General Features of Our Approach to NESM & NEMD

Our main goal is to reach an understanding connecting microscopic and mesoscopic models to analogs in the Real World of Macroscopic Physical Phenomena. We strive for simplicity. Our models are mainly classical and nonrelativistic and typically two-dimensional. The main lines of thought we follow can be traced to Abraham, Alder, Ashurst, Bhattacharya, Boltzmann, Bridgman, Bulgac, Debye, De Rocco, Dettmann, Duvall, Euler, Evans, Fermi, Feynman, Ford, Galton, Gauss, Gibbs, Jaynes, Hamilton, Holian, Kawai, Kratky, Krivtsov, Kusnezov, Lagrange, Landau, Lifshitz, Liouville, Lyapunov, Mareschal, Maxwell, the Mayers, Moran, Morriss, Newton, Nosé, Occam, Pars, Patra, Posch, Rahman, Rice, Ruelle, Sommerfeld, Sprott, Steiner, Stell, Stull, Thoreau, Travis, Uhlenbeck, Vineyard, von Neumann, Wainwright, Wojciechowski, Wood, Zwanzig. Feynman’s ideas of pursuing definite examples, along with his and Alder’s efforts toward simplicity are always with us.

Most of what you see will be in two dimensions, with graphic illustrations, using FORTRAN and gnuplot and PowerPoint as our main expository tools, not because these are perfect but because we haven’t yet found anything better.

In order to teach students rather than course material it is useful to have questions. This is the main job of the student, not just for himself, but for all of us.

Let us thank Baidurya Bhattacharya for making this possible.
1. Ideal Gas Thermometer → Temperature/Entropy

2. Isokinetic “Gaussian” Molecular Dynamics

3. Nosé and Nosé-Hoover Mechanics

4. The Boltzmann Equation and Entropy

5. The Krook-Boltzmann Equation, $\eta$ and $k$

6. Direct Simulation Monte Carlo

7. Nosé-Hoover Knots from Yang and Wang

**William G. Hoover**

Ruby Valley Nevada

December 2016
Mechanics plus Temperature (and Heat) → Thermodynamics.

We have the luxury of using the ideal-gas temperature scale

<table>
<thead>
<tr>
<th>Substance and its state</th>
<th>Defining point (range)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K</td>
</tr>
<tr>
<td>Triple point of hydrogen</td>
<td>13.8033</td>
</tr>
<tr>
<td>Triple point of neon</td>
<td>24.5561</td>
</tr>
<tr>
<td>Triple point of oxygen</td>
<td>54.3584</td>
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<tr>
<td>Triple point of argon</td>
<td>83.8058</td>
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<tr>
<td>Triple point of mercury</td>
<td>234.3156</td>
</tr>
<tr>
<td>Triple point of water[Note 1]</td>
<td>273.16</td>
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<tr>
<td>Melting point of gallium</td>
<td>302.9146</td>
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<tr>
<td>Freezing point of indium</td>
<td>429.7485</td>
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<tr>
<td>Freezing point of tin</td>
<td>505.078</td>
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<tr>
<td>Freezing point of zinc</td>
<td>692.677</td>
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<td>Freezing point of aluminum</td>
<td>933.473</td>
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<tr>
<td>Freezing point of silver</td>
<td>1,234.53</td>
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<tr>
<td>Freezing point of gold</td>
<td>1,337.33</td>
</tr>
<tr>
<td>Freezing point of copper</td>
<td>1,357.77</td>
</tr>
</tbody>
</table>

Titanium melts at $T = 3034\,^\circ\text{F}$.

Temperature in the sun = $15,000,000\,^\circ\text{K}$.

Temperature in the H Bomb is a few times greater than that of the sun.

Plotting $PV/Nk$ at low number density defines the ideal-gas temperature scale.

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**Ideal-Gas Thermometer: Microscopic Mechanics → Thermodynamics**

Gibbs’ Statistical Mechanics in the Microcanonical Ensemble *

\[
\Omega_{\text{ideal}} = (1/N!) \prod (\int dq \int dp / h) \propto (V/N)^N (E/N)^{DN/2}
\]

$\Omega_i$ is the number of states, with $(dq \, dp / h)^{DN}$ corresponding to a “state” →

\[
\Omega_{i+F} = \Omega_i (E - E_F) \Omega_F (E_F) = \Omega_i (E_i) \Omega_F (E - E_i)
\]

Thermal equilibrium corresponds to maximizing the number of states by varying the fluid energy. The ideal-gas energy states comprise a $DN$-dimensional hypersphere.

Taking the logarithm of the number of states makes the maximization step easy:

Maximizing $\ln \Omega \rightarrow (\delta \ln \Omega_i / \delta E_i) = (\delta \ln \Omega_f / \delta E_f) = DN/(2E) = (1/kT)$

This definition of temperature makes thermometry possible and gives the Zeroth Law of Thermodynamics: $T_1 = T_2$ and $T_1 = T_3 \rightarrow T_2 = T_3$

* Good references are Molecular Dynamics and Computational Statistical Mechanics @williamhoover.info
Next Consider Mechanical Evaluation of Pressure, in 2D

\[
P_{xx} = \sum \left( \frac{2mv_x}{L_y} \right) \left( \frac{v_x}{2L_x} \right) = \frac{NkT_{xx}}{V}
\]

Notice that both pressure and temperature can be second-rank tensors. Two directions are involved: [1] the orientation of the wall on which the force per unit area is measured; and [2] the direction of the force. At equilibrium the pressure and the temperature are scalars. We will show this for the ideal gas using the Boltzmann equation which \( \rightarrow \) Maxwell-Boltzmann f.

