Kharagpur Lectures

Simple Systems with Thermal Constraints

1. The Lucy Fluid, a Prototypical Simple System
2. Simulation with Newtonian mechanics
3. Simulation with Gauss' mechanics
4. Simulation with Hoover-Leete mechanics
5. Simulation with Nosé-Hoover mechanics
6. Multi-moment Thermostated Oscillators
7. The ϕ^4 Model for Heat Conduction
8. Harmonic Chain Dynamics
9. Bit-Reversible Levesque-Verlet Dynamics

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Simple Systems Under Thermal Constraints
Summary Conclusions

The Lucy fluid in two dimensions is a simple model system .

Newton, Gauss, Hoover-Leete, and Nosé-Hoover mechanics are about equally costly .

For small systems ergodicity can be promoted through velocity moments .

Shockwave studies show that temperature can (briefly) be a tensor .

The scale of shockwave structure is the mean free path .

Smooth-particle weighting functions provide continuous field variables .

The ϕ^4 model provides Fourier's law and chaos , even in one dimension .

1. Lucy Fluid, a Prototypical Simple System

Simple Systems Under Thermal Constraints

The Lucy Fluid is a Prototypical Simple System

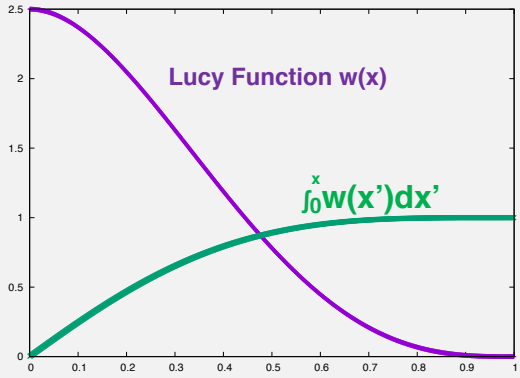
$\Phi = \Sigma\phi$ **with** $\phi(r< h) \alpha\ 1 - 6(r/h)^2 + 8(r/h)^3 - 3(r/h)^4$

Simplicity aids analysis .
Simulations take minutes .
Code development takes a few hours .
Two-Dimensional, in order to simplify graphics .
Equilibrium equation of state is easily characterized .
Atomistic Equations of Motion same in 2D and 3D .
Boundary Conditions and Constraints likewise .

Lucy weight function in one dimension

Normalization such that $\int_0^1 w(x)dx = 1$

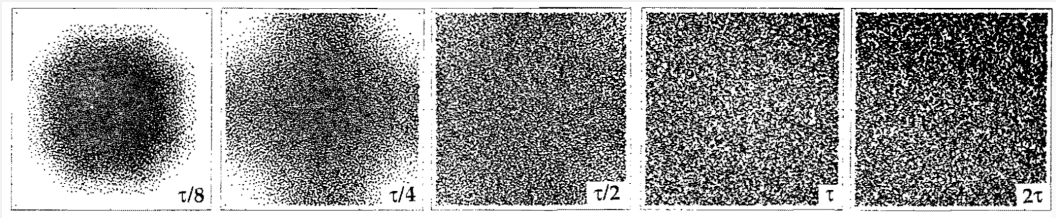
w(r) can also serve as a weak repulsive potential



0 < separation = x < 1

Simple Systems Based on the Lucy Fluid

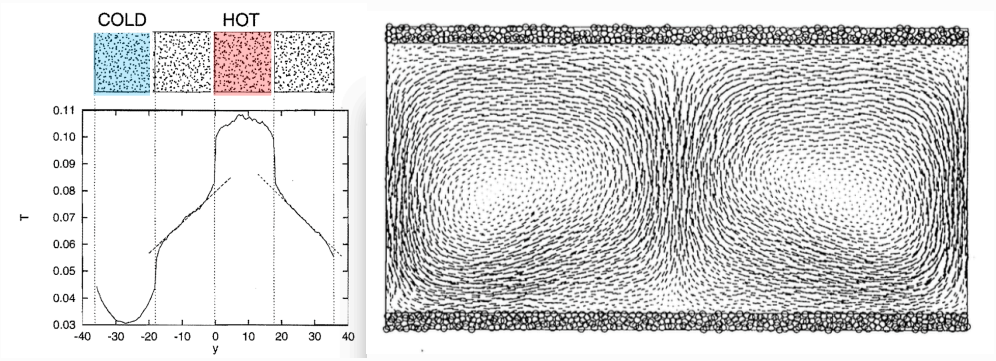
The system is typically , though not necessarily , two-dimensional with a relatively weak repulsive potential . From the numerical standpoint it is optimum due to the very smooth nature of the equations of motion . One of the problems that we looked into is the confined expansion of a hot fluid into a container four times the original area *. Snapshots of the motion include those shown here , where τ is the sound-traversal time .



* **Wm. G. Hoover and H.A. Posch, Physical Review E 59,** 1770-1776 **(1999) .**

Simple Systems Based on the Lucy Fluid

By using two thermostated regions it is possible to measure the heat conductivity [#] . If a gravitational field is added Rayleigh-Bénard instability can result [*] . Lucy's potential has been investigated for many problems .

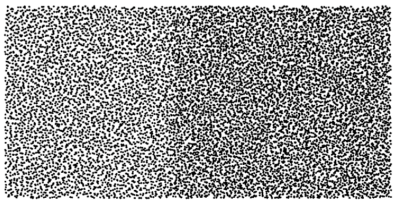


[#] **Physical Review E 54,** 5142-5145 **(1996) ;** [*] **Physical Review E 52 ,** 1711-1720 **(1995) .**

Simple Systems Based on the Lucy Fluid

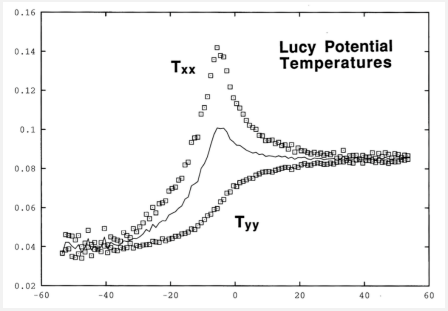
By using two moving regions , the entrance cool and the exit hot , we can maintain a stationary shockwave with Lucy-fluid forces[*] .

