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At equilibrium Nosé's 1984 revolutionary thermostat idea linked Newton's mechanics with Gibbs' statistical mechanics. His work expanded the scope of isothermal and isobaric simulations. Nosé–Hoover dynamics has subsequently facilitated the simulation and detailed understanding of *nonequilibrium* problems. The fractal phase-space distributions, and their close link to the Lyapunov spectrum, provide a novel explanation of irreversibility and a rich field for exploration.

1. Introduction to Nosé's mechanics

In the simple-fluid molecular dynamics of the 1960s and 1970s the *usual* Hamiltonian was the sum of the kinetic and pair-potential energies K and Φ:

$$\mathcal{H}_{\text{Usual}} = K + \Phi; \quad K = \sum \left[\frac{p^2}{2m} \right];$$

$$\Phi = \sum_{\text{pairs}} \phi(r) \rightarrow \{ m\ddot{r} = \dot{p} = F(r) = -\nabla\Phi \}.$$

By the early 1970s *non*equilibrium simulations were emerging, and temperature control (as measured by kinetic energy) of dynamical simulations was being implemented by *ad hoc* velocity scaling [1,2].

In the 1980s temperature control underwent a qualitative change. Shuichi Nosé was responsible for it [3,4]. He discovered a most *unusual*, even revolutionary, temperature-dependent Hamiltonian for thermostating # degrees of freedom:

$$\mathcal{H}_{\text{Nosé}} = \left[\frac{p_s^2}{2M} \right] + \sum \left[\frac{p^2}{2ms^2} \right] + \Phi(q) + \# kT \ln s.$$

His new Hamiltonian included the extra pair of conjugate control variables (s, p_s) as well as a thermostat mass M setting the control-variable timescale. Nosé preferred to interpret s as a "time-scaling" (as opposed to "mass-scaling") variable. The new variable controlled the kinetic energy through feedback. Nosé's augmented ("extended-system") Hamiltonian led directly to his new (in 1984) equations of motion:

$$\left\{ \dot{q} = \frac{p}{ms^2}; \dot{p} = F(q) \right\};$$

$$\dot{s} = \frac{p_s}{M}; \quad \dot{p}_s = \sum \left[\frac{p^2}{ms^3} - \frac{kT}{s} \right].$$

His related "time-scaled" equations of motion contain the extra factor s:

$$\{ \dot{q}, \dot{p}, \dot{s}, \dot{p}_s \} \rightarrow \{ s\dot{q}, s\dot{p}, s\dot{s}, s\dot{p}_s \}.$$

These new "time-scaled" equations are as follows:

$$\left\{ \dot{q} = \frac{p}{ms}; \dot{p} = sF(q) \right\};$$

$$\dot{s} = \frac{sp_s}{M}; \quad \dot{p}_s = \sum \left[\frac{p^2}{ms^2} - kT \right].$$

Nosé proved that *either* set of equations, original or time-scaled, generates the canonical distribution (assuming ergodicity) for the $(q, p') \equiv (q, p/s)$ variables provided that the time averages are properly weighted. See his two 1984 papers [3,4] and his 1991 review [5] for the details.

Nosé stated that his work was strongly influenced by Hans Andersen's 1980 work [6] in which the *pressure*

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fluctuations characterising an isobaric ensemble were implemented by a deterministic feedback force controlling volume. Andersen's idea of using an extended Hamiltonian to regulate the pressure had independently been applied to the simulation of nonequilibrium bulk and shear viscosities [7]. Nosé's breakthrough was the imposition of canonical *temperature* fluctuations implemented by an extended-system feedback force controlling kinetic energy.

2. Nosé and Nosé–Hoover mechanics

As Nosé pointed out in his 1984 papers, his scaled equations of motion can be usefully rewritten by replacing the scaled momentum with a new "real" momentum: $[(p/s) \rightarrow p]$. Here I indicate this new momentum by p in the rewritten equations:

$$\left\{ \dot{r} = \frac{p}{m}; \dot{p} = F(\{r\}) - \frac{p_s}{M} p \right\};$$
$$\dot{s} = \frac{sp_s}{M}; \quad \dot{p}_s = \sum \left[\frac{p^2}{m} - kT \right].$$

After meeting Nosé in Paris in 1984 I wrote a paper [8] emphasizing both the importance of the scaled equations of motion and the complete irrelevance of the scaling variable s. The scaling variable can be completely ignored by writing the remaining motion equations as follows:

$$\{ m\ddot{r} = \dot{p} = F(\{r\}) - \zeta m\dot{r} = F(r) - \zeta p \};$$

$$\dot{\zeta} = \frac{[(K/K_0) - 1]}{\tau^2}; \quad \zeta = \frac{p_s}{\#kT\tau^2} = \frac{p_s}{M},$$

where τ is a phenomenological relaxation time. The friction coefficient $\zeta \propto p_s$, which can be either positive or negative, obeys a feedback equation which controls the kinetic energy K to make its time average equal to K_0. Applications of the three simpler equations proliferated and, on the strength of my 1985 paper, these equations were called the "Nosé–Hoover" thermostat equations. The earlier *ad hoc* thermostating equations of Woodcock and Ashurst corresponded to the special "Gaussian Isokinetic" case of Nosé's equations:

$$(M \propto \tau^2 \rightarrow 0) \rightarrow \left(\zeta \rightarrow \zeta_{\text{Gauss}} = \frac{\sum \dot{r} \cdot F}{\sum (p^2/m)} \right).$$