Microscopic Mechanics \( \rightarrow \) Thermodynamics

J Willard Gibbs’ Statistical Mechanics *

\[
\Omega_i = \left( \frac{1}{N!} \right) \prod \left( \int \int \frac{dq}{h} dp \right) \propto \left( \frac{V}{N} \right)^N \left( \frac{E}{N} \right)^{DN/2}
\]

Mechanical Coupling \( \rightarrow \) \( \Omega_{i+F} = \Omega_i(V - V_F) \Omega_f(V_f) = \Omega_i(V_i) \Omega_f(V - V_f) \) (1839-1903)

Mechanical equilibrium corresponds to maximizing the number of states by varying the fluid volume. The ideal-gas volume states comprise an N-dimensional hypevolume \( V^N \). Again, taking the logarithm of the number of states makes the maximization step easy:

\[
\text{Maximizing } \ln \Omega \rightarrow \left( \frac{\partial \ln \Omega}{\partial V_i} \right) = \left( \frac{\partial \ln \Omega_f}{\partial V_f} \right) = \left( \frac{N}{V} \right) = \left( \frac{P}{kT} \right)
\]

This ideal-gas pressure makes it easy to describe mechanical equilibria and gives the Zeroth Law of Mechanics/Dynamics if \( P_1 = P_2 \) and \( P_1 = P_3 \) \( \Rightarrow \) \( P_2 = P_3 \)

* J. W. Gibbs, Elementary Principles in Statistical Mechanics (Dover, 1960), originally 1902
Thermodynamic Entropy $S$ Corresponds to $k \ln \Omega$

$$e^{(S/k)} = \Omega(E, V) \propto (1/N!) \int \cdots \int (dqdp/h) \propto (V/N)^N \sqrt{E/N}^{DN}$$

$$\sum(p^2/2m) = E, \text{ a many-dimensional spherical surface with radius } (2mE)^{1/2}$$

1. Entropy is a state function depending upon $E$ and $V$.
2. Entropy increases in the absence of a constraint.
3. Entropy is an extensive quantity for identical particles.

For an ideal gas $(S/Nk) = \ln (V/N) + (D/2) \ln (E/N) + \text{constant}^*$

$$TdS = dE + PdV \ (\text{Combined First and Second Laws})$$

The microcanonical entropy shown here deviates only negligibly – as $(1/N)$ – from Gibbs’ canonical entropy where the momentum integral is $(2\pi m kT)^{1/2}$ per degree of freedom.

The Mayers’ Statistical Mechanics expresses the hypervolume of a $DN$-dimensional hypersphere in terms of Gaussian integrals, which are “gamma functions”.

What about using the Configurational Temperature from Landau/Lifshitz?*

$$\langle \nabla^2 \mathcal{H} \rangle = \langle (\nabla \mathcal{H})^2 \rangle / kT \rightarrow kT_C \equiv \langle (\nabla \mathcal{H})^2 \rangle / \langle \nabla^2 \mathcal{H} \rangle.$$  

$$kT \int \left[ (\nabla^2 \Phi) e^{-\Phi/kT} \right] dr = \int (\nabla \Phi)^2 e^{-\Phi/kT} dr$$

This is just an application of integration by parts:

$$\int du \, v = -\int dv \, u \text{ where } u = \nabla \Phi \text{ and } v = e^{-\Phi/kT} \text{ where }$$

$\Phi$ vanishes at the two endpoints of the integrals.

There is a comprehensive literature detailing (or obscuring) what is a relatively simple idea with plenty of generalizations. Unfortunately it appears to be just a dead end. If you would like to read more see Carlos Braga and Karl Travis’ two papers in the Journal of Chemical Physics: 123, 134101 (2005) and 124, 104102 (2006).
An apparent disadvantage is the occasional vanishing of the denominator. Think about gravitational field forces!

An apparent advantage is the lack of dependence on velocity, where the local velocity might be hard to determine accurately.

Steady rotation increases the forces without increasing temperature so that configurational temperature seems rather unphysical.

2. Isokinetic “Gaussian” Molecular Dynamics

Ordinarily \( \frac{dK}{dt} = -(d\Phi/dt) \). The upshot of a classic concept, Gauss’ “Principle of Least Constraint”, \( \sum \delta(F_c)^2 = 0 \), is a motion equation of the form \( \frac{dK}{dt} = -(d\Phi/dt) + \sum F \cdot v \) as we shall see. Remember that Gauss was famous for “Least Squares” already. This idea is not a panacea, and gives incorrect results sometimes.

Pars’ text is a good reference for classical variational principles.
Molecular Dynamics at Constant $T_{xx}$ Using Gauss’ Principle of Least Constraint (1829 - 1982)

The desired constraint is: $\sum m v_x^2 = N k T_{xx}$.

