# Equations of Motion and Numerical Integration

# Integrators

We want to solve, numerically Hamilton's Equations

$$\begin{aligned}\dot{x}_i &= \frac{p_i}{m_i} \\ \dot{p}_i &= \frac{-\partial\phi(\mathbf{x})}{\partial x_i} = F_i(\mathbf{x})\end{aligned}$$

where

$$\begin{aligned}H &= \sum_i \frac{p_i^2}{2m_i} + \phi(\mathbf{x}) \\ \dot{x}_i &= \frac{\partial H}{\partial p_i} \\ \dot{p}_i &= -\frac{\partial H}{\partial x_i}\end{aligned}$$

# Liouville Operator Formalism and Numerical Integrators

## The Problem

Develop a formalism that can be used to construct algorithms that in a consistent and simple way.

The algorithms should be reversible and exact to some order in the time step.

The algorithms should reflect as many analytical properties of the true dynamics as possible. In particular, conserved quantities should be generated.

# Symplectic Property

Hamiltonian flows possess the symplectic property,

$$\mathbf{J}(t)\mathbf{M}\mathbf{J}^T(t) \;=\; \mathbf{M}$$

where

$$\mathbf{J}(t) \;=\; \begin{pmatrix} \frac{\partial \mathbf{p}(t)}{\partial \mathbf{p}(0)} & \frac{\partial \mathbf{p}(t)}{\partial \mathbf{q}(0)} \\ \frac{\partial \mathbf{q}(t)}{\partial \mathbf{p}(0)} & \frac{\partial \mathbf{q}(t)}{\partial \mathbf{q}(0)} \end{pmatrix}$$

$$\mathbf{M} \;=\; \begin{pmatrix} 0 & \mathbf{I} \\ -\mathbf{I} & 0 \end{pmatrix}$$

which implies phase space volume preservation, $\det \mathbf{J}(t) = 1$.

# Symplectic Property

In addition, the converse is true. The symplectic property implies the existence of a Hamiltonian!! If the dynamics arises from a Hamiltonian, then, of course, the Hamiltonian is conserved.

Lets design, reversible symplectic algorithms!!

# The Formalism

Assume a set of coupled first order differential equations with

$$\begin{aligned} \dot{x}_i &= \frac{p_i}{m_i} \\ \dot{p}_i &= \frac{-\partial \phi(\mathbf{x})}{\partial x_i} = F_i(\mathbf{x}) \end{aligned}$$

The time dependence of any function of the $\mathbf{x}$ and $\mathbf{p}$ can be written as

$$\begin{aligned} \dot{\Gamma} &= \sum_{i=1}^{N} \frac{p_i}{m_i} \frac{\partial \Gamma}{\partial x_i} + \sum_{i=1}^{N} F_i(\mathbf{x}) \frac{\partial \Gamma}{\partial p_i} \\ \dot{\Gamma} &= iL\,\Gamma \\ \Gamma(t) &= e^{iLt}\Gamma(0) \end{aligned}$$

where $L$ is called the Liouville operator.

If $\Gamma = \{\mathbf{x}, \mathbf{p}\}$ then the state of the system at time $t$ is written in very nice form. Can this formalism be used to generate numerical solutions?

# The Trotter Formula

The analogy that the Liouville operator formalism gives with quantum mechanics can be exploited and a short time approximation to the time evolution operator constructed

$$
\begin{aligned}
e^{iLt} &= \left[e^{\frac{iLt}{P}}\right]^P \\
e^{iLt} &= \left[e^{\frac{iL_1\Delta t}{2}} e^{iL_2\Delta t} e^{\frac{iL_1\Delta t}{2}}\right]^P + \mathcal{O}(t\Delta t^2)
\end{aligned}
$$

where

$$
\begin{aligned}
iL &= iL_1 + iL_2 \\
\Delta t &= \frac{t}{P}
\end{aligned}
$$

# The Trotter-Suzuki Formula

The state of the system at time, $t$ is thus generated by $P$ succesive applications of the short time approximation to the initial state $\Gamma(0)$

$$\begin{aligned}\Gamma(\Delta t) &= e^{\frac{iL_1\Delta t}{2}} e^{iL_2\Delta t} e^{\frac{iL_1\Delta t}{2}} \Gamma(0)\\ &\cdot\\ &\cdot\\ \Gamma(t) &= e^{\frac{iL_1\Delta t}{2}} e^{iL_2\Delta t} e^{\frac{iL_1\Delta t}{2}} \Gamma(t-\Delta t)\end{aligned}$$

While the Trotter-Suzuki formula is not exact, it has GREAT properties.