1.35→



0.90→

FIG. 1. Snapshot of the 12 960-particle shock wave simulation described in the text. Particles enter at the left and leave at the right. Fourth-order Runge-Kutta integration of the motion equations with a timestep of 0.025 is used.

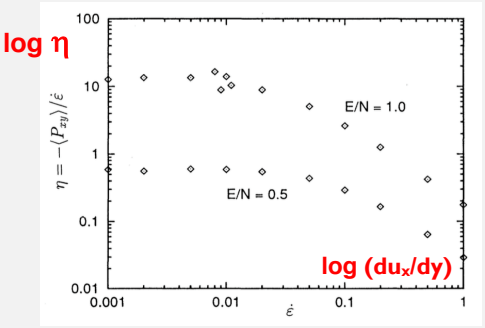


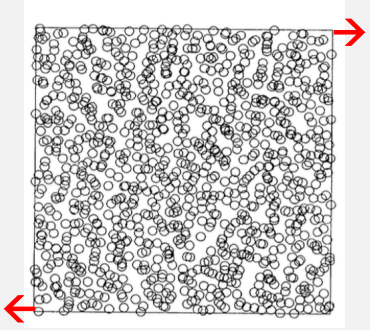
The range of the forces is 3 with entrance and exit speeds 1.35 and 0.90 → compression of 3/2 .
The maximum for the Lucy potential $\phi(0) = 0.17684$ is of the order of the temperature maximum .
The number of particles in the simulation cycles between 144 x 72 and 143 x 72 .

[#] **Oyeon Kum and the Hoovers , Physical Review E 56,** 462-465 **(1997) .**

Simple Systems Based on the Lucy Fluid

Steady Isothermal Shear simulations make it possible to measure the shear viscosity as a function of the thermodynamic state *. The left plot illustrates the energy dependence of η as a function of strain rate . The right plot illustrates the structure induced by simple shear on the fluid .





* H.A. Posch, W. G. Hoover, and O. Kum, Physical Review E 52, 1711-1720 (1995) .

The Lucy Fluid, a Prototypical Simple System + Constraints

Lenin's Question : What to do ?

Our Answer : Look into *thermal* constraints with a 10 x 10 periodic fluid using Lucy's Potential with a maximum range h = 3 :

$$\phi\,(r< h) \propto 1 - 6(r/h)^2 + 8(r/h)^3 - 3(r/h)^4$$

[Two continuous derivatives *everywhere*]

Boundary Conditions :

```
if(x.gt.+5) x = x – 10
if(x.lt.+5) x = x + 10
if(y.gt.+5) y = y – 10
if(y.lt.–5) y = y + 10
```

Initial Conditions :

```
index = 0
do i = 1,10
do j = 1,10
index = index + 1
x(index) = i – 5.5d00
y(index) = j = 5.5d00
enddo
enddo

px = rund(intx,inty) – 0.5d00
py = rund(intx,inty) - 0.5d00
```

The routine `rund(intx,inty)` generates 2^{22} pseudorandom numbers in the range from 0 to 1 .

The Lucy Fluid, a Prototypical Simple System

The velocities will take on a Maxwell-Boltzmann distribution by themselves .
The only help that they need is first to have their average value removed :

```
px(i) = px(i) – (sumpx/100)
```

and

```
py(i) = py(i) – (sumpy/100)
```

Next, their mean-squared value needs to be imposed :

```
px(i) = px(i)*dsqrt(100*T/sumpxpx)
```

$\phi\ (r< h) \alpha\ 1 - 6(r/h)^2 + 8(r/h)^3 - 3(r/h)^4$

[Two continuous derivatives *everywhere*]

Next comes RK4 Newtonian Motion !

Initial Conditions :

```
index = 0
do i = 1,10
do j = 1,10
index = index + 1
x(index) = I – 5.5d00
y(index) = j = 5.5d00
enddo
enddo

px = rund(intx,inty) – 0.5d00
py = rund(intx,inty) - 0.5d00
```

Boundary Conditions :

```
if(x.gt.+5) x = x – 10
if(x.lt.+5) x = x + 10
if(y.gt.+5) y = y – 10
if(y.lt.-5) y = y + 10
```

2. Newtonian Motion with the Lucy Fluid

The Lucy Fluid, a Prototypical Simple System

Next comes RK4 Newtonian Motion !

ϕ (r< h) α 1 – 6(r/h)^2 + 8(r/h)^3 – 3(r/h)^4

[Two continuous derivatives *everywhere*]
The derivative is computed as wp(r) .

There are 400 differential equations to solve :

```
xdot(i) = px(i)
ydot(i) = py(i)
pxdot(i) = fx(i)
pydot(i) = fy(i)
```

A very conservative value dt = 0.01d00 replaced by two steps at dt = 0.005d00 can reveal errors in the differential equations [if the two agree but do not conserve energy then the differential equations are to blame] .

```
do i = 1,99
do j = i+1,100
if(xij.lt.-5) xij = xij + 10 *
if(xij.gt.+5) xij = xij - 10
rij = dsqrt(xij*xij + yij*yij)
if(rij.lt.3) then
fx(i) = fx(i) - (xij/rij)*wp(rij)
fx(j) = fx(j) + (xij/rij)*wp(rij)
fy(i) = fy(i) - (yij/rij)*wp(rij)
fy(i) = fy(j) + (yij/rij)*wp(rij)
endif
enddo
enddo
```

Remember that `xij = x(i) – x(j)`
and likewise `yij = y(i) – y(j)`

The Lucy Fluid, a Prototypical Simple System

2 . RK4 Newtonian Motion

A Few Minutes on the laptop provide a solution to a time of 1000 .

