by "velocity rescaling", enforcing fixed kinetic temperatures on "fluid-wall" boundary particles.

The resulting nonlinear viscous heat-conducting flows were stable, satisfied the Second Law of Thermodynamics, and produced transport coefficients close to experimental rare-gas values. Typical simulations, carried out at Argonne, Brookhaven, Livermore, Los Alamos, and Orsay, used tens of hours of computer time to follow hundreds of particles for tens of thousands of timesteps.

THE PRESENT:

Shuichi Nosé linked Molecular dynamics to Gibbs' ensemble theory in 1984; he extended Newtonian mechanics to generate Gibbs' NVT and NPT statistical-mechanical ensembles. The "Nosé-Hoover" form of Nosé's equations of motion generalizes the friction-coefficient formulation of velocity scaling which follows from Gauss' Principle of Least Constraint:

$$dp/dt = F - \zeta(t)p \; ; \; \zeta_{GAUSS} = \Sigma[F\cdot(p/m)]/\Sigma[(p^2/m)] \; .$$

Shuichi Nosé showed that a more-general integral-feedback relation:

$$d\zeta_{NH}/dt = \Delta K/(\langle K\rangle\tau^2) \; ; \; \Delta K = K - \langle K\rangle \; ; \; K = \Sigma[(p^2/2m)] \; ; \; \langle K\rangle = (3NkT/2) \; ,$$

with an adjustable thermostat response time τ, generates Gibbs' canonical distribution. This idea was a fundamental advance for which Nosé received an IBM-Japan Science Prize.

At equilibrium the friction coefficient ζ_{NH} has a root-mean-squared value of τ^{-1} and influences temperature fluctuations of order $N^{-1/2}$. Numerical trajectories can be obtained by generalizing[1] Stoermer's centered-difference algorithm:

$$(r_+ - 2r_o + r_-)/dt^2 = (F_o/m) - \zeta_o(r_+ - r_-)/(2dt) \; ; \; (\zeta_+ - \zeta_-)/(2dt) = (\Delta K_o)/(\langle K\rangle\tau^2) \; .$$

The subscripts (-,o,+) indicate times (t-dt,t,t+dt). This symmetric time-reversible structure is remarkably stable. Symmetric equations can have no long-term tendency for energy gain or loss, because the reversed solution would then show the opposite tendency. The same remarkable stability applies in nonequilibrium simulations.

Away from equilibrium the Gaussian and Nosé-Hoover equations of motion provide a mechanical basis for the Second Law of Thermodynamics. This connection between reversible microscopic mechanics and irreversible thermodynamics is fundamentally important. Consider the simplest two-dimensional example: a Newtonian system linking two reservoirs maintained HOT and COLD by two Nosé-Hoover friction coefficients. Simplify by assuming equal particle numbers and relaxation times in the two reservoirs:

$$d\zeta_{HOT}/dt = \Delta K_{HOT}/(NkT_{HOT}\tau^2) \; ; \; d\zeta_{COLD}/dt = \Delta K_{COLD}/(NkT_{COLD}\tau^2) \; .$$

In the reservoirs Nosé-Hoover equations of motion apply: $(dp/dt = F(r) - \zeta p)$. Two steps show that these solutions are consistent with the Second Law. First, consider the quantity:

$$C(q,p,\zeta) = \Phi(q) + K(p) + [NkT(\zeta\tau^2 + \int\zeta dt)]_{HOT} + [NkT(\zeta\tau^2 + \int\zeta dt)]_{COLD} \; .$$

Chain-rule differentiation shows that the time derivative $dC(q,p,\zeta)/dt$ vanishes. C is a constant of the motion! Thus, in a steady state the two time integrals must cancel:

$$NkT_{HOT}\int\zeta_{HOT}dt + NkT_{COLD}\int\zeta_{COLD}dt = 0 \; .$$

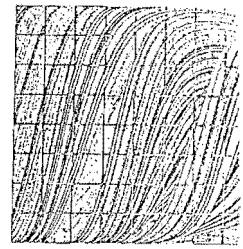
This result is an energy-balance requirement: in the absence of external work, heat taken in must balance heat lost. Thus the magnitude of ζ_{COLD} must exceed the magnitude of ζ_{HOT}. That is, $|\zeta_{COLD}| > |\zeta_{HOT}|$. Second, consider the geometric

requirement that the comoving phase-space density $f(q,p,\zeta,t)$ cannot decrease in nonequilibrium steady state: $df/dt > 0$. Liouville's Theorem connects the fricti coefficient integrals and the comoving phase-space probability density $f(q,p,\zeta,t$

$$\ln[f(q,p,\zeta,t)/f(q,p,\zeta,0)] = N\int\zeta_{HOT}dt + N\int\zeta_{COLD}dt > 0 \ .$$