3. Dettmann's Hamiltonian for Nosé–Hoover dynamics

About a dozen years after meeting Nosé–san in Paris, prior to a CECAM meeting, I met Carl Dettmann in Lyon, also at a CECAM gathering (July, 1996), another happy coincidence. Carl's background in transformations for astrophysical applications made it possible for him to answer my question: "Is there a Hamiltonian giving

Nosé's scaled equations without the need for time scaling?". Carl had the answer early the very next day [9,10]:

$$\mathcal{H}_{\text{Dettmann}} \equiv s\mathcal{H}_{\text{Nosé}}$$

$$= s \left[\frac{p_s^2}{2M} \right] + s \sum \left[\frac{p^2}{2ms^2} \right] + s\Phi + s \#kT \ln s$$

$$\equiv 0(!) \rightarrow \{ m\ddot{r} = F(\{r\}) - \zeta m\dot{r} \};$$

$$\dot{\zeta} = \frac{[(K/K_0) - 1]}{\tau^2}; \quad K_0 = \frac{\#}{2} kT; \quad \zeta = \frac{p_s}{\#kT\tau^2};$$

$$M = \#kT\tau^2.$$

In retrospect it seems surprising that it took so long (a dozen years) for the Hamiltonian generating the Nosé–Hoover equations to be discovered. Nosé had written the equivalent Lagrangian in his second 1984 paper [4] but not the Hamiltonian, with its essential value, *zero*.

Along with many others inspired by Nosé's work I had pursued this problem for years. Nosé's Hamiltonian, with the usual kinetic energy divided by s^2 and the logarithmic temperature-dependent potential for s, $\#kT \ln s$, certainly suggests whole families of modified Hamiltonians for investigation [11]. For instance, Winkler [12] studied the consequences of dividing the momenta by s^2 rather than s. Had he tried $\sqrt{s}$ instead, he would have discovered Dettmann's result. Kusnezov *et al.* [13] generalized the scaling approach by including arbitrary *functions* of $\{q, p\}$ rather than just powers of s. It is very interesting that the much simpler idea, dividing/multiplying the kinetic/potential energy by s, was undiscovered until July of 1996 [9]. Once known it was promptly rediscovered, about a year later, in connection with the development of symplectic "Nosé–Poincaré" integrators [14].

The most mysterious feature of Nosé's Hamiltonian (and Dettmann's) is the "time-scaling" (or mass-scaling) variable "s". The significance of s is not apparent. Evidently it is dimensionless, like an angle, and its conjugate (angular) momentum p_s is proportional to the friction coefficient ζ. The mystery of s' identity need not be solved, as "s" soon disappears. In the final "Nosé–Hoover" form of the motion equations, although they can be traced back to Dettmann's Hamiltonian, "s" does not appear at all.

A less mysterious direct route (suggested by Brad Holian) to the same destination, the Nosé–Hoover equations, begins with the somewhat *ad hoc* control equation—which can be related to Gauss' Principle of Least Constraint [15] and to Hamilton's Principle of Least Action [16]:

$$m\ddot{r} = F(\{r\}) - \zeta m\dot{r},$$

together with the question: "What must the control variable ζ be in order to produce Gibbs' canonical constant-temperature phase-space distribution?" The answer is the

Nosé–Hoover recipe for ζ:

$$\dot{\zeta} = \frac{[(K/K_0) - 1]}{\tau^2}.$$

Of course the *complete* canonical distribution cannot be obtained numerically. In fact, unless the dynamics is sufficiently "mixing" the phase-space distribution depends on the initial conditions as well as the thermostat timescale set by M or τ. Particularly poor timescale choices can lead to the Toda-potential oscillations described in detail in pages 27–35 of Ref. [17].

4. Dynamics away from equilibrium, Leete's Hamiltonian

Generating canonical distributions directly from dynamics was a boon to the simulation activities that followed Alder and Wainwright's, and Fermi's, and Vineyard's lead in the 1950s and 1960s. All that was required was to add the control force involving the friction coefficient ζ to the ordinary equations of motion derived from $\mathcal{H}_{\text{Usual}}$.

Away from equilibrium Nosé's Hamiltonian route to the control equations hit a roadblock. There is no consistent way (known to me) to introduce a second temperature into the Nosé (or the Dettman) Hamiltonian. Finding a solution to this problem remains a major challenge. By contrast, the Nosé–Hoover dynamic approach can deal with any number of temperatures. For *any* degree of freedom q_i, thermostated to its own individual temperature T_i, the equation of motion is as follows:

$$m_i \ddot{q}_i = F_i(\{q\}) - m_i \zeta_i \dot{q}_i; \quad \dot{\zeta}_i = \frac{\left[(m\dot{q}_i^2/kT_i) - 1\right]}{\tau_i^2},$$

where τ_i describes the rate at which q_i interacts with its thermostat at the temperature T_i.