The density is calculated at each particle, by summing up the weight function w_{Lucy} :

```
Do I = 1,100
rho(i) = w(0.0d00)
enddo
do i = 1,99
do j = i+1,100
rho(i) = rho(i) + w(dsqrt(xij*xij + yij*yij))
rho(j) – rho(j) + w(dsqrt(xij*xij + yij*yij))
enddo
enddo
```

Apply periodic boundaries in computing `xij` **and** `yij`

The total energy E = 100 is conserved to 9-figure accuracy at a time of 1000. The kinetic energy, averaged from time = 500 to 1000 is 45.58 and the potential is 54.42 where the potential energy is the sum of `rho(i)/2` **for all 100 particles . Whether or not to include w(0) in the potential energy is an arbitrary choice .**

3 . RK4 Thermostated Motions
Gauss Dynamics for the Lucy Fluid

The Lucy Fluid, a Prototypical Simple System

3 . RK4 Thermostated Motions

A Few Minutes on the laptop provide a solution to a time of 1000 .

We have seen that the Gauss, Hoover-Leete, and Nosé-Hoover thermostats can be used to keep the kinetic energy constant [Gauss or Hoover-Leete] or to constrain its time-averaged value [Nosé-Hoover] . In the Gauss case it is only necessary to start out with an initial kinetic energy of 45.58 which can be preserved by computing the isokinetic friction coefficient and applying it at each timestep :

```
fz = 0.0d00
twoK = 0.0d00
do i = 1,100
fz = fz + px(i)*fx(i) + py(i)*fy(i)
twoK = twoK + px(i)*px(i) + py(i)*py(i)
enddo

do i = 1,100
fx(i) = fx(i) – (fz/twoK)*px(i)
fy(i) = fy(i) – (fz/twoK)*py(i)
enddo
```

[Remember $\zeta_{Gauss} = \Sigma$ F•p / Σ p•p

Gauss Dynamics

The kinetic energy remains constant to ten figures and the mean total energy , averaged from time 500 to time 1000 is 100.07 , close to the Newtonian value .

4. RK4 Thermostated Motions
Hoover-Leete Dynamics for the Lucy Fluid

The Lucy Fluid, a Prototypical Simple System

4 . RK4 Thermostated Motions

A Few Minutes on the laptop provide a solution to a time of 1000 .

We have seen that the Gauss, Hoover-Leete, and Nosé-Hoover thermostats can be used to keep the kinetic energy constant [Gauss or Hoover-Leete] or to constrain its time-averaged value [Nosé-Hoover] . In the Hoover-Leete case it is only necessary to start out with an initial kinetic energy of 45.58 which is preserved by computing scaled velocities at each timestep :

```
do i = 1,100
xdot(i) = px(i)*dsqrt(ekq/ekp)
ydot(i) = py(i)*dsqrt(ekq/ekp)
pxdot(i) = fx(i)
pydot(i) = fy(i)
enddo
```

$\mathcal{H} = 2(K_p K_q)^{1/2} - K_q + \Phi$

[Remember `(dq/dt) = p*dsqrt(ekq/ekp)`]

Hoover-Leete Dynamics

The kinetic energy remains constant to ten figures and the mean total energy , averaged from time 500 to time 1000 is 99.93 , close to the Newtonian value .

5 . RK4 Thermostated Motions
Nosé-Hoover Dynamics for the Lucy Fluid

The Lucy Fluid, a Prototypical Simple System

5 . RK4 Thermostated Motions

A Few Minutes on the laptop provide a solution to a time of 1000 .

We have seen that the Gauss, Hoover-Leete, and Nosé-Hoover thermostats can be used to keep the kinetic energy constant [Gauss or Hoover-Leete] or to constrain its time-averaged value [Nosé-Hoover] . In the Nosé-Hoover case the initial kinetic energy is unimportant as feedback will drive it to a mean value of 45.58. Rather than solving just the 400 { x,y,px,py } equations it is necessary to solve 401, with the last one giving the Nosé-Hoover friction coefficient ζ :

```
sumpp = 0
do i = 1,100
sumpp = sumpp + px(i)**2 + py(i)**2
enddo

zdot = sumpp – 2*45.58d00
```

One can just as well use

```
zdot = ( sumpp/(2*45.58d00) ) - 1
```

Remember :

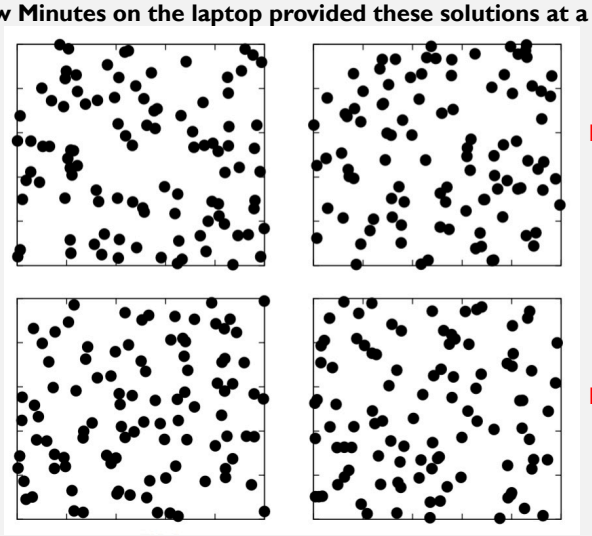
```
fx(i) = fx(i) – z*px(i)
fy(i) = fy(i) – z*py(i)
```

Nosé-Hoover Dynamics

The total mean total energy , averaged from time 500 to time 1000 is 100.02 , close to the Newtonian value .

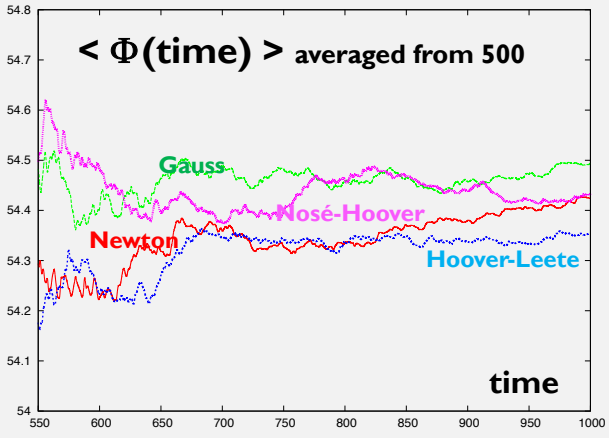
2-5. RK4 Thermostated Motions with dt = 0.01

A Few Minutes on the laptop provided these solutions at a time of 1000 .



