Canonical Temperature Control by Molecular Dynamics[1,2]

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Abstract

"Pedagogical derivations for Nosé's dynamics can be developed in two different ways, (i) by starting with a temperature-dependent Hamiltonian in which the variable s scales the time or the mass, or (ii) by requiring that the equations of motion generate the canonical distribution including a Gaussian distribution in the friction coefficient ζ. Nosé's papers follow the former approach. Because the latter approach is not only constructive and simple, but also can be generalized to other forms of the equations of motion, we illustrate it here. We begin by considering the probability density $f(q,p,\zeta)$ in an extended phase space which includes ζ as well as all pairs of phase variables q and p. This density $f(q,p,\zeta)$ satisfies the conservation of probability (Liouville's Continuity Equation)"

$$(\partial f/\partial t) + \sum(\partial(\dot{q}f)/\partial q) + \sum(\partial(\dot{p}f)/\partial p) + \sum(\partial(\dot{\zeta}f)/\partial\zeta) = 0 \ .$$

The multi-authored "review"[1] motivated our quoting the history of Nosé and Nosé-Hoover mechanics, aptly described on page 31 of Bill's 1986 *Molecular Dynamics* book, reproduced above[2].

Keywords: Cell Model, Nosé and Nosé-Hoover Mechanics, Continuity Equation

I. INTRODUCTION

In 1984 Shuichi Nosé discovered a canonical form of molecular dynamics[3,4] consistent with Gibbs' canonical ensemble probability density, $f \propto e^{-\mathcal{H}(q,p)/kT}$. Bill was struck by the revolutionary nature of Nosé's papers. As a result he arranged to attend a workshop meeting at Orsay, just outside Paris, where he and Nosé were scheduled to talk about molecular dynamics. A stroke of luck brought Bill and Shuichi together a few days earlier, purely by accident, at a Paris train station. Bill identified Shuichi by his large suitcase bearing the label "NOSE". The two arranged to meet for technical discussions on a bench in front of the Notre Dame Cathedral. Bill brought with him a list of about a dozen questions for Shuichi. Both came away with a better understanding of Nosé's discovery. Shuichi's two papers were difficult reading for Bill. They involved "scaling the time" so as to provide the Gaussian canonical distribution of velocities along with the Boltzmann-factor $\propto e^{-\Phi/kT}$ probability density for the coordinates and $e^{-K/kT}$ for the scaled momenta, $\{ \ (p/s) \ \}$. All this Nosé accomplished by introducing a time-scaling variable s along with its conjugate momentum p_s. Nosé's two papers, with about 20 pages of algebra, provided a novel and highly-productive connection of molecular dynamics to Gibbs' canonical statistical mechanics.

The concept of time-scaling, relating "real" time to "virtual" time, made reading Nosé's papers a heavy lift. To simplify this task Bill hit upon the idea of applying Nosé's ideas to a simple example problem, the one-dimensional harmonic oscillator. He began a manuscript[5] in Orsay and completed it in Lausanne after the Orsay workshop, thanks to a kind invitation from Philippe Choquard to visit his home and the Lausanne laboratory. Along with Harald Posch and Franz Vesely, Bill pursued the oscillator problem further in Vienna[6]. They found periodic, toroidal, and chaotic multifractal solutions of the oscillator equations. The simplest case considered is described by three ordinary differential equations (enough for chaos) giving the evolution of the coordinate q, momentum p, and friction coefficient ζ :

$$\{ \ \dot{q} = p \ ; \ \dot{p} = -q - \zeta p \ ; \ \dot{\zeta} = p^2 - 1 \ \} \ [\ \text{Nosé}' - \text{Hoover Oscillator} \ ] \ .$$

It is easy to use the continuity equation to confirm that the steady-state canonical distribution $f \propto e^{-(q^2+p^2+\zeta^2)/2}$ is consistent with these Nosé-Hoover motion equations.