Equivalently, $\sum 2 m v_x \dot{v}_x = \sum 2 m v_x \left[ F_x + F_c + \delta F_c \right]$,

which can be combined with Gauss’s $\sum 2 F_c \delta F_c = 0$,

by using a Lagrange Multiplier $\zeta$ to give

$$2 m v_x \zeta + 2 F_c = 0 \rightarrow F_c = -\zeta m v_x.$$ 

Finally, $\sum 2 m v_x \dot{v}_x = \sum 2 m v_x \left[ F_x - \zeta m v_x \right] = 0$;

$$\zeta_{\text{Gauss}} = \frac{\sum v_x F_x}{\sum m v_x^2}.$$ 

Molecular Dynamics at constant $T_{xx}$ Using a Standard Lagrange Multiplier *

The Lagrange multiplier method leads to

$$\mathcal{H}_{HL} = 2 \sqrt{K_q K_p} - K_q + \Phi \text{ (Hoover – Leete)}$$

where $K_q = \left(\frac{m q^2}{2}\right)$; $K_p = \left(\frac{p^2}{2m}\right)$.

This gives the following equations of motion:

$$\{ \dot{p} = F ; \dot{q} = \left(\frac{p}{m}\right) \sqrt{\left(\frac{K_q}{K_p}\right)} \}.$$ 

Sample Problem: Three masses with periodic boundary conditions

Choose a normal mode with $\omega^2 = 3$ solving three motion equations.

* For references see our arXiv 1303.6190 paper: Hamiltonian Thermostats Fail to Promote Heat Flow
Sample Problem #1: Three masses with periodic boundary conditions
Choose a normal mode with $\omega^2 = 3$ solving three motion equations.

$x, y, \text{ and } z \text{ are the displacements of the particles}$

\[ \ddot{x} = y + z - 2x \; ; \; \ddot{y} = z + x - 2y \; ; \; \ddot{z} = x + y - 2z \]
\[ x = \cos(\sqrt{3}t) \; ; \; y = \cos(\sqrt{3}[t - \tau/3]) \; ; \; z = \cos(\sqrt{3}[t + \tau/3]) \]

This moving wave has constant kinetic and potential energies.
For this system’s isokinetic problems $\zeta_{\text{Gauss}} = 0$ and $K_q = K_p$.

Sample Problem #2: Two masses in steady rotation with one spring.

RK4 solution of 4 equations for Particle 1.
There are 628 timesteps of $dt = 0.01$ each.
It isn’t necessary to add the centrifugal forces ($\omega^2 r/2$) to the spring forces. Those forces arise automatically from the motion.

Spring force is $(1 - r)$ and with a speed of unity the centrifugal force is $r/2 \rightarrow r = 2$. You should be able to verify that the initial values
\[ \{ x_1 = 1 ; y_1 = 0 ; p_{x1} = 0 ; p_{y1} = 1 \} \]
are those for which the radial acceleration is zero. Notice that the four variables for Particle 2 are just the negatives of those for Particle 1.
\[ r_{12} = \sqrt{((x_1 - x_2)^2 + (y_1 - y_2)^2)} \]
\[ f_{x1} = (x_2 - x_1)(r_{12} - 1)/r_{12} \]
\[ f_{y1} = (y_2 - y_1)(r_{12} - 1)/r_{12} \]

It is also easy to see that the virial theorem is satisfied. Consider the theorem for the $x$ coordinate of Particle 1. The $x$ coordinate is $(r/2)\cos(t) = \cos(t) \rightarrow < x \dot{x} > = < (d/dt)(xx) > - < x^2 > = 0 - (1/2)$.
A good way to start on such problems is to write the Lagrangian (in terms of the coordinates and velocities) in order to discover the momenta and the Hamiltonian equations of motion they obey.
Sample Problem # 3: Five masses in steady rotation with four springs.

Characteristics of the motion are:
1. Initial values of \( p_y \) are equal to the x coordinates \( \Omega = 1 \).
2. Initial values of all the radial accelerations vanish.
3. The potential energies for Newton, Hoover-Leete, and Gauss Dynamics with Kinetic Energies initially equal to 7.
4. Fourth-Order Runge-Kutta timestep = 0.001.

Spring forces are \( 10(1 - r) \) and centrifugal forces are \( r \). You should be able to verify that the initial values given below are those for which all the radial accelerations vanish.

Initial values:

\[
x_1 = -19/7.1; \quad x_2 = -10/7.1; \quad x_3 = 0; \quad x_4 = +10/7.1; \quad x_5 = +19/7.1
\]

The RK4 solution of 8 equations for Particles 1 and 2: 628 timesteps of \( dt = 0.01 \) each.

It isn't necessary to add the centrifugal forces \( \{\omega^2r\} \) to the spring forces. Those forces arise automatically from the motion.

Spring forces are \( 10(1 - r) \) and centrifugal forces are \( r \). You should be able to verify that the initial values given below are those for which all the radial accelerations vanish.

Initial values of \( p_y \) are equal to the x coordinates \( \Omega = 1 \).

Potential energies for Newton, Hoover-Leete, and Gauss Dynamics with Kinetic Energies initially equal to 7.
Fourth-Order Runge-Kutta timestep = 0.001.
3. Nosé and Nosé-Hoover Mechanics *

* Nosé’s 1984 papers [ Molecular Physics + Journal of Chemical Physics ] and mine in Physical Review A.