2-5. RK4 Thermostated Motions with dt = 0.01

A Few Minutes on the laptop provided these solutions at a time of 1000 .



2-5 . RK4 Thermostated Motions

All four dynamics agree as to equation of state within a part per thousand .
None of these approaches presents any numerical difficulties .
The additional programming is no more than ten lines .
The Nosé-Hoover equations present no difficulty in choosing a relaxation time .
The Lucy Function provides a handy method for defining an interpolating field .
We can explore the usefulness of defining temperature as a fluctuation .

$kT_{xx} = < v_x v_x > - < v_x >^2$ and $kT_{yy} = < v_y v_y > - < v_y >^2$

1 . Begin by defining a regular xy grid (we will use a million points)
2 . At each grid point compute the velocity and its square as ratios :

$$< v > = \Sigma\, v_j\, w(r_G - r_j) / \Sigma\, w(r_G - r_j)$$
$$< v^2 > = \Sigma\, v_j\, v_j\, w(r_G - r_j) / \Sigma\, w(r_G - r_j)$$

3 . Compare averages computed with Lucy's function (maximum at r = 0)
to averages computed with a symmetric quartic with maximum at r = (3/2)
4 . We anticipated that the differences will be significant with a winner and loser .

Simple Systems with Thermal Constraints

Simulation with Newtonian mechanics considering defining local temperature

$$< v > = \Sigma\, v_j\, w(r_G - r_j) / \Sigma\, w(r_G - r_j)$$
$$< v^2 > = \Sigma\, v_j\, v_j\, w(r_G - r_j) / \Sigma\, w(r_G - r_j)$$

These averages require summing over particles and the grid .
Neither Lucy's weight function nor one which is zero at the origin give good values of the kinetic temperature. They are about 10% lower than expected . What about the configurational temperature ?

Landau and Lifshitz → $kT_c = < \nabla \mathcal{H} >^2 / < \nabla^2 \mathcal{H} >$

Unfortunately the curvature of $\mathcal{H}$ can have either sign.
Evidently this is an excellent area for new research !

6. Multi-Moment Thermostated Oscillators

Simple Systems with Thermal Constraints

6. Multi-Moment Thermostated Oscillators

The harmonic oscillator, with $\mathcal{H} = K + \Phi = (1/2)(q^2 + p^2)$, can be "thermostated" through any of its even moments : $< q^2 , q^4 , q^2p^2 , p^2 , p^4 \ldots >$. Evidently the moments cannot be constants of the motion so that some form of integral control, based on feedback , needs to be used. Nosé-Hoover "integral control" of the kinetic energy is the simplest illustration of this idea :

$$(dq/dt) = p \; ; \; (dp/dt) = -q - \zeta p \; ; \; (d\zeta/dt) = [p^2 - 1]/\tau^2 \; .$$

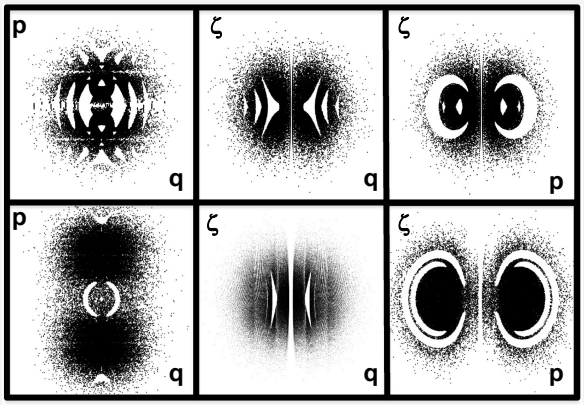
A flurry of interest in the configurational temperature led to investigations of "coordinate", or better yet "force" moments . Braga and Travis pointed out that the configurational analog of the Nosé-Hoover oscillator problem is simply a relabeling of the variables :

$$(dq/dt) = p - \xi q \; ; \; (dp/dt) = -q \; ; \; (d\xi/dt) = [q^2 - 1]/\tau^2 \; .$$

The same symmetry could be applied to thermostating $< q^4 >$ or $< q^6 >$.

Simple Systems with Thermal Constraints

6. Multi-Moment Thermostated Oscillators



To make a ζ section simply plot p(q) if the product $\zeta_{old}\,\zeta_{new}$ is negative .

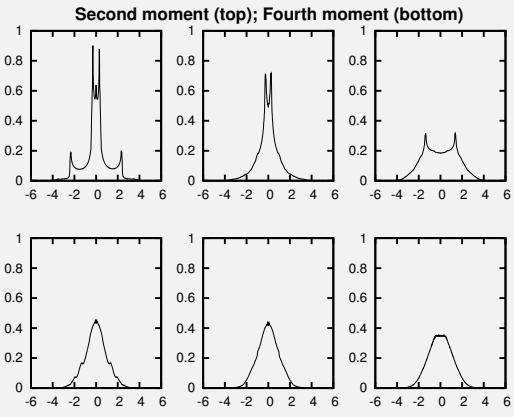
In the top row $< p^4 >$ is controlled with the feedback equation $(d\zeta/dt) = p^4 - 3p^2$.

In the bottom row $< p^6 >$ is controlled with the feedback equation $(d\zeta/dt) = p^6 - 5p^4$.

All six sections are chaotic but not ergodic . We know of no foolproof path to ergodicity . Holes in cross-sections for 3-dimensional problems clearly show a lack of ergodicity .

Simple Systems with Thermal Constraints

6. Multi-Moment Thermostated Oscillators



Probability density for { q, p, ζ } from left to right

Gibbs' canonical ensemble gives a Gaussian distribution for { q,p } and the Nosé-Hoover equations are consistent with a Gaussian distribution for the friction coefficient ζ .

Here we show the probability densities for all three variables { q,p, ζ } from simulations that control the second moment (Nosé-Hoover) as well as those that control the fourth moment by solving the integral-feedback equations :

$(dq/dt) = p$; $(dp/dt) = -q - \zeta p^3$; $(d\zeta/dt) = p^4 - 3p^2$.

None of the distributions is close to Gaussian .