In the years since 1984 the Nosé-Hoover motion equations have become the standard algorithmic technique for isothermal simulations. Tens of thousands of citations of Nosé and Hoover's papers testify to their value in stimulating additional thermostat research, both at and away from, equilibrium. There are occasional setbacks. See particularly the relatively recent Reference 1 responsible for the present work. Although described as a review that article entirely misstates the history of thermostatted mechanics and ignores the vast computational literature on applications to chaotic irreversible processes. In addition to our own work[7] see also the fundamental contributions of Dettmann, Evans, and Morriss[8–10]. Among many other developments Dettmann and Morriss discovered a Hamiltonian $\mathcal{H}_{\rm DM} = s\mathcal{H}_{\rm Nosé}$ which generates the Nosé-Hoover equations directly, without the need for a separate time-scaling step. Demonstrating this connection is an interesting exercise for the reader.

It is particularly noteworthy that nonequilibrium simulations are the primary beneficiary of all the work on deterministic thermostats. Isoenergetic, isokinetic, and isobaric thermostats all have provided new algorithms linking time-reversible equations of motion to irreversible simulations. The papers by Bauer, Bulgac, and Kusnezov provide a useful guide to the construction of new algorithms[11].

II. AN INTERESTING TOY PROBLEM EXAMPLE

Here we provide an interesting toy problem[7] suited to illustrating both approaches to canonical simulations, scaling the time, and introducing time-reversible friction. The two subsections following these different approachs can provide *identical* (x,y) trajectories, but with *different* (p_x,p_y) momenta. The system explored here is a one-body "wanderer" problem remeniscent of the Einstein cell model of solid state physics. The two-dimensional (x,y) motion takes place within a periodic square of sidelength 2, centered on the origin $(x,y) = (0,0)$. Four fixed scatterers, at the corners $(x,y) = (\pm 1, \pm 1)$, influence the motion of the wanderer particle. The potential furnished by the four scatterers has the very smooth form $\phi(r<1) = (1-r^2)^4$. The conventional Hamiltonian equations of motion are

$$\{\ \dot x = p_x \ ; \ \dot y = p_y \ ; \ \dot p_x = \sum 8dx(1-r^2)^3 \ ; \ \dot p_y = \sum 8dy(1-r^2)^3 \ \}.$$

The sums include only those scatterers, if any, with deviations $r = \sqrt{(dx^2+dy^2)}$ from the wanderer less than unity. For simplicity we take an initial condition with a (conserved)

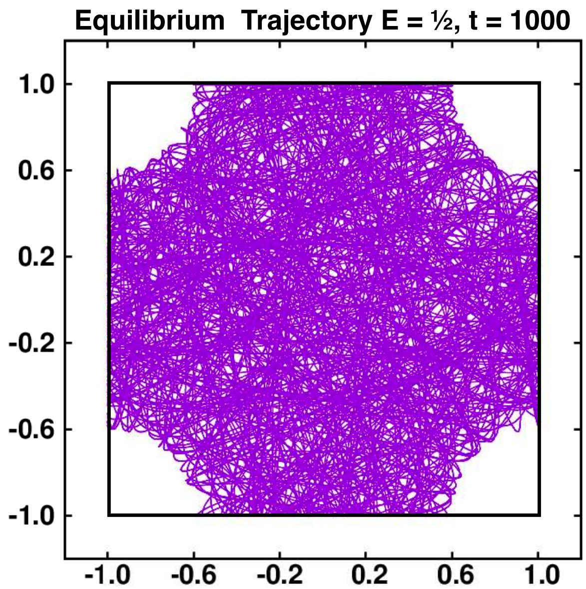

FIG. 1: A million-timestep trajectory with $dt = 0.001$ and periodic boundaries in the x and y directions. The initial condition is $p = (0.6, 0.8)$ with $(x, y) = (0, 0)$. The total energy agrees with the initial to eleven-figure accuracy at the conclusion of the run. The maximum potential energy of 1/2 occurs along four quarter-circles centered at $(\pm 1, \pm 1)$, with radii $0.398878 = \sqrt{1 - 2^{-1/4}}$.

energy of 0.5 : $(x, y, p_x, p_y) = (0, 0, 0.6, 0.8)$. Let us summarize the two approaches to the Nosé-Hoover equations, Nosé's, based on his 1984 papers[3,4], and Hoover's, based on his 1985 work[5].