# Reversiblity

First, as $\exp(iL_i\Delta t)\exp(-iL_i\Delta t) = 1$ the unitary property of the time evolution operator is exactly preserved.

All algorithms generated by this formalism will be time reversible.

# Symplectic Property

The Trotter-Suzuki approach allows an error analysis to be performed and error bounds to be constructed. Applying the BCH formula to the integrator yields,

$$
\begin{aligned}
e^{i\tilde{L}\Delta t} &= e^{\Delta t\left[iL+\sum_{k=1}^{\infty}\Delta t^{2k}C^{(k)}\right]} = e^{\Delta t\left[iL+\sum_{k=1}^{\infty}\Delta t^{2k}i\tilde{L}^{(k)}\right]} \\
\prod_{k=1}^{P} e^{i\tilde{L}\Delta t} &= e^{P\Delta t\left[iL+\sum_{k=1}^{\infty}\Delta t^{2k}i\tilde{L}^{(k)}\right]} = e^{t\left[iL+\sum_{k=1}^{\infty}\Delta t^{2k}i\tilde{L}^{(k)}\right]}
\end{aligned} \quad ,
$$

because the commutator of any two Liouville operators yields a third,

$$
\tilde{L}^{(k)} = \tilde{G}^{(k)} \cdot \nabla_x
$$

and, for example,

$$
\begin{aligned}
C^{(1)} &= \frac{1}{24}[L_1 + 2L_2, [L_1, L_2]] \\
&\equiv i\tilde{L}^{(1)}
\end{aligned}
$$

That is, Lioville operators are composed of first derivities $iL = G(x)\cdot\nabla_x$ and communators of two operators of this form, yield a third of this form.

# Symplectic Property

Therefore, the integrator generates the solution to the continuous time equations of motion,

$$\begin{aligned} \mathbf{x}(t) &= e^{i\tilde{L}t}\mathbf{x}(0) \\ \dot{\mathbf{x}}(t) &= (i\tilde{L})e^{i\tilde{L}t}x(0) = i\tilde{L}\mathbf{x}(t) \\ \dot{\mathbf{x}} &= \sum_{k=0}^{\infty} \tilde{G}^{(k)}(\mathbf{x})\Delta t^{2k} \end{aligned}$$

at intervals, $n\Delta t$, where $n$ is an integer and $\tilde{G}^{(0)}(\mathbf{x}) \equiv G(\mathbf{x})$. Thus, the dynamics is correct up to the desired order!!

# Symplectic Property

The above analysis allows the choice of decomposition, $L = L_1 + L_2$ to be connected directly to properties of the "flow" generated by the integrator.

For example, if the original equations are Hamiltonian, and $iL_1, iL_2$ are each derivable from Hamiltonians, $h_1(\mathbf{p}, \mathbf{q}) + h_2(\mathbf{p}, \mathbf{q}) = H(\mathbf{p}, \mathbf{q})$, then each $\tilde{G}^{(k)}(\mathbf{p}, \mathbf{q})$ is Hamiltonian, $\tilde{G}^{(k)}(\mathbf{p}, \mathbf{q}) = \nabla_\Gamma \tilde{H}^{(k)}(\mathbf{p}, \mathbf{q})$.

That is, the commutator of two Hamiltonian Liouville operators yields a third, whose associated Hamiltonian is given by the Poisson bracket, $h_3 = \{h_1, h_2\}$,

$$\{h_1, h_2\} = \frac{\partial h_2}{\partial p}\frac{\partial h_1}{\partial q} - \frac{\partial h_2}{\partial q}\frac{\partial h_1}{\partial p}$$

Note, the rich analogies with quantum mechanics!

# Symplectic Property

Therefore one can define a Hamiltonian

$$\tilde{H} = \sum_k \tilde{H}^{(k)}(\mathbf{x})\Delta t^{2k} = H + \mathcal{O}(\Delta t^2)$$

which generates the "dynamics" of the interator and is exactly preserved by the integrator. The integrator is, therefore, symplectic!!!!!!!!

# Symplectic Property

First, since $\tilde{H}$ is conserved, $\Delta H = \tilde{H} - H$ is bounded. There is no secular growth in the total energy.

Second, since $\tilde{H}$ is conserved, closed orbits can exist. They are not the orbits of $H$ but deviate by at most $\mathcal{O}(\Delta t^2)$.

Of course, $\Delta t$ must be within the radius of convergence of the series defining $\tilde{H}$.