Simple Systems with Thermal Constraints

6. Multi-Moment Thermostated Oscillators

In Physics Letters A 211, 253-257 (1996) Bill and Brad Holian showed that *simultaneous thermostating* of the second and fourth moments, $< p^2 >$ and $< p^4 >$ very likely gives an ergodic distribution extending Gibbs' two-dimensional Gaussian to a four-dimensional distribution Gaussian in all four variables { q,p,ζ,ξ } .

The equations of motion are :

$$\{ (dq/dt) = p \; ; (dp/dt) = -q - \zeta p - \xi p^3 \; ; (d\zeta/dt) = p^2 - 1 \; ; (d\xi/dt) = p^4 - 3p^2 \}$$

In The Journal of Chemical Physics 97, 2635-2643 (1992) Martyna, Klein, and Tuckerman suggested thermostating the thermostat variable(s) :

$$\{ (dq/dt) = p \; ; (dp/dt) = -q - \zeta p \; ; (d\zeta/dt) = p^2 - 1 - \xi\zeta \; ; (d\xi/dt) = \zeta^2 - 1 \}$$

Liouville's phase-space continuity equation shows that $(\partial f/\partial t) = 0$ for both of these four-dimensional sets of equations if f(q,p,ζ,ξ) is Gaussian in all four variables . A variety of many-body problems have been solved successfully using these ideas .

Simple Systems with Thermal Constraints

6. Hoover-Holian Thermostated Oscillator

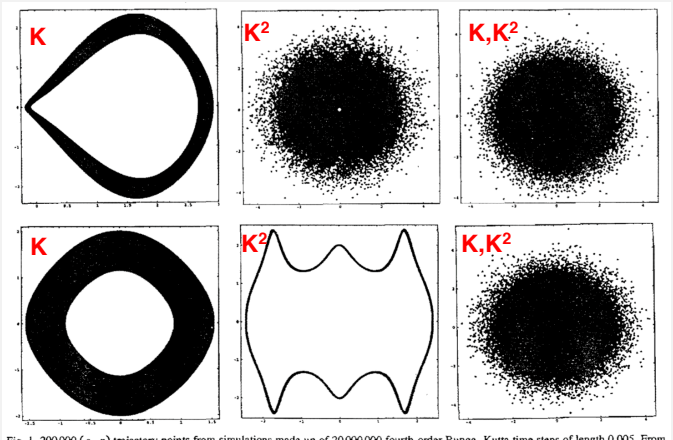


Fig. 1. 200 000 (q, p) trajectory points from simulations made up of 20 000 000 fourth-order Runge–Kutta time steps of length 0.005. From left to right the trajectories were generated with $\langle K \rangle$ control, $\langle K^2 \rangle$ control, and simultaneous $\langle K \rangle$ and $\langle K^2 \rangle$ control. The initial condition for the upper row is $\{q, p, \zeta, \xi\} = \{2, 2, 0, 0\}$, while that for the lower row is $\{0, 2, 0, 0\}$. In all cases, the relaxation times, τ_ζ and τ_ξ, were equal to unity.

These simulations constrain The mean values of p^2 or p^4 or both using two different initial conditions . When the results depend upon the initial conditions they are clearly *not* ergodic. When both moments are controlled not only do the results *look* similar . Also, the values of the second, fourth, and sixth moments are all very close to the known results : $< p^2, p^4, p^6 > = 1, 3, 15$.

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Simple Systems with Thermal Constraints

6. Simultaneous control of $< p^2, p^4, p^6 >$!

In the 90s Brad Holian, Harald Posch, and I concluded that it was unlikely that all three moments could be controlled simultaneously . With a fixed timestep it is clear that eventually a point too far from the origin would appear (because the Gaussian extends to infinity) so that no fixed timestep algorithm can run forever . In 2015, working with Clint Sprott, we came across Nosé oscillator problems that required an adaptive integrator to solve . Sure enough , if the adaptive integrator is applied to the three-moment control , there is no problem following the solution for long times . The main check of the calculation is the set of moments as the five-dimensional phase space is far too complex for good topological studies . One can check to make sure that the largest Lyapunov exponent is independent of the initial conditions , taking a few hundred initial conditions and then running the two with the highest and lowest Lyapunov exponents longer , tens or hundreds of billions of timesteps , and confirming that the two values tend to agree within the expected statistical errors , proportional to $time^{-1/2}$. Let's look at the details →

Simple Systems with Thermal Constraints

6. Simultaneous adaptive control of $< p^2, p^4, p^6 >$!

```
Comparison of two RK4 solutions requires very little new programming :
call rk(xx,xxp,dt/2)
call rk(xx,xxp,dt/2)
call rk(yy,yyp,dt/1)

error = error + (xx(i) - yy(i))***2
if(error.lt.10.0d00**-24) dt = dt*2
if(error.gt.10.0d00**-20) dt = dt/2

yy(i) = xx(i)

pdot = - q - z*p - y*p*p*p - x*p*p*p*p*p
zdot = p*p - 1
ydot = p*p*p*p - 3*p*p
xdot = p*p*p*p*p*p - 5*p*p*p*p
```

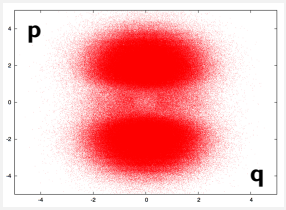
The mean timestep < dt > turns out to be very close to dt = 0.001 .

Simple Systems with Thermal Constraints *

6. Simultaneous adaptive control of $< p^2, p^4, p^6 >$!

(qp) Results after 1×10^9 timesteps : `1.002, 3.024, 15.226, 1.00000, 3.00000, 15.00002`
(qp) Results after 4×10^9 timesteps : `1.001, 3.010, 15.145, 1.00000, 3.00000, 15.00001`

Notice that the fixed moments of momentum are quite precise while the coordinate moments are not . This situation would be reversed if the coordinates' moments had been selected for the constraints .



This sampling of 1 000 000 { q,p } points looks rather unlike the Gaussian distribution for Gibbs' canonical ensemble. Why is there this apparent disagreement ?

* Carol described the application of adaptive integration to Nosé and Nosé-Hoover oscillators .