Tom Leete and I used a Lagrange multiplier route to an equilibrium thermostat, in the early 1980's [18]:

$$\mathcal{H}_{\text{Leete}} = \sqrt{4KK_0} + \Phi; \quad K = \sum \frac{p^2}{2m};$$

$$K_0 = \sum \frac{m\dot{q}^2}{2}.$$

It is possible that this idea, which keeps the kinetic energy K_0 constant, while K varies, could somehow be modified so as to be made suitable for *nonequilibrium* simulations. Unlike Dettmann's Hamiltonian, Leete's requires no special initial value. Unfortunately the initial conditions can easily spoil the requirement that $K \simeq K_0$.

When Carol and I visited Japan in 1989–1990, we were quick to take advantage of Nosé's thermostat ideas. Working with Tony De Groot, back at Livermore, and with several other colleagues, some in Japan, we simulated the plastic indentation of silicon, pressing an indentor into a thermostated specimen, represented by more than a million Stillinger-Weber silicon atoms [19,20] (See figure 1).
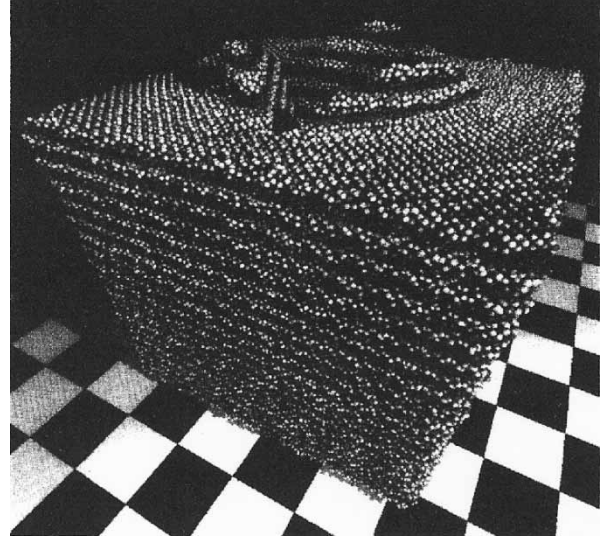

Figure 1. Indentation of a thermostated Stillinger-Weber silicon sample using a rigid indentor. See Refs [19,20] for details.

In order to clarify the new ideas associated with Nosé's thermostat, let us detail three further examples: (i) a particle in a constant external field, (ii) a harmonic oscillator, with and without temperature gradient, and (iii) a two-dimensional heat-conducting crystal. For simplicity in what follows I choose the various parameters (masses, field strength, force constants, ...) equal to unity, corresponding to expressing the problems in "reduced units".

5. Field-driven dissipative motion

Perhaps the simplest pedagogical example [21] of Nosé and Nosé–Hoover dynamics is the steady motion of a thermostated particle in a gravitational field, $\phi = -q$. In the absence of a thermostat the particle accelerates continuously:

$$\mathcal{H}_{\text{Usual}} = \frac{p^2}{2} - q \rightarrow \left\{\ddot{q} = 1 \rightarrow \dot{q} = t \rightarrow q = \frac{t^2}{2}\right\}.$$

By adding friction we would expect a stationary nonequilibrium state. Nosé's Hamiltonian for this problem adds the new variables $(s, p_s) = (s, \zeta)$. The resulting motion remains Hamiltonian, and the kinetic energy $p^2/2$ increases quadratically in time while $\dot{q}^2/2$ approaches zero:

$$\mathcal{H}_{\text{Nosé}} = \frac{p^2}{2s^2} - q + \ln s + \frac{\zeta^2}{2} \rightarrow \dot{q} = \frac{p}{s^2}; \quad \dot{p} = 1;$$

$$\dot{s} = \dot{\zeta}, \quad \dot{\zeta} = \frac{p^2}{s^3} - \frac{1}{s} \rightarrow (q, p, s, \zeta) = (\ln t, t, t, 1).$$

"Scaling the time", multiplies the four rate equations by s and results in a different solution, in which the kinetic energy $p^2/2$ diverges *exponentially* with time while $\dot{q}^2/2$

is constant:

$$\dot{q} = \frac{p}{s}; \quad \dot{p} = s; \quad \dot{s} = s\zeta;$$

$$\dot{\zeta} = \frac{p^2}{s^2} - 1 \rightarrow$$

$$(q, p, s, \zeta) = (t, e^t, e^t, 1).$$

These same equations of motion, with the same solution, follow from Dettmann's Hamiltonian (a *non*equilibrium Hamiltonian in this case):

$$\mathcal{H}_{\text{Dettmann}} = \frac{p^2}{2s} - qs + s\ln s + \frac{s\zeta^2}{2} = 0.$$

The equivalent "Nosé–Hoover" equations—just three first-order equations, rather than four, as s is finally absent—have a simpler finite and stationary solution, in accord with our physical expectations:

$$\ddot{q} = 1 - \zeta\dot{q}; \quad \dot{\zeta} = \dot{q}^2 - 1 \rightarrow (q, \dot{q}, \zeta) = (t, 1, 1),$$

The velocity reaches a stable stationary state, in which gravitational energy is steadily converted to heat by the Nosé–Hoover thermostat. We consider next a harmonic oscillator, which illustrates the complexity which can be associated with realistic nonequilibrium states.