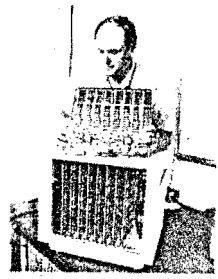
Together with our first result, $|\zeta_{COLD}| > |\zeta_{HOT}|$, this inequality shows that ζ_{COLD} i positive and ζ_{HOT} is negative. Thus the friction coefficients necessarily *inject* heat at T_{HOT} ($\zeta_{HOT} < 0$) and *extract* heat at T_{COLD} ($\zeta_{COLD} > 0$), giving a steady-sta flow from hot to cold consistent with the Second Law of Thermodynamics. It is remarkable that the *irreversible* Second Law of Thermodynamics can be derived fro *time-reversible* mechanics. Time-reversible heat reservoirs made this possible. link between mechanics and thermodynamics is more comprehensive than it was in Boltzmann's day. A topological consequence of the inequality $\langle df/dt \rangle > 0$ is that the steady-state probability density must diverge, collapsing onto a multifractal strange attractor with fractional dimensionality. One of the simplest such examples, a single ball wandering through a periodic Pachinko Palace, generates t Poincaré Section shown in the **Figure.**

Our capacity to simulate nonequilibrium processes is undergoing rapid technological change. Tony De Groot and his SPRINT[2] parallel-processor computer, built at the Livermore Laboratory as a University of California at Davis Ph. D. thesis project, are shown in the **Figure.** This machine duplicates CRAY performance at 1/1000 of the cost. The SPRINT uses a linked list to locate up to a million atoms in 64 processors, transferring atomic coordinates between processors at the end of each Stoermer time step. Atoms within each processor are further divided into cells, with each cell holding just a few atoms. The transfer operations take a negligible fraction of the clock time per time step, measured at 31 seconds for 1,000,000 particles with 64 processors.

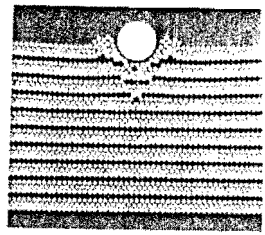


THE FUTURE:

Without further improvements in technology a CRAY-size investment in SPRINT technology would make possible dynamic simulations of *billion*-atom samples nearly a micron in size. Because continuum mechanics should be useful at the micron scale the future will see successful modelling blending atomistic and continuum calculations. We are preparing for this future by studying the dynamics of large nonequilibrium systems important in precision engineering Processing. The **Figure** shows a single videotape frame from a SPRINT indentor simulation with a small cold Lennard-Jones crystal.



Generating new ideas through new technology requires cooperation among many very talented individuals to coordinate the best in physics, programming, and computer graphics. Such a cooperative interactive approach is essential to applying the new ideas through new technology. This work is very much a joint effort, involving Tony De Groot, Bill Moran, Mike Allison, and Irv Stowers at Livermore, Brad Holian and Art Voter at Los Alamos, Harald Posch at Vienna, Sigeo Ihara at Hitachi-Kokubunji, and Toshio Kawai and my wife Carol at Keio. Work performed at the Lawrence Livermore National Laboratory was supported by the United States Department of Energy under University of California Contract W-7405-Eng-48. Work performed at Keio University was supported by the Japan Society for the Promotion of Science. I specially thank Taisuke Boku and Shuichi Nosé for their help with the computing facilities at Keio University.



1. B. L. Holian, A. J. De Groot, W. G. Hoover and C. G. Hoover, "Time-Reversible Equilibrium and Nonequilibrium Isothermal-Isobaric Simulations with Centered-Difference Stoermer Algorithms"(submitted to Physical Review A, January, 1990).
2. A. J. De Groot, S. R. Parker, and E. M. Johansson, in SVD and Signal Processing: Algorithms, Applications and Architectures, (North-Holland, Amsterdam, 1988)