Simple Systems with Thermal Constraints

6. Multi-Moment Thermostated Oscillators

For a many-body system the various thermostats are consistent with one another and with Gibbs' canonical distribution. For small systems, with a few degrees of freedom, there are relatively large differences. The Gauss and Nosé-Hoover thermostats are relatively not necessarily easy to generalize.

Suppose for example that it is desired to constrain the fourth moment rather than the second , so that $< p^4 >$ is constant . The constraint equation suggests trying

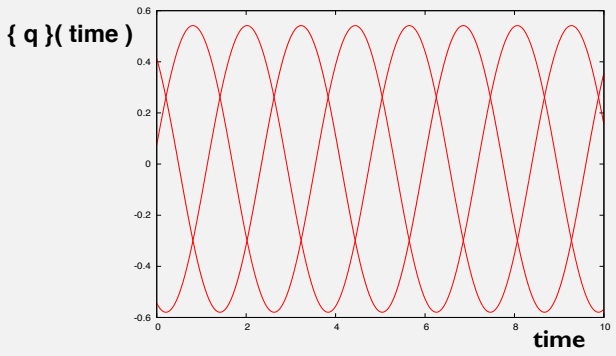
$$(dp/dt) = F - \zeta p^3 \text{ with } p^3(dp/dt) = 0 = Fp^3 - \zeta p^6$$

It turns out that this idea fails , as without controlling the center of mass of the three-oscillator problem the system simply moves away from the origin . In the early days of nonequilibrium molecular dynamics Bill Ashurst thermostated manybody systems by [1] subtracting the center-of-mass velocity and then [2] rescaling the second moment to reproduce T . Although my attempts to use two Lagrange multiplier constraints to control the moment and the center of mass failed with a conservative timestep of 0.001 zeroing of the center of mass followed by a rescaling of the fourth moment successfully reached a "normal mode" which can be followed by reducing dt : 0.1 → 0.001 . The next graphic shows the result.

Simple Systems with Thermal Constraints

6. Multi-Moment Thermostated Oscillators

Here is the result of solving the oscillator equations with a rescaling of the fourth moment, $p(1)^4 + p(2)^4 + p(3)^4$. This could be viewed as an example of "operator splitting", where two or more parts of the differential equation are applied in a sequence rather than simultaneously. Here are the coordinates of a travelling three-particle wave with the fourth velocity moment held constant.



7. The ϕ^4 Model for Heat Conduction

Simple Systems with Thermal Constraints

7. The ϕ^4 Model for Heat Conduction

$$\mathcal{H} = K(p) + \Sigma(1/2)(q_i - q_j)^2 + \Sigma(1/4)q^4$$

Although the harmonic chain is particularly useful for evaluating integration algorithms it is of little use away from equilibrium . Two examples make this clear . Energy and momentum travel along a harmonic chain ***at the velocity of sound*** . In more "realistic" systems heat obeys Fourier's $Q_x = -\kappa(dT/dx)$. Flow proceeds outward from a source as the ***square root*** of the time . This qualitative difference (linear *versus* square root) can be understood . It is due to the scattering of the phonons which travel at the sound speed. The mean free path of molecules in air is about a hundred nanometers and can be nicely described by the Boltzmann equation . Scattering in the ϕ^4 model Is local with energy conservation but without any long wavelength phonons .

7. Simple Systems with Thermal Constraints -- An aside regarding the diffusion of mass and heat [reminiscent of the Central Limit Theorem]

7. Why Does Heat Travel as the Square Root of time ?

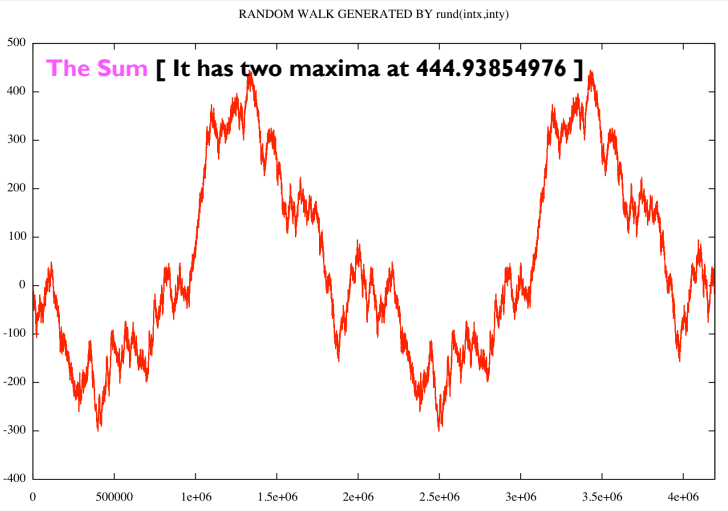
A simple explanation can be based on squaring the sum of N steps of unit length and averaging : $< L^2 > = < (\Sigma \mathcal{U})^2 > = N$ (because the steps are not correlated) . There is a huge literature on "random walks" including recurrence and fractal dimension . Although the sum of all possible walks gives the binomial distribution which approximates the Gaussian distribution for large N the diffusion equation : $(\partial\rho / \partial t) = (\partial^2\rho / \partial x^2)$ does not have a Gaussian as its solution . Because the diffusion equation provides an effect traveling faster than the speed of sound it is unphysical .

The many problems introduced by dimensionality , self-avoidance , time delay , and stochastic models make this area of mathematics interesting today . One might expect that solutions of the Boltzmann Equation would agree with solutions of the diffusion equation but no doubt this is an example of problems in which taking limits has to be done carefully (if at all) . There is similarity to computing $< x^2 > \approx N$, ln(N) , O(1) using lattice dynamics in one , two , and three dimensions .

The Maxwell-Cattaneo equation , $Q + \tau(\partial Q/\partial t) = -(\partial T/\partial x)$, for instance , can be used to limit the speed of the response to gradients , but can exhibit other problems , such as negative temperature .

7. Simple Systems with Thermal Constraints --
[an Aside regarding pseudorandom numbers]

7. Random walk using rund(intx,inty) = rund(0,0)
initially and using up all 2^{22} available steps .




```
sum = 0.0d00
do i = 1,2**22
step = rund(intx,inty) - 0.5d00
sum = sum + step
write(77,77) i, step, sum
enddo
```

The square root of 2^{22} is 2048 and 2048 x (1/2) is of the order of the maximum excursion from the origin . Our deterministic random numbers are perfectly adequate for this if the periodicity of the sum is acceptable .