A. Nosé's Approach: Scaling the Time

The first step in Nosé's derivation is to augment the conventional Hamiltonian $K + \Phi$, with (s, p_s), the time-scaling variable s and its conjugate momentum p_s:

$$\mathcal{H} = (K/s^2) + \Phi + (p_s^2/2) + \ln(s) \text{ [Nosé's Hamiltonian] } .$$

Next, the resulting equations of motion, $(\dot{x}, \dot{y}, \dot{s}, \dot{p}_x, \dot{p}_y, \dot{p}_s)$:

$$\{ \ \dot{x} = (p_x/s^2) \ ; \ \dot{y} = (p_y/s^2) \ ; \ \dot{s} = p_s \ \} \text{ Coordinates } ;$$

$$\{ \ \dot{p}_x = F_x \ ; \ \dot{p}_y = F_y \ ; \ \dot{p}_s = (p_x^2 + p_y^2)/s^3 - (1/s) \ \} \text{ Momenta } ,$$

are multiplied by s, "scaling the time". Third, and last, the "scaled momenta", (p_x/s) and

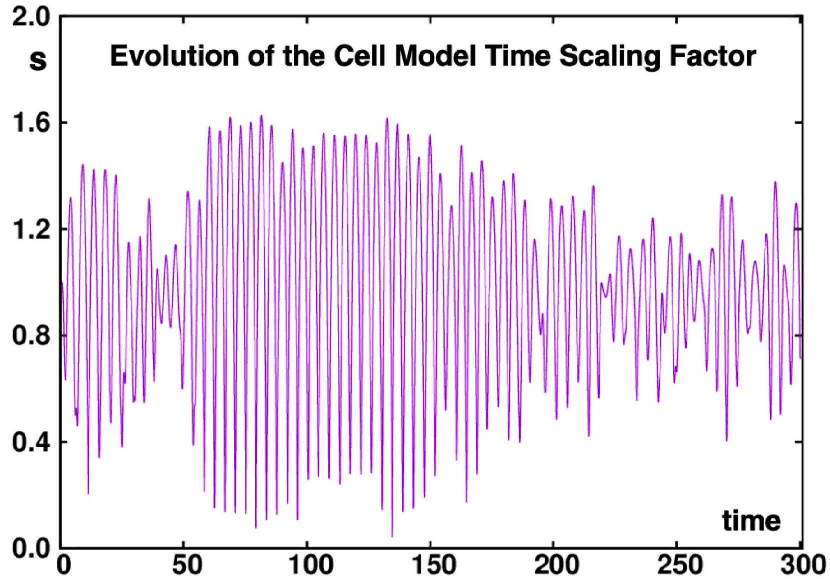

FIG. 2: Evolution of the time-scaling factor s for the Toy Model cell model for the initial 300 000 fourth-order Runge-Kutta timesteps of 0.001.

(p_y/s), are replaced by p_x and p_y. The resulting equations of motion are the Nosé-Hoover equations:

$$\{ \ \dot{x} = p_x \ ; \ \dot{y} = p_y \ ; \ \dot{p}_x = F_x - \zeta p_x \ ; \ \dot{p}_y = F_y - \zeta p_y \ ; \ \dot{\zeta} = K - 1/2 \ \} \ [\ \text{Nosé} - \text{Hoover} \ ]$$

Despite the smooth nature of the potential function, solutions of the Nosé equations are typically stiff. **Figure 2** illustrates the evolution of the time-scaling factor s for the cell-model problem of **Figure 1**.