Shuichi Nosé’s Mechanics for an Oscillator (1984)

\[ 2\mathcal{H}_N = \left(\frac{p}{s}\right)^2 + q^2 + T \ln(s^2) + (\zeta^2) ; \]

\[ \dot{q} = \left(\frac{p}{s^2}\right) ; \quad \dot{p} = -q ; \quad \dot{s} = \zeta ; \quad \dot{\zeta} = \left(\frac{p^2}{s^3}\right) - \left(\frac{T}{s}\right) ; \]

\[ \Downarrow \]

\[ \dot{q} = \frac{p}{s} ; \quad \dot{p} = -qs ; \quad \dot{s} = s\zeta ; \quad \dot{\zeta} = \left(\frac{p^2}{s^2}\right) - T ; \]

\[ \dot{q} = p ; \quad \dot{p} = -q - \zeta p ; \quad \dot{s} = s\zeta ; \quad \dot{\zeta} = p^2 - T . \]

Two steps are involved here:

[ 1 ] **Scaling the time** with \( s \) (line 2 \( \rightarrow \) line 3) and

[ 2 ] **Redefining the momentum**, \( (p / s) \rightarrow p \).

Alternatively one can compute the acceleration \( \ddot{q} \).
To what extent is the **Continuity Equation** Obvious?

An important observation:
During the short time \( dt \) the flow into the fixed Eulerian bin is \( f v dt \) from the left with a loss \( -f v dt \) on the right. Evidently the change in \( f dx \) during \( dt \) becomes \(-\partial f/\partial t\) so that the conservation law in one dimension is \((\partial f/\partial t) = -\partial(fv)/\partial x\). There is nothing to stop us from summing up contributions in the \( x \) and \( y \) and \( z \) directions if desired, or even in all the phase-space directions if we would like to prove **Liouville’s Theorem**.

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**Liouville’s Steady Flow Equation for Nosé Mechanics**

\[
(\partial f/\partial t) = -\nabla \cdot (fv) = 0 \ [\text{Is This Obvious?}]^*.
\]

\[
2\mathcal{H} \equiv (p/s)^2 + q^2 + \ln(s^2) + \zeta^2 \ [\text{Nosé!}]
\]

For simplicity, we set the temperature equal to unity in what follows.

\[
\mathcal{H} \rightarrow \dot{q} = (p/s^2) ; \quad \dot{p} = -q ; \quad \dot{s} = \zeta ; \quad \dot{\zeta} = (p^2/s^2) - (1/s)
\]

\[
\mathcal{H} \rightarrow f(q, p, s, \zeta) = (1/s)e^{-[(p/s)^2+q^2+\zeta^2]/2}
\]

Because \( \nabla \cdot v \) vanishes we just need to show that \( v \cdot \nabla f \) vanishes:

\[
\dot{q}(\partial f/\partial q) = (p/s^2)(-qf) ; \quad \dot{p}(\partial f/\partial p) = (-q)(-pf/s^2) ;
\]

\[
\dot{s}(\partial f/\partial s) = (\zeta)[(p^2f/s^2)-(f/s)] ; \quad \dot{\zeta}(\partial f/\partial \zeta) = [(p^2f/s^2)-(1/s)][-\zeta f].
\]

* Here \( f \) is a conserved quantity, like mass density or probability density, with a velocity \( v \).
Nosé-Hoover (1985) and Dettmann (1996) Mechanics *

\[ 2\mathcal{H} = \left(\frac{p^2}{s}\right) + sq^2 + st\ln(s^2) + s(\zeta^2) \equiv 0; \]
\[ \dot{q} = \frac{p}{s}; \quad p = -qs; \quad s = s\zeta; \]
\[ \dot{s} = s\zeta; \]
\[ \dot{\zeta} = \left(\frac{p^2}{2s^2}\right) - \frac{(q^2)}{2} - \left(\frac{T}{2}\right)\ln(s^2) - T - \frac{(\zeta^2)}{2} = \left(\frac{p}{s}\right)^2 - T. \]

Redefining \((p/s) \to p; \quad q = p; \quad \dot{p} = -q - \zeta p; \quad \dot{\zeta} = p^2 - T.\)

Alternatively \(\ddot{q} = \left(\frac{\dot{p}}{s}\right) - \dot{q}(\dot{s}/s) = -q - \zeta \dot{q}\) with \(\dot{\zeta} = q^2 - T.\)

Notice the two very different expressions for the \(d\zeta/dt\).
Notice that \(s\) is unneeded in the acceleration equation.


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Nosé-Hoover (1985) Mechanics

Suppose \(f(q, p, \zeta) = e^{-\phi/kT}e^{-\gamma/kT}e^{-\zeta^2/2}.\)

Suppose also \(\dot{p} = F - \zeta p \to \dot{\zeta} = \left(\frac{p^2}{mkT}\right) - 1]s\dot{s}^2.\)

Then \(\{ \dot{q} = (p/m); \quad \dot{p} = F - \zeta p; \quad \dot{s} = s\zeta, \}\)

This motion is an application of the phase-space Continuity Equation:

\[ 0 \equiv \left(\frac{\partial f}{\partial t}\right) = -\nabla \cdot (fv) = -f\nabla \cdot v - v \cdot (\nabla f) \quad \text{where} \quad -f\nabla \cdot v = f\zeta \quad \text{and} \quad -v \cdot (\nabla f) = -p \cdot \left(\frac{Ff}{kT}\right) - (F - \zeta p) \cdot (-p/mkT)f - \left(\frac{p^2}{mkT}\right) - 1](-\zeta f).\]

Nosé-Hoover mechanics gives Gibbs’ statistical mechanics!