Question for the students : why does The Sum repeat ?

It turned out to be a Good Idea to plot The Sum of the points rather than the points themselves . Though the 4 194 304 pseudorandom points *can* be distinguished on a 24" screen they cannot be successfully entered into PowerPoint. Just too much info !

Simple Systems with Thermal Constraints

7. The ϕ^4 Model for Heat Conduction

$$\mathcal{H} = K(p) + \Sigma(1/2)(q_i - q_j)^2 + \Sigma(1/4)q^4$$

Shockwaves are supersonic [travel faster than the sound speed] with a "jump" discontinuity in pressure, density, entropy, and energy . Such a pressure jump in the harmonic chain spreads out as the *cube root* of the time . For harmonic and anharmonic simulations see B. L Holian and G. K. Straub in Physical Review B 18, 1593-1608 **(1978) .**

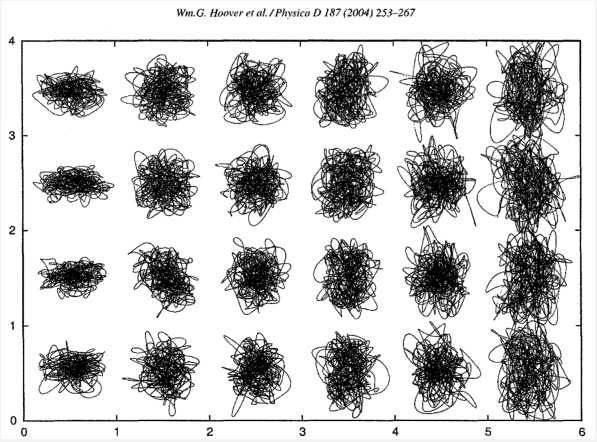
The unphysical harmonic behavior is most easily cured with a tethering potential. The resulting scatter of phonons results in ordinary Fourier conductivity . Aoki and Kusnezov emphasized that the phi-4 model, with simple quartic tethering makes possible the study of heat conductivity in a variety of one-, two- and three-dimensional lattices . The Hamiltonian for the model is the usual harmonic Hamiltonian plus a sum of quartic tethers . In the one-dimensional case, where the { q } represent displacements from the regular lattice sites it is simplest to choose all the parameters equal to unity . Let's look at the two-dimensional case .

Simple Systems with Nosé-Hoover Control

7. The ϕ^4 Model for Heat Conduction

$$\mathcal{H} = K(p) + \Sigma(1/2)(q_i - q_j)^2 + \Sigma(1/4)q^4$$

T = 0.005



T = 0.015

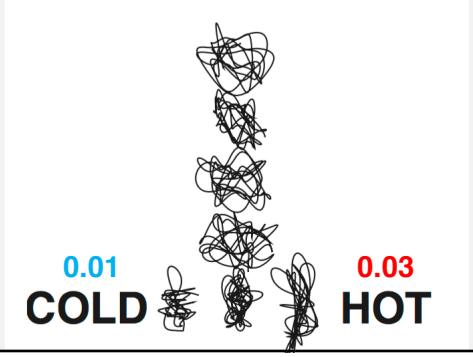
There are 16 Newtonian particles of the 24 total .

Simple Nosé-Hoover flow with ϕ^4 Thermometer

7. The ϕ^4 Model for Heat Conduction

$$\mathcal{H} = K(p) + \Sigma(1/2)(q_i - q_j)^2 + \Sigma(1/4)q^4$$

ϕ^4 Thermometer registers 0.024 .

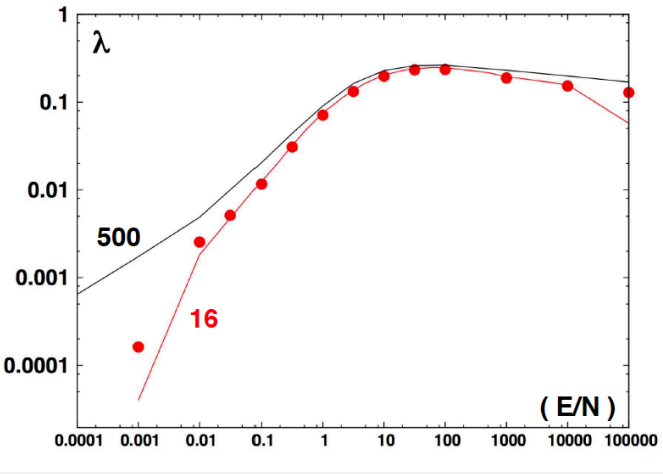


The thermometer "measures" a temperature about ten percent higher than the kinetic temperature of the Newtonian particle's 0.021 . The measurement depends very little on the length of the thermometer which was varied from 4 (as shown here) to 21 .

The conductivity of the ϕ^4 model is insensitive to system size . Although the model is harmonic at low temperature and non-conducting at high temperature, where particles simply oscillate in quartic wells, there is a very wide range where Fourier's Law describes the hot-to-cold heat flow .

Simple Systems Under Thermal Constraints

7. The ϕ^4 Model for Heat Conduction



Typically systems which exhibit ordinary (linear) transport have chaotic dynamics . In chaotic systems two nearby trajectories separate from one another exponentially rapidly in time, as $e^{+\lambda t}$. The graphic here illustrates that exponential growth for 16 and 500 particle chains of ϕ^4 particles.

The plot, which shows the variation of the Lyapunov exponent* with energy , reveals a range of chaotic behavior over about ten orders of magnitude in temperature .

* Technically, the λ here is the *largest* one .

Simple Systems Under Thermal Constraints

Points to remember and consider :

Two-dimensional Lucy-Fluid simulations provide insight into shear and heat flows , hydrodynamic instabilities like Rayleigh-Bénard , and steady shockwaves .

Many thermostat types are available with both instantaneous and time-averaged control of velocity , energy , temperature , . . .