6. Harmonic oscillator, at and away from equilibrium

After first meeting Shuichi in Paris in 1984, I learned more about his mechanics by studying the thermostated harmonic oscillator problem, first in Lausanne [8] and then in Vienna, with Harald Posch and Franz Vesely [22]. In terms of the oscillator mass m, force constant κ, thermal energy mkT, and thermostat relaxation time τ the problem is a set of three coupled ordinary differential equations:

$$\dot{q} = p/m; \quad \dot{p} = -\kappa q - \zeta p; \quad \dot{\zeta} = \frac{[(p^2/mkT) - 1]}{\tau^2},$$

When expressed in terms of dimensionless "reduced" variables, the equations depend upon a single dimensionless parameter, the ratio of the oscillator period to the relaxation time. In their simplest form, the reduced thermostated oscillator equations for q and p are

$$\dot{q} = p; \quad \dot{p} = -q - \zeta p;$$

where the reduced friction coefficient ζ is obtained from any of three equivalent choices for the third differential equation:

$$\dot{\zeta} = \frac{p^2}{T} - 1 \text{ or } \dot{\zeta} = [p^2 - 1]/\tau^2 \text{ or } \dot{\zeta} = p^2 - T.$$

These relatively simple equations for $(\dot{q}, \dot{p}, \dot{\zeta})$ surprised us with their relatively complicated solutions with many interesting special cases. Depending upon the initial conditions, the trajectories made up not only an infinite number of regular "tubes", each surrounding a quasiperiodic family of stable periodic orbits—but also an unstable

chaotic sea, surrounding all the tubes, and filling up the rest of the phase space. The union of all these complicated distributions can be expressed as a simple three-dimensional Gaussian distribution, the simple stationary solution of Liouville's probability density flow equation $\partial f/\partial t \equiv 0$ in the phase space:

$$\partial f/\partial t \equiv 0 \rightarrow f \propto \exp\left[\frac{-q^2 - p^2}{2kT}\right]\exp\left[\frac{-\zeta^2}{2}\right]$$

$$= e^{-\mathcal{H}_{\text{Usual}}/kT}e^{-\zeta^2/2}.$$

The probability density of the friction coefficient ζ here is Gaussian too, just as is the distribution of the coordinate q and the momentum p.

The thermostated harmonic oscillator problem offers striking evidence for the inefficiencies of time scaling. Consider, as a typical example, the simple periodic orbit detailed in Figure I.21 of Ref. [17] and figure 7 of Ref. [22]. Good energy conservation for this orbit with the fourth-order Runge–Kutta method requires $dt = 0.0000001$ for Nosé's original equations of motion and $dt = 0.01$ for the Nosé–Hoover equations. A detailed investigation shows that the time-scaling factor s is the culprit, leading to phase-space speeds,

$$v_{\text{Phase}} = \sqrt{(\dot{q})^2 + (\dot{p})^2 + (\dot{s})^2 + (\dot{p}_s)^2},$$

exceeding Nosé–Hoover and Dettmann speeds by more than four orders of magnitude! But even with the time-scaling difficulty removed, the Nosé–Hoover oscillator *still* lacks ergodicity.

By adding a *second* control variable ξ, controlling either the fourth moment [17,23] $\langle p^4 \rangle$ or ζ itself [24], the (q, p, ζ, ξ) phase-space distribution *can* be made ergodic for the oscillator, without the contained complexity of the infinite family of regular tube solutions. The "chain of thermostats" approach [24], controlling ζ with ξ,

$$\dot{q} = p; \quad \dot{p} = -q - \zeta p; \quad \dot{\zeta} = p^2 - T - \xi\zeta;$$

$$\dot{\xi} = \zeta^2 - T,$$

describes a *non*equilibrium problem if T is made to depend upon the coordinate q:

$$T_q = 1 + \epsilon\tanh/(q) \rightarrow [T_{-\infty} = 1 - \epsilon; T_{+\infty} = 1 + \epsilon].$$