To what extent is the **Continuity Equation** Obvious?

An important observation:
During the short time $dt$ the flow into the fixed Eulerian bin is $fvdt$ from the left with a loss $-fvdt$ on the right. Evidently the change in $fdx$ during $dt$ becomes $-(\partial f/\partial x)dx$ so that the conservation law in one dimension is $\frac{\partial f}{\partial t} = -\frac{\partial (fv)}{\partial x}$. There is nothing to stop us from summing up contributions in the x and y and z directions if desired, or even in all the phase-space directions if we would like to prove **Liouville's Theorem**.

**Liouville's Steady Flow with Nosé-Hoover Mechanics**

\[ \frac{\partial f}{\partial t} = -\nabla \cdot (fv) \quad \text{[Is this Obvious ?]} \]

\[ H = (p^2/2) + s^2 - s \ln(s^2) \]

\[ \xi = (1/2) \left( (p^2/2) - q^2 - \xi^2 - \ln(s^2) \right) - 1 = (p^2/2) - 1. \]

\[ H \longrightarrow f(q, p, s, \xi) \propto \left( p^2/2 + s^2 + s^4/2 \right). \]

Because the motion is Hamiltonian we know that $H$ is a constant of the motion. But we also know that $\int_{NH} = -f_{NH} \nabla \cdot v$, which is nonzero:

\[ \{ q = p ; p = -q - \xi p ; \xi = p^2 - 1 \} \rightarrow \nabla \cdot v = (\partial \xi/\partial p) = -\xi. \]

In fact, if we start with $\xi(t = 0) = 1$, \n
\[ v = -\xi \rightarrow f \propto e^{-\xi/2}. \]

so that $f$ is not constant although $H$ is zero, suggesting that $f$ is everywhere the same.

Perhaps this is a good student puzzle? Yes Indeed!

Although the distribution function has a somewhat peculiar denominator it is well-behaved from the numerical standpoint.
The Three Sections of the Nosé & NH Generate Conservative Tori and Points in the Chaotic Sea

Initial periodic orbits \( \{q, p, \zeta\} = (\pm 1.2144, 0, 0) \) incremented by \( \pm 0.1 \). The 12th increments lie in the chaotic sea.

This complexity is typical of Hamiltonian mixtures of chaos and toroidal solutions.

Initial condition \( \{q, p, \zeta\} = (2.4, 0, 0) \) generates points in the chaotic sea.

A Long Torus Penetrates the Chaotic Sea in 18 Places

\[
\begin{align*}
\dot{q} &= p \\
\dot{p} &= -q - \zeta p \\
\dot{\zeta} &= (p^2 - 1)
\end{align*}
\]

Initial condition \( \{q, p, \zeta\} = (2.4, 0, 2.4) \)
Two Long Tori Penetrate the Chaotic Sea

\[
\begin{align*}
\dot{q} &= p \\
\dot{p} &= -q - \zeta p \\
\dot{\zeta} &= 10(p^2 - 1)
\end{align*}
\]

Initial condition \( \{q,p,\zeta\} = (\pm 1.6, 0, 0) \)

Nosé is extremely stiff (and slow to compute), here the thick line.

Nosé-Hoover is much more efficient, here the thinner projection.

Chaotic starts: \((q,p,\zeta) = (3310)\) and \((q,p,\zeta) = (330)\), both to time = 100.

Fourth-order Runge-Kutta integration with \(dt = 0.001\) and \(dt = 0.01\).

\(\mathcal{H}\) is 9 here, not 0!
Lyapunov Exponents for Nosé & Nosé-Hoover Mechanics

Initial condition: \((q,p,s, \xi) = (2.4, 0, e^{-2.88}, 0)\) so that \(\mathcal{H} = 0\).

\(< \lambda >_{\text{Nosé}} \) differs from \(< \lambda >_{\text{NH}}\) by a factor of \(1/<s>_{\text{NH}} = 3.28 = 1/s >_{\text{N}}\).

\(\mathcal{H}_\text{NH} = 0:\)

\[\frac{dq}{dt} = \left(\frac{p}{s}\right); \quad \frac{dp}{dt} = -sq; \quad \frac{ds}{dt} = sz; \quad \frac{d\xi}{dt} = \left(\frac{p}{s}\right)^2 - 1\]

\(\lambda_1 \rightarrow 0.0138\)

Nosé-Hoover Equations:

\[\frac{dq}{dt} = p; \quad \frac{dp}{dt} = -q - \xi p; \quad \frac{d\xi}{dt} = p^2 - 1\]
4. The Boltzmann Equation and Entropy

When does Boltzmann’s Equation for \( f(r,p,t) \) apply?

1. When the density is low so that \( PV = NKT \).
2. When collisions occur at points (not Enskog, not Knudsen).
3. When collision orientations are random (\( P_{xx} = P_{yy} \)).