Nosé's three-step "derivation" of the Nosé-Hoover equations looks like magic rather than straightforward mechanics. His highly original search for a time scale linking isoenergetic and isothermal motion equations used three unconventional steps in scaling the time. In their February 2006 Physics Today obituary of Shuichi, Yosuke Kataoka and Michael L. Klein recall that his two 1984 articles were "somewhat delayed by referees who had difficulty accepting the new and highly original formulation".

By contrast, Hoover's derivation of the Nosé-Hoover equations relies on the phase-space continuity equation, an analog of Liouville's Theorem, a standby of conventional statistical mechanics. We summarize that next.

B. Hoover's Approach: The Continuity Equation

After a couple of weeks of study, in France and Switzerland, Hoover found a straightforward path to both the isothermal and the isobaric Nosé-Hoover equations. The basis is the continuity equation for the conservation of probability in phase space, Liouville's Theorem. For simplicity we illustrate the isothermal steps for a single degree of freedom. We begin with the assumption that the motion equations, $\{ \dot{p} = F - \zeta p \}$, include a friction coefficient depending on the phase variables, $\zeta(q,p)$. We also assume that an exponential form, $e^{-\mathcal{F}(\zeta)}$, multiplies the conventional canonical Gibbs' distribution $f(q,p,t) \propto e^{-\mathcal{H}/kT}$. Suppose that the equations of motion need nothing more than a linear friction coefficient, $\dot{p} = F - \zeta p$, to acquire an extended canonical solution, $f \propto \exp[-\Phi/T - K/T - \mathcal{F}(\zeta)]$. For a steady-state Liouville's Theorem, the continuity equation in the extended (q,p,ζ) phase space, implies that $(\partial f/\partial t)$ vanishes:

$$(\partial(\dot{q}f)/\partial q) + (\partial(\dot{p}f)/\partial p) + (\partial(\dot{\zeta}f)/\partial\zeta) = -(\partial f/\partial t) \equiv 0 \ .$$

Two relations describing the flow in (q,p) space provide the Nosé-Hoover distribution function. For simplicity we write the relations for a single canonical pair and choose the temperature, Boltzmann's constant, mass, and the relaxation time of the frictional force, $-\zeta p$ all equal to unity:

$$(\partial(\dot{q}f)/\partial q) + (\partial(\dot{p}f)/\partial p) = -(\partial(\dot{\zeta}f)/\partial\zeta) = -\dot{\zeta}(\partial f/\partial\zeta) = -(d\mathcal{F}/d\zeta)\dot{\zeta}f \ ;$$

$$(\partial(\dot{q}f)/\partial q) + (\partial(\dot{p}f)/\partial p) = pFf + (F - \zeta p)(-pf) - \zeta f = \zeta(p^2 - 1)f \ .$$

The joint solution of these two flow relations, $\mathcal{F}(\zeta) = (\zeta^2/2)$ and $\dot{\zeta} = p^2 - 1$, gives Gibbs' canonical distribution, augmented by a Gaussian distribution of the friction coefficient :

$$f \propto \exp[-\mathcal{H} - (\zeta^2/2)\ ] \longrightarrow \dot{\zeta} = (p^2 - 1) \ ,$$

$$\dot{p} = F - \zeta p \ ; \ \dot{\zeta} \propto K - 1/2 \ \} \ [\ \text{Nosé} - \text{Hoover Equations}\ ] \ .$$

This is the simplest form of the Nosé-Hoover algorithm and its one-step derivation is arguably the simpler of the two routes to this time-reversible deterministic canonical dynamics.