Control of the fourth moment [17,23,25] provides an alternative set of equations:

$$\dot{q} = p; \quad \dot{p} = -q - \zeta p - \xi p^3; \quad \dot{\zeta} = p^2 - T_q;$$

$$\dot{\xi} = p^4 - 3p^2 T_q.$$

For small ϵ nothing out of the ordinary occurs with either approach. The phase-space distribution is close to Gaussian in each of the four variables. But larger ϵ values, corresponding to larger temperature gradients, $dT/dx \leq \epsilon$, provide interesting phase-space projections. Figure 2 shows five time exposures of an ergodic
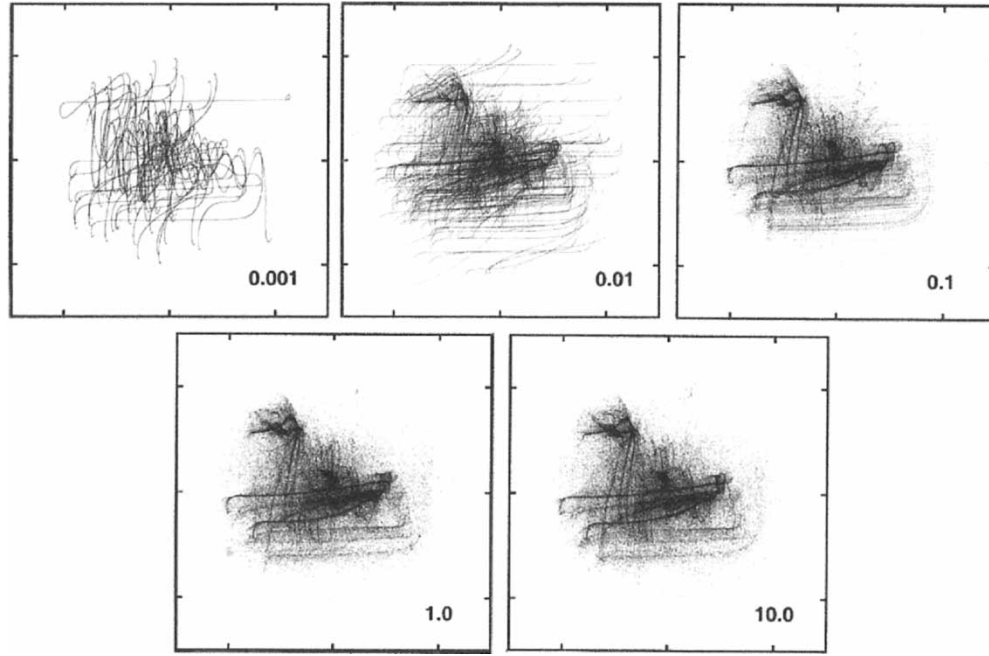
Figure 2. The Skiing Goose: development of a multifractal phase-space distribution from a one-dimensional trajectory. The intervals between the plotted trajectory points in this (ζ, ξ) projection are $\{dt, 10dt, 10^2 dt, 10^3 dt, 10^4 dt\}$, where dt is the fourth-order Runge–Kutta timestep, 0.001. See Ref. [25] for details.

four-dimensional trajectory [25] with $\epsilon = 1$, projected into the two-dimensional (ζ, ξ) plane. The transformation of a one-dimensional (q, p, ζ, ξ) trajectory into a 1.77 *fractional*-dimensional "fractal" projected (ζ, ξ) distribution [the "Skiing Goose" rather than a two-dimensional Gaussian] is clearly visible in figure 2. The underlying distribution in four dimensions is a 2.56-dimensional "strange attractor".

This type of transformation, to a *fractal* distribution, is in fact *typical* of nonequilibrium systems treated with Nosé–Hoover mechanics. Let us consider next a many-body example [26], before turning to the more general situation [27,28], together with the implications for nonequilibrium statistical mechanics.

7. Heat conducting crystal

"ϕ^4" crystals [29,30] are probably the simplest model systems with ordinary Fourier conductivity in one, two, or three dimensions. The ϕ^4 particles interact with nearest-neighbor Hooke's-law springs and are additionally tethered to their lattice sites with a quartic potential. Figure 3 shows individual particle trajectories [26] for a crystal with a single "hot" particle (upper right) and a single "cold" one (lower left). The phase space, with 32 coordinates, 32 momenta, and two friction coefficients $(\zeta_{HOT}, \zeta_{COLD})$ is 66-dimensional, impossible to visualize directly. But the distribution is nevertheless fractal. This can be shown by following the rate of expansion, in phase space, of a small element of volume, $\otimes = \Pi(dq dp) \times d\zeta_{HOT} d\zeta_{COLD}$:

$$d \ln \otimes / dt = -\zeta_{HOT} - \zeta_{COLD} = \sum_i \lambda_i(t).$$

The 66 instantaneous Lyapunov exponents $\{\lambda_1(t), \lambda_2(t), \ldots, \lambda_{66}(t)\}$ give the rates of expansion or contraction of particular infinitesimal 1-, 2-, ..., 66-dimensional volumes in the 66-dimensional phase space. The *largest* exponent (when time-averaged), $\lambda_1 \equiv \langle \lambda_1(t) \rangle$, gives the average rate at which two nearby trajectories separate. The sum of the largest two exponents, $\lambda_1 + \lambda_2$, corresponds to the rate at which an *area* defined by three nearby trajectories, increases. For this example the first 53 exponents, whose sum describes the growth rate of a
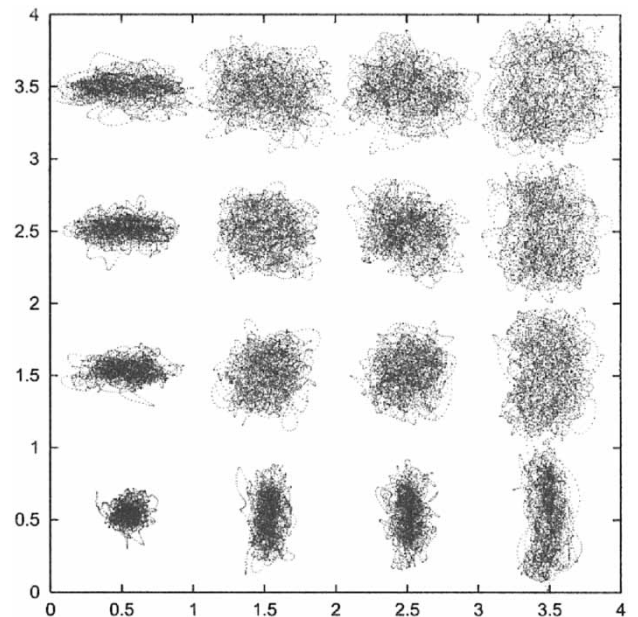

Figure 3. Trajectories in a 4×4-particle conducting solid described with Nosé–Hoover thermostated dynamics. The upper right and lower left particles are respectively "hot" and "cold". See Ref. [26] for details.
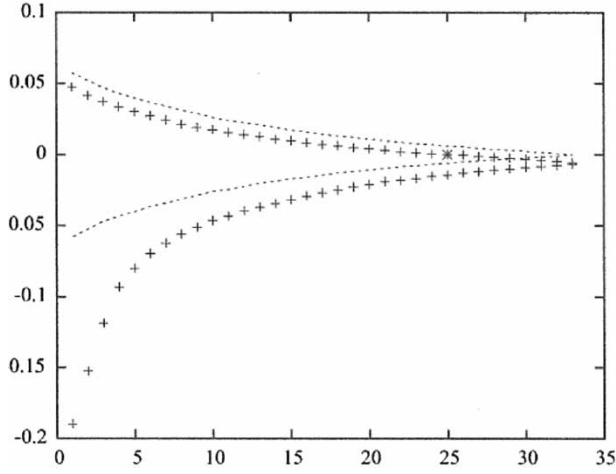
Figure 4. Equilibrium (dashes) and nonequilibrium (plus signs) Lyapunov spectra for the 16-particle solid of figure 3. The underlying information dimension of the multifractal nonequilibrium distribution function is 53.5. At equilibrium the dimensionality is 66. See Ref. [26] for details.

53-dimensional phase-space volume, have a positive sum, while adding on half the 54th exponent changes the sign from positive to negative. See figure 4 for the exponent values. In geometric terms this vanishing exponent sum means that the steady-state dimensionality of the phase-space distribution is between 53 and 54 (actually 53.5 according to Kaplan and Yorke's conjectured [25] *linear* interpolation between the last positive and first negative sums). The reduction in dimensionality of $\Delta D = 66 - 53.5 = 12.5$ describes the extreme rarity of nonequilibrium states relative to equilibrium ones for this system.

8. The general situation

Generally Nosé–Hoover mechanics makes it possible to connect the time-rates-of-change of phase volume $\otimes$, probability density f, and external entropy S to the friction coefficients $\{\zeta_i(T_i)\}$ and to the time-averaged Lyapunov spectrum $\{\lambda_i \equiv \langle \lambda_i(t) \rangle\}$, where the angular brackets indicate a *long*time average:

$$-\langle d \ln \otimes / dt \rangle \equiv +\langle d \ln f / dt \rangle \equiv \sum_i \langle \zeta_i \rangle \equiv \langle \dot{S}/k \rangle$$

$$\equiv -\sum_i \langle \lambda_i(t) \rangle = -\sum_i \lambda_i \geq 0.$$

The final inequality is the Second Law of Thermodynamics. The chain of inequalities relates the loss of microscopic phase-space dimensionality to the macroscopic rate of entropy production.

These connections between dynamics, thermodynamics, and chaos theory appear to be quite general, but are most easily established with Nosé–Hoover mechanics. In an important independent development Jarzynski [31] used the exact connection between phase volume and the Nosé–Hoover friction coefficient ζ to establish his free energy identity for nonequilibrium systems. This identity

relates the *nonequilibrium* finite-time work W (averaged over an initial canonical ensemble) to the equilibrium reversible-work Helmholtz free energy change:

$$\langle e^{W/kT} \rangle \equiv e^{-\Delta A/kT}.$$

Although the practical utility of the identity is limited [32], its pedagogical importance in linking equilibrium and nonequilibrium processes [33] is a profound and stimulating benefit of Nosé's work.