These restrictions are all related to the basic assumption

\[
f(r_1, r_2, p_1, p_2) = f(r, p_1)f(r, p_2) *
\]

Remarkably, the Boltzmann Equation obeys the Second Law. That is, the Boltzmann Equation is irreversible and provides quantitative viscosities \( \eta \) and conductivities \( \kappa \).

\[
\dot{f} \equiv \left( \frac{df}{dt} \right) = \left( \frac{\partial f}{\partial t} \right) + v \cdot \left( \frac{\partial f}{\partial r} \right) + \left( \frac{F}{m} \right) \cdot \left( \frac{\partial f}{\partial v} \right) = \left( \frac{\partial f}{\partial t} \right)_{\text{collisions}}
\]

\( \left( \frac{\partial f}{\partial t} \right)_{\text{collisions}} \) is calculated from two-body collisions by combining the collisional “losses” with reversed-inverse collisions which give “gains”. This expression gives the comoving time derivative following the motion.

* These \( f(\ldots) \) functions are all probability densities in phase spaces.
Boltzmann’s Treatment of Two-Body Collisions

\[ \left( \frac{\partial f}{\partial t} \right)_{\text{collisions}} = \text{“Gain”} - \text{“Loss”} \alpha \left[ f_3 f_4 - f_1 f_2 \right] \]

For the soft repulsive potential \( \phi(r) = (1 - r^2)^4 \)
a typical pair of collisions is shown below.

The “loss” velocities are indicated by arrows.
The “gain” collision is inverted in space and time.
The “gain” collision begins at the circled blue dots and finishes at the plain end points lacking the dots.

Boltzmann’s Proof of the H-Theorem, \((dS/dt) \geq 0\).

\[
\frac{\dot{S}}{Nk} = -(d/dt) \left( f \ln f \right) = - \int dp_1 \int dp_2 \Gamma_{12} \left[ \ln(1 + \ln f) \right] \dot{f} = \\
- \int dp_1 \int dp_2 \Gamma \ln f_1 \left[ f_3 f_4 - f_1 f_2 \right] = - \frac{1}{4} \int dp_1 \int dp_2 \Gamma \ln(f_1 f_2 / f_3 f_4) \left[ f_3 f_4 - f_1 f_2 \right]
\]

For simplicity we imagine that the system is homogeneous and isolated so that integrating over space is unnecessary. Notice also that \( f \) is normalized so that its integral is constant. The collision rates of corresponding gains and losses are identical as both of them are integrated over the entire velocity space.

This irreversible result is surprising as the motion is reversible. Unless \( \ln f \) is conserved, as in \( A + Bv + Cv^2 \), the entropy \( S \) increases. Evidently equilibrium corresponds to the Maxwell-Boltzmann Gaussian distribution!
Boltzmann’s Proof of the H-Theorem, \((dS/dt) \geq 0\).

This irreversible result is surprising as the motion is reversible. Unless \(\ln f\) is conserved, as in \(A + Bv + Cv^2\), the entropy \(S\) increases. Evidently equilibrium corresponds to the Maxwell-Boltzmann Gaussian distribution!

The surprise is usually stated as two paradoxes:

**Zermélo**: If the equations of motion are reversible then any trajectory obeying the H-Theorem disobeys it if reversed.

**Poincaré**: If the equations of motion obey Liouville’s Theorem then any initial state, no matter how odd, will recur in future.

Boltzmann’s Proof of the H-Theorem, \((dS/dt) \geq 0\).

**Poincaré**: If the equations of motion obey Liouville’s Theorem then any initial state, no matter how odd, will recur in future.

To prove this consider a small phase volume \(\Delta\Omega\) and follow it long enough that the new volume \(\Delta\Omega'\) does not overlap the old. Call \(\Delta\Omega''\) all of the volume ever covered (in infinitely long time) which was originally in \(\Delta\Omega'\). Then it must be the case that the latter includes \(\Delta\Omega\). Otherwise the volume \(\Delta\Omega + \Delta\Omega''\) would have to violate Liouville’s Theorem. This “Recurrence Theorem” is called Poincaré’s Recurrence Paradox. Do not be dismayed that the time required to recur exceeds the age of the Universe for about a dozen argon atoms at liquid density.
Maxwell-Boltzmann Distribution

Detailed balance suggests that $f_1 f_2 = f_3 f_4$ at equilibrium.

What happens to $\Sigma \ln[f(v)]$ when a collision occurs?

Evidently *it must be conserved*.

We know that collisions conserve mass, momentum, energy.

Therefore $\ln[f(v)] = \alpha + \beta v + \gamma v^2$ where $(\alpha, \beta, \gamma)$ are constants.

Evidently in the frame where $<v>$ vanishes $f(v)$ must be Maxwell-Boltzmann with $f(v) = \exp(-mv^2/kT)/(2\pi mkT)^{3/2}$.

It is useful to remember the identity

$$2\pi = \int 2\pi r \exp(-r^2/2) \, dr = \left[ \int \exp(-x^2/2) \, dx \right] \left[ \int \exp(-y^2/2) \, dy \right].$$

The H Theorem, together with detailed balance, shows that collisions cause a system to come to thermal equilibrium with velocities matching the Maxwell-Boltzmann distribution.