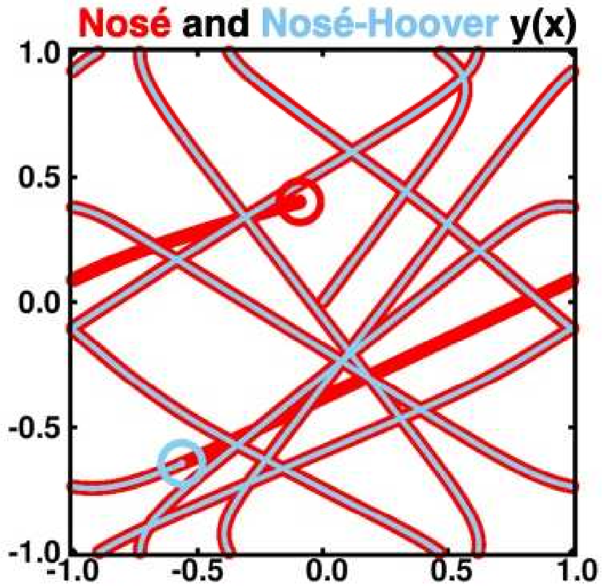

FIG. 3: Evolution of the cell model coordinates (x, y) from Nosé's Hamiltonian (red, and concluding at the open red circle just above the origin) are compared to those from the Nosé-Hoover motion eequations (blue, and ceasing at the blue open circle at lower left). The two approaches follow *identical trajectories*, but at *different rates*. Here the results of 20 0000 fourth-order Runge-Kutta timesteps are displayed for both sets of motion equations with initial conditions $(x, y, s, p_x, p_y, p_s = \zeta) = (0, 0, 1, 0.6, 0.8, 0)$.

From the standpoint of simplicity Hoover's assumption of a friction coefficient (which turns out to be the momentum p_s conjugate to Nosé's s) is preferable to the time-scaling Hamiltonian and the redefinition of momentum in Nosé's work. It is noteworthy too, that a dozen years later, Dettmann and Morriss found a Hamiltonian which automatically accomplishes Nosé's program[8,9].

III. SUMMARY

We have outlined two approaches to the Nosé-Hoover motion equations. Both were well established in 1984. Both have stimulated the development of deterministic thermostats, with nonequilibrium steady-state simulations generating fractal phase-space distributions. The 1984 and 1986 Paris workshops stimulated a simple example problem[12]. By 1987 deterministic time-reversible thermostatting was used to resolve Loschmidt's paradox for thermostatted steady states[13]. **Figure 3** shows two solutions of the motion equations with initial conditions $(x, y, s, p_x, p_y, p_s) = (0, 0, 1, 0.6, 0.8, 0)$. Comparing the two shows that the Nosé version is "stiffer" than the Nosé-Hoover. The culprit is the small denominator in the differential equation for $p_s : \dot{p}_s = (p^2/s^3) - (1/s)$. See the discussion in pages 123-126 of our book of Kharagpur lectures[7].

This toy model problem presents the opportunity for future work studying heat transfer between the horizontal and vertical degrees of freedom and the challenge of displaying graphic evidence for strange attractors in a six-dimensional phase space.

IV. ACKNOWLEDGMENT

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V. APPENDIX

Two aspects of programming thermostatted mechanics for the cell model are worth describing here. Looping over the four fixed scatterers in computing the forces or the energy is simplest with stored arrays of the scatterers' x and y coordinates;

```
dimension xj(4),yj(4)
xj(1) = +1 ; yj(1) = +1 ; xj(2) = -1 ; yj(2) = +1
xj(3) = -1 ; yj(3) = -1 ; xj(4) = +1 ; yj(4) = -1
```

To illustrate the use of these arrays consider the computation of the energy:

```
phi = 0 ; do j = 1,4
dx = x - xj(j) ; dy = y - yj(j) ; rr = dx*dx + dy*dy
if(rr.lt.1) phi = phi + (1 - rr)**4 ; end do
```

After each Runge-Kutta integration step the four checks of the periodic boundaries need to be implemented:

```
if(x.gt.+1) x = x - 2
if(x.lt.-1) x = x + 2
if(y.gt.+1) y = y - 2
if(y.lt.-1) y = y + 2
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