By eliminating the propagation of long waves the ϕ^4 model provides simple examples of systems obeying Fourier's Law in one , two , and three dimensions .

Problem :

Does the one-dimensional harmonic chain provide insight into the shockwave problem ? The motion of such a chain , where we choose the force constant and particle mass equal to unity , is governed by nearest-neighbor linear forces :

$\{ F_i = q_{i+1} - 2q_i + q_{i-1} \}$ reminiscent of the wave equation $(d/dt)^2 q = c^2 (d/dx)^2 q$.

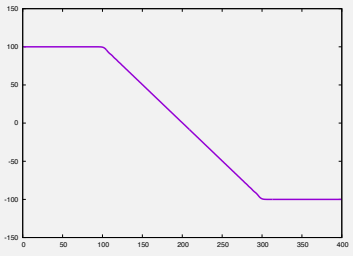
We can generate a "shockwave" through the collision of two mirror-image systems .

8. Harmonic Chain Dynamics

Dynamics of a 400-particle harmonic chain with initial velocities of +1 and -1

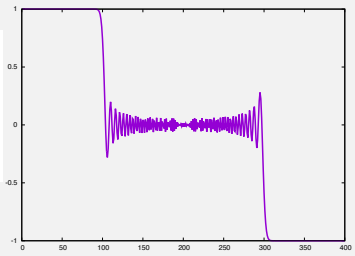
From the analogy with the wave equation we expect that the sound (or maybe shock) speed will be unity . The { q } in the equations of motion can represent either coordinate values or displacements . We choose displacements so that the initial { q } are all zero . We choose to look at the coordinates and velocities and forces at a time of 100 when we expect half the particles to have been affected by the "shock" . The calculations below confirm the expectations .

Displacements at time 100

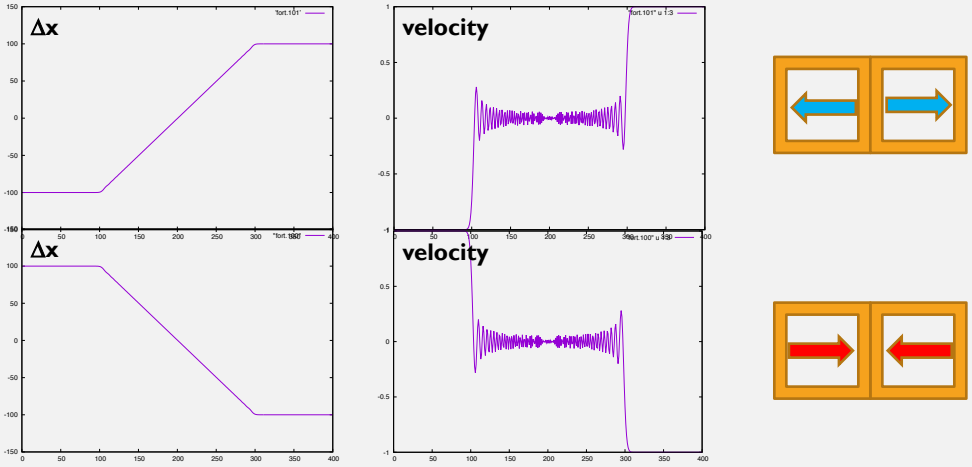



```
do i = 1,N-1
xij    = x(i) - x(i+1)
f(i)   = f(i)   - xij
f(i+1) = f(i+1) + xij
enddo
```

Velocities at time 100



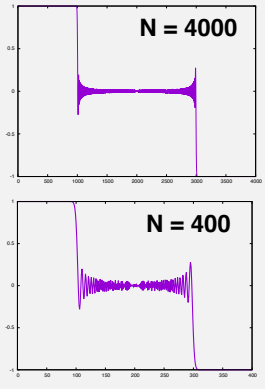
Compression = Expansion in Harmonic Chains



In a typical fluid case one would obtain a shockwave or a rarefaction fan .
The harmonic chain solutions just change sign and exhibit no asymmetry .

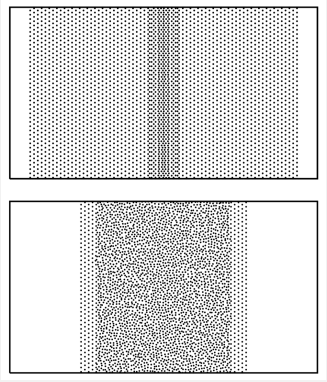
Dynamics of a 400-particle harmonic chain with initial velocities of +1 and -1

The harmonic chain problem has a long and continuing history . The solution can be written in terms of Bessel functions . It turns out that the easiest way to find the Bessel functions is to solve the corresponding harmonic chain problem ! Look at "Molecular Dynamics of Shock Waves in One-Dimensional Chains" by B L Holian and G K Straub in Physical Review B 18 , 1593-1608 **(1978) . There is no obvious visual difference between the velocities shown here for two different system sizes . Note that the analytic solution shows that the shockwidth varies as the cube root of the time (vanishing on the macroscopic scale ; large on the microscale) .**



More realistic models of interparticle forces show that the shockwidth is governed by viscosity and is only a few particle diameters . The profile is planar in 3D and a straight line in 2D .

The snapshots at the right show a 2D shock at two different times using a smooth finite-range repulsive potential .



9. Levesque-Verlet Dynamics

Simulations of Irreversible Processes Using the Levesque-Verlet Integer Leapfrog Algorithm

Carol has explained that *integer arithmetic* makes it possible to *reverse* any leapfrog history . The shockwave problem is an interesting example because it includes an irreversible process converting cold low-density fluid into hot compressed fluid with a greater entropy .

If one begins a simulation with hot compressed fluid expanding into a vacuum rather than a shock one sees a "rarefaction fan" in which states of nearly the same entropy vary smoothly from the original density to low density . It seems to me that the velocity gradient , which produces entropy through the viscosity , gets smaller as the system size is increased . In the shockwave things are different : the velocity gradient stays at the inverse mean free path so that the viscous entropy production does not change as the system size is increased .

The rarefaction fan is also irreversible , but for another reason . When , as is usual , the sound velocity is an increasing function of density , the denser part of a rightmoving wave moves faster than the rarefied part . A shockwave is formed !