5. The Krook-Boltzmann Equation, $\eta$ and $\kappa$

Max Krook
1913-1985
Cambridge(s)
The Krook-Boltzmann Equation is Similar and Simpler

\[
(df/dt) = (f_{LTE} - f)/\tau \text{, where } \tau \text{ is the collision time .}
\]

Now the H Theorem can be proved in a single line :

\[
(dS/dt) = \langle -Nk [1 + \ln f] [f_{LTE} - f]/\tau = -Nk[\ln (f/f_{LTE})][f_{LTE} - f]\rangle
\]

Local Thermodynamic Equilibrium means having exactly the same density, velocity, and energy.
For Maxwell molecules this KB approximation is exact.

We illustrate its consequences for simple shear and for steady heat flow.

---

The Krook-Boltzmann Equation is Similar and Simpler

Suppose that the distribution function has a linear increase in \( u \) with \( y \) and that \( P_{xy} = P_{yx} = -\eta(du/dy) \):

\[
\begin{align*}
    f_{LTE} &\propto e^{-(m[v_x - \bar{v}_x]^2/2kT)}e^{-(mv_y^2/2kT)}
    \\
    (\partial f/\partial t) + v \cdot (\partial f/\partial r) + (F/m) \cdot (\partial f/\partial v) &\simeq 0 + (mv_y \bar{v}_x/kT)f_{LTE} = (f_{LTE} - f)/\tau
    \\
    f &\approx f_{LTE}[1 - \dot{\epsilon} (mv_x v_y/kT)] \rightarrow P_{xy} = -(NkT/V)\dot{\epsilon}\tau \rightarrow \eta = (NkT/V)\tau = P_{eq}\tau.
\end{align*}
\]

This density-independence of viscosity is a major success of the Boltzmann Equation!
The Krook-Boltzmann Equation is Similar and Simpler

Suppose that the distribution function has a linear decrease in T with x and that $Q_x = -\kappa (dT/dx)$:

$$f_{LTE} \propto (P/kT)e^{-mv^2/2kT}/(2\pi mkT)^{D/2}$$

$$\dot{f} = (\partial f/\partial t) + v \cdot (\partial f/\partial \tau) + (F/m) \cdot (\partial f/\partial \nu) \approx$$

$$0 - v_x (d\ln T/dx) f_{LTE}[ (D/2) + 1 - (mv^2/2kT) ] + 0 = [ f_{LTE} - f ]/\tau$$

$$\Delta f = v_x \tau (d\ln T/dx) f_{LTE}[ (D/2) + 1 - (mv^2/2kT) ] \rightarrow$$

$$J = 0 ; Q = -(d\ln T/dx)(5/2)\rho \tau (kT/m) \rightarrow \kappa = P\tau C_P$$

This density-independence of conductivity is another Boltzmann Equation success!

6. Direct Simulation Monte Carlo
Direct Simulation Monte Carlo (developed by Græme Bird) provides simple solutions, both analytic and numerical.

Divide the space into “zones” or cells, each with several particles. Some cells can act as boundary conditions as in a shock wave. The basic algorithm then advances each particle for a time $dt$. The number of collisions in each zone is computed from $< |v_{ij}| >$. Pairs of particles in each zone are then selected for collision with The impact parameters are chosen randomly. The advantages of this method are speed and simplicity.

The Krook-Boltzmann idea would replace a particle with one drawn from the LTE (Local Thermodynamic Equilibrium) distribution.

Ideal-Gas Thermometry – Massive Particle in a Thermal Bath

The Model: $M = 100$ with $V = 1$ and $m = 1$ with a Maxwell-Boltzmann distribution

Two Solution Methods:
1. Expand the Gaussian integrals for the bath in $(m/M)^{1/2}$.
2. Carry out a simulation along the lines of Krook-Boltzmann:

Algorithm for the Simulation:
Choose a Maxwell – Boltzmann bath particle $v$ in 1D, 2D, or 3D. Choose a random “impact parameter” in the 2D case. Compute the momentum/energy changes in a collision with $V$. Weight these changes with the relative speed, $I (v-V)I$. Sum up a million or so collisions.

Simulation is certainly faster and likely more accurate!
Reminder : How to Choose a Gaussian random number with \( \text{rund}(\text{intx}, \text{inty}) \)
random where \( \text{rund} \) returns a random number in the interval \([ 0 \text{ to } 1 ]\).

\[
\begin{align*}
\text{intx} &= 0 \\
\text{inty} &= 0 \\
10 & \text{ vx} = 10 \cdot \text{dsqrt}(T) \cdot (\text{rund}(\text{intx}, \text{inty}) - 0.5d00) \\
& \text{ Boltz} = \text{dexp}(-\text{vx} \cdot \text{vx}/(T+T)) \\
& \text{ If}(\text{rund}(\text{intx}, \text{inty}).\gt.\text{Boltz} \text{ go to } 10
\end{align*}
\]

The Box-Muller algorithm is a more sophisticated method for generating Gaussian random velocities, as Carol mentioned. See Wikipedia for details.