The fractal nature of the nonequilibrium distributions, together with the time reversibility of the motion equations, also provides a physical interpretation of irreversibility [34,35]. Motion in the forward direction is invariably less unstable than motion in the reverse direction;

$$\lambda_{\text{forward}} \equiv -\lambda_{\text{backward}} \rightarrow \left[\sum_{\text{forward}} \lambda_i \leq 0; \otimes \rightarrow 0 \right]$$

$$\leftrightarrow \left[\sum_{\text{backward}} \lambda_i \geq 0; \otimes \rightarrow \infty \right].$$

Thus *any* uncertainty or perturbation to a trajectory, no matter how small, will, when reversed, cause the trajectory to choose the direction of increasing entropy with overwhelming probability.

Nosé's work not only made it possible to simulate systems *at* equilibrium. It also contributed, in an unexpected way, to a detailed understanding of systems far from equilibrium. There remains much more to do. In particular, the *optimization* of thermostats and the *analyses* of reduced phase-space dimensionalities are fertile research fields for the future. There is also considerable activity in thermostated integration algorithms, both at, and away from, equilibrium [36–38]. The title and text of [37] show that in 2001 Nosé was still unaware of Dettmann's 1996 derivation [9] of the Nosé–Hoover thermostat *without* time scaling.

9. Historical remarks

Shuichi Nosé's thermostat ideas were so novel in 1984 that it took me months to understand them. We first met on a train platform at the Orly airport, in Paris. It was fortunate for me that his suitcase bore a large label: "NOSE". We talked on the train and arranged for a long technical conversation on a bench in front of Notre Dame. I had a list of 12 questions which had puzzled me about his ideas (mainly having to do with the significance of "*s*"), and we went through them thoroughly. That conversation changed the direction of my research career. I had been working on nonequilibrium simulations, but without the analytic tools provided by Nosé's fresh approach.

Nosé–san kindly invited me for a sabbatical year at Keio University 1989–1990. A fringe benefit of this invitation was my marriage to Carol, in preparation for living together in Japan. My son Nathan's family was already established in Tokyo, where my first grandson,

Beau Chiyofuji Hoover, was born during a February blizzard in 1992. Carol's sister Sandi, her mother Mabel, my daughter Frannie's family, and my own parents Edgar and Mary also visited Japan and got acquainted with Shuichi, his son Atsushi, and his wife Ibuki. We made many other friends in Japan and are forever grateful to Shuichi for his kindness and inspiration and to his family and colleagues for the memories which he has left with us.

Acknowledgements

References

[1] L. Woodcock. Isothermal molecular dynamics calculations for liquid salts. *Chem. Phys. Lett.*, **10**, 257 (1971).

[2] W.T. Ashurst, W.G. Hoover. Dense fluid shear viscosity *via* nonequilibrium molecular dynamics. *Phys. Rev. A*, **11**, 658 (1975).

[3] S. Nosé. A molecular dynamics method for simulations in the canonical ensemble. *Mol. Phys.*, **52**, 255 (1984).

[4] S. Nosé, A. Unified. Formulation of the constant temperature molecular dynamics methods. *J. Chem. Phys.*, **81**, 511 (1984) Section IIB.

[5] S. Nosé. Constant temperature molecular dynamics methods. Progress of Theoretical Physics Supplement In *Molecular Dynamics Simulations*, S. Nosé (Ed.), 103, pp. 1–46 (1991).

[6] H.C. Andersen. Molecular dynamics simulations at constant pressure and/or temperature. *J. Chem. Phys.*, **72**, 2384 (1980).

[7] W.G. Hoover. Adiabatic Hamiltonian deformation, linear response theory, and nonequilibrium molecular dynamics. In *Systems Far From Equilibrium*, Lecture Notes in Physics[Proceedings of the Sitges Conference on Statistical Mechanics, June 1980, Sitges, Spain.] H. Araki, J. Ehlers, K. Hepp, R. Rippenhahn, H.A. Weidenmüller, J. Zittartz (Eds.), 132, pp. 373–380, Springer-Verlag, New York (1980).

[8] W.G. Hoover. Canonical dynamics: equilibrium phase-space distributions. *Phys. Rev. A*, **31**, 1695 (1985).

[9] Wm. G. Hoover. Mécanique de Nonéquilibre à la Californienne. *Physica A*, **240**, 1 (1997).

[10] C.P. Dettmann, G.P. Morriss. Hamiltonian reformulation and pairing of Lyapunov Exponents for Nosé–Hoover dynamics. *Phys. Rev. E*, **55**, 3693 (1997).

[11] W.G. Hoover. Generalization of Nosé's isothermal molecular dynamics: NonHamiltonian dynamics for the canonical ensemble. *Phys. Rev. A*, **40**, 2814 (1989).

[12] R.G. Winkler. Extended-phase-space isothermal molecular dynamics: canonical harmonic oscillator. *Phys. Rev. A*, **45**, 2250 (1992).

[13] D. Kusnezov, A. Bulgac, W. Bauer. Canonical ensembles from chaos. *Ann. Phys. (New York)*, **204**, 155 (1990).

[14] S.D. Bond, B.J. Leimkuhler, B.B. Laird. The Nosé–Poincaré method for constant temperature molecular dynamics. *J. Comput. Phys.*, **151**, 114 (1999).