For the details of the analytic approach as well as the result of an elastic collision of \( M \) with \( v \) and \( m \) with \( v \) see HHP in Physical Review E 48, 3196-3198 (1993):

\[
\begin{align*}
\dot{\mathbf{x}}' &= \left( (M - m)/(M + m) \right) \dot{\mathbf{x}} + 2 \left( m/(M + m) \right) \mathbf{x} \\
\dot{\mathbf{x}}' &= \left( (m - M)/(M + m) \right) \dot{\mathbf{x}} + 2 \left( M/(M + m) \right) \mathbf{x}
\end{align*}
\]

Thermal Equilibration – Energy Change for \( M = 100 \) in a bath with \( m = 1 \) at \( T \)

200 million-collision averages at temperatures 1, 2, \ldots 200

Energy change, due to collisions, for a hard disk of mass $M$ and unit speed with an equilibrium bath of point particles with mass $m = M/100$ and temperature $T_x$. Zero energy change corresponds precisely to that temperature (50 for disks, 33.333 … for spheres, open circles in the figure) for which the disk kinetic energy equals the mean bath energy $\langle m v^2 / k \rangle$. Also shown are analogous results for a hard sphere immersed in a hard-sphere ideal-gas thermometer.

Some points of interest that could use investigation

Smooth-particle averages provide local quantities:

\[ F(r) \equiv \sum F_j w(r - r_j) \text{ where } w(r) \propto 1 - 6(r/h)^2 + 8(r/h)^3 - 3(r/h)^4 \]

Computing the local temperature involves a local Average of two velocity moments: \[ < (v - <v>)^2 > \].

An instantaneous recipe would be handy. One idea is to eliminate the “self contribution” to the local temperature. Irving and Kirkwood, and later Hardy, seem to have confused several researchers.
Ensembles versus trajectories and atomistic mechanics versus continuum mechanics contain examples.

Lucy’s weight function and a weight function which vanishes at $r = 0$:

$$w(r) = 30r^2(1 - r)^2.$$
Lucy’s and Monaghan’s weight functions

Lucy ≈ 1 – 6r^2 + 8r^3 – 3r^4; Monaghan ≈ 1 – 6r^2 + 6r^3 \rightarrow 2(1 – r)^3

1. Peak at Zero
2. Very Smooth
3. Normalized
4. Finite Range

7. Nosé-Hoover Knots from Yang and Wang
Interlocking Rings in Oscillator Phase Space

\[
\begin{align*}
\frac{dq}{dt} &= p ; \quad \frac{dp}{dt} = -q - \zeta p ; \\
\frac{dz}{dt} &= p^2 - T ; \quad T = 1 + \varepsilon \tanh(q)
\end{align*}
\]

The topology of knots is fascinating, even in the case of just three rings.
Knots are Everywhere!

Piotr Pieranski’s research in Poznań, Poland:
He has written software for simplifying, classifying, and even untangling knots by increasing the diameter of the rope to its maximum.

“The invariant Tori of Knot Type and the Interlinked Invariant Tori in the Nosé-Hoover System”
Lei Wang and Xiao-Song Yang, arXiv 1501.03375

[A somewhat stiffer Nosé-Hoover oscillator: \( (dq/dt) = p \); \( (dp/dt) = -q - \zeta p \); \( (d\zeta/dt) = 10(p^2 - 1) \)]

Initial \( (q,p,\zeta) = (-0.72,0,0) \) and \( (2.4,0,0) \)

Pairs of Tori turn out to be interlinked!
Is This a Nosé–Hoover Knot?

\[ \dot{q} = p \]
\[ \dot{p} = -q - \zeta p \]
\[ \dot{\zeta} = 10(p^2 - 1) \]

Initial condition
\[ \{q, p, \zeta\} = (1.6, 0, 0) \]

\[ p > 0 \; ; \; p < 0 \]
Is This a Nosé – Hoover Knot?

\[
\begin{align*}
\dot{q} &= p & \text{Initial condition} \\
\dot{p} &= -q - \zeta p & \{q, p, \zeta\} = (2.4, 0, 2.4) \\
\dot{\zeta} &= (p^2 - 1) & \zeta > 0 \ ; \ \zeta < 0
\end{align*}
\]

Is This a Nosé – Hoover Knot?

\[
\begin{align*}
\dot{q} &= p & \text{Initial condition} \\
\dot{p} &= -q - \zeta p & \{q, p, \zeta\} = (1.6, 0, 0) \\
\dot{\zeta} &= 10(p^2 - 1) & \zeta > 0 \ ; \ \zeta < 0
\end{align*}
\]
Summary of things it would be good to know up to the present

1. Temperature is best measured with the ideal-gas thermometer.
2. Gauss and Hoover-Leete algorithms are isokinetic and useful.
3. Nosé mechanics is unnecessarily stiff and not very useful.*
4. Nosé-Hoover mechanics is convenient and robust.
5. The Boltzmann Equation covers many applications beyond $\eta$, $\kappa$.
6. The linear Krook-Boltzmann equation is nearly as useful as is $B$.
7. Direct Simulation Monte Carlo is a simple tool for gas problems.
8. Knots should appeal to those interested in topology and chaos.

* These problems demonstrate the usefulness of adaptive integration, already explained by Carol.

Things it would be good to think about:

1. How to make a Boltzmann Equation boundary condition for $P_{xy}$?
2. Can you solve the Krook-Boltzmann equation for a shockwave?
3. Is entropy a dynamical property of a single dynamical system?