[15] D.J. Evans, W.G. Hoover, B.H. Failor, B. Moran, A.J.C. Ladd. Nonequilibrium molecular dynamics *via* Gauss' principle of least constraint. *Phys. Rev. A*, **28**, 1016 (1983).

[16] Wm. G. Hoover. Time reversibility in nonequilibrium thermomechanics. *Physica D*, **112**, 225 (1998).

[17] Wm.G. Hoover. *Molecular Dynamics*, H. Araki, J. Ehlers, K. Hepp, R. Rippenhahn, H.A. Weidenmüller, J. Zittartz (Eds.), 258, Springer-Verlag, New York (1986).

[18] T.M. Leete. The Hamiltonian dynamics of constrained Lagrangian systems. [Thesis, West Virginia University] (1979); W.G. Hoover, Atomistic nonequilibrium computer simulations. Physica A, **118**, 111 (1983).

[19] W.G. Hoover, A.J. De Groot, C.G. Hoover, I.F. Stowers, T. Kawai, B.L. Holian, T. Boku, S. Ihara, J. Belak. Large-scale elastic–plastic indentation simulations *via* nonequilibrium molecular dynamics. *Phys. Rev. A*, **42**, 5844 (1990).

[20] J.S. Kallman, W.G. Hoover, C.G. Hoover, A.J. De Groot, S.M. Lee, F. Wooten. Molecular dynamics of silicon indentation. *Phys. Rev. B*, **47**, 7705 (1993).

[21] W.G. Hoover. Reversible mechanics and time's arrow. *Phys. Rev. A*, **37**, 252 (1988).

[22] H.A. Posch, W.G. Hoover, F.J. Vesely. Canonical dynamics of the Nosé oscillator: stability, order, and chaos. *Phys. Rev. A*, **33**, 4253 (1986).

[23] Wm. G. Hoover, B.L. Holian. Kinetic moments method for the canonical ensemble distribution. *Phys. Lett. A*, **211**, 253 (1996).

[24] C.J. Martyna, M.L. Klein, M. Tuckerman. Nosé–Hoover chains— the canonical ensemble *via* continuous dynamics. *J. Chem. Phys.*, **97**, 2635 (1992).

[25] Wm.G. Hoover, C.G. Hoover, H.A. Posch, J.A. Codelli. The second law of thermodynamics and multifractal distribution functions: bin counting, pair correlations, and the [definite failure of the] Kaplan–Yorke conjecture. *Commun. Nonlinear Sci. Num. Simul.*, **12**, 214 (2007) (Available online 7 April 2005.).

[26] Wm. G. Hoover, H.A. Posch, K. Aoki, D. Kusnezov. Remarks on NonHamiltonian statistical mechanics: Lyapunov exponents and phase-space dimensionality loss. *Europhys. Lett.*, **60**, 337 (2002).

[27] Wm.G. Hoover. *Computational Statistical Mechanics*, Elsevier, New York (1991).

[28] Wm.G. Hoover. *Computer Simulation, Time Reversibility, and Chaos*, World Scientific Publishing, Singapore (1999, 2001).

[29] K. Aoki, D. Kusnezov. Bulk properties of anharmonic chains in strong thermal gradients: Nonequilibrium "ϕ^4" theory. *Phys. Lett. A*, **265**, 250 (2000).

[30] Wm. G. Hoover, K. Aoki, C.G. Hoover, S.V. De Groot. Time-reversible deterministic thermostats. *Physica D*, **187**, 253 (2004).

[31] C. Jarzynski. Nonequilibrium equality for free energy differences. *Phys. Rev. Lett.*, **78**, 2690 (1997).

[32] H. Oberhofer, C. Dellago, P.L. Geissler. Biased sampling of nonequilibrium trajectories: can fast switching simulations outperform conventional free energy calculation methods? *J. Phys. Chem. B*, **109**, 6902 (2005).

[33] R.C. Lua, A.Y. Grosberg. Practical applicability of the Jarzynski relation in statistical mechanics: a pedagogical example. *J. Phys. Chem. B*, **109**, 6805 (2005).

[34] B. Moran, W.G. Hoover, S. Bestiale. Diffusion in a periodic Lorentz gas. *J. Stat. Phys.*, **48**, 709 (1987).

[35] B.L. Holian, W.G. Hoover, H.A. Posch. Resolution of Loschmidt's paradox: the origin of irreversible behavior in reversible atomistic dynamics. *Phys. Rev. Lett.*, **59**, 10 (1987).

[36] B.L. Holian, A.J. De Groot, Wm.G. Hoover, C.G. Hoover. Time-reversible equilibrium and nonequilibrium isothermal–isobaric simulations with centered-difference Stoermer algorithms. *Phys. Rev. A*, **41**, 4552 (1990).

[37] S. Nosé. An improved symplectic integrator for Nosé–Poincaré thermostat. *J. Phys. Soc. Jpn.*, **70**, 75 (2001).

[38] A. Samoletov, M. Chaplain, C. Dettmann. The Smoluchowski thermostat. (2006), (2006 preprint, http://arxiv.org/abs/physics/0412163).