# Simple Algorithms

Consider the most basic Trotter-Suzuki break up possible

$$\begin{aligned} iL_1 &= \frac{F(x)}{m}\frac{\partial}{\partial \mathrm{v}} \\ iL_2 &= \mathrm{v}\frac{\partial}{\partial x} \end{aligned}$$

where the momenta has been replaced by the more traditional velocity due to the extreme simplicity of the Hamiltonian system in question.m

Here, $h_1 = \phi(x)$ and $h_2 = p^2/2m$.

# Simple Algorithms : Tools

In order to evaluate the action of the approximate evolution operator on $\Gamma$ we need to apply the translation operator,

$$\begin{aligned}\exp\left[a\frac{d}{dx}\right] f(x) &= \sum_{k=0} \frac{a^k}{k!}\frac{d^k f(x)}{dx^k} \\ &= f(x+a)\end{aligned}$$

and

$$\exp\left[a\frac{d}{dx}\right] g(y) = g(y)$$

if $y$ is independent of $x$.

# Simple Algorithms : Evaluation

Thus, the action of this short time evolution operator on $x$ and v gives

$$\begin{aligned} x(\Delta t) &= e^{\frac{iL_1 \Delta t}{2}} e^{iL_2 \Delta t} x(0) \\ &= e^{\frac{iL_1 \Delta t}{2}} \left[ x(0) + \mathrm{v}(0)\Delta t \right] \\ &= x(0) + \mathrm{v}(0)t + \frac{F(x(0))\Delta t^2}{2m} \end{aligned}$$

and

$$\mathrm{v}(\Delta t) = \mathrm{v}(0) + \frac{\Delta t}{2m}\left[F(x(0)) + F(x(\Delta t))\right]$$

where the identity $\exp(c\frac{\partial}{\partial x})f(x) = f(x+c)$ is used.

# Simple Algorithms : Evaluation

This is famous velocity Verlet algorithm!!!!

$$\begin{aligned} x(\Delta t) &= x(0) + \mathrm{v}(0)t + \frac{F(x(0))\Delta t^2}{2m} \\ \mathrm{v}(\Delta t) &= \mathrm{v}(0) + \frac{\Delta t}{2m}\left[F(x(0)) + F(x(\Delta t))\right] \end{aligned}$$

# Simple Algorithms

Velocity Verlet is Symplectic! This can be seen by generating the Jacobian analytically and testing it (YUCH!!) or by realizing that $iL_1$ is derivable from $h_1 = \phi(x)$ and $iL_2$ is derivable from $h_2 = p^2/2m$. Thus, Velocity Verlet is derivable from a Hamiltonian.

For example, velocity Verlet integration of $H = p^2/2m + m\omega^2 x^2/2$ conserves

$$\tilde{H}(p, q; \Delta t) = \left( \frac{p^2 \left[1 - \left(\frac{\omega \Delta t}{2}\right)^2\right]^{-\frac{1}{2}}}{2m} + \frac{m\omega^2 q^2 \left[1 - \left(\frac{\omega \Delta t}{2}\right)^2\right]^{\frac{1}{2}}}{2} \right) \frac{\cos^{-1}\left(1 - \frac{\omega^2 \Delta t^2}{2}\right)}{|\omega \Delta t|}$$

The integrator has closed orbits for $\omega\Delta t < 2$ and yields a good approximation to the true trajectories if $\omega\Delta t << 2$ (i.e. $\lim_{\omega\Delta t \to 0} \tilde{H}(p, q; \Delta t) = H(p, q)$).

In $\lim_{\omega\Delta t \to 2}$, the shadow conserved quantity diverges.. Closed orbits are replaced by hyperbolic, unbound orbits and the integrator becomes unstable. These limitations haunt even the more complex integrators described next.

# Multiple Time Step Integration

Velocities Verlet works GREAT but ...

1) Fast motion caused by strong short range forces: Vibrations in molecules, Path Integrals limit the time step.

2) Long range forces: Molecular and atomic fluids, clusters, have long range forces that are computational expensive to calculate.

3) Combinations of the above are typically present.

How can we use the power of our approach to midigate these difficulties?

# Multiple Time Step Integration

## Reference System Propagator Algorithm: RESPA

Here we take the break up

$$
\begin{aligned}
iL_2 &= \frac{F_{ref}(x)}{m}\frac{\partial}{\partial \mathrm{v}} + \mathrm{v}\frac{\partial}{\partial x} \\
iL_1 &= \frac{\Delta F(x)}{m}\frac{\partial}{\partial \mathrm{v}}
\end{aligned}
$$

where

$$
\Delta F(x) = F(x) - F_{ref}(x)
$$

which is based on the decomposition,

$$
\begin{aligned}
h_1 &= \frac{p^2}{2m} + \phi_{ref}(x) \\
h_2 &= \phi(x) - \phi_{ref}(x)
\end{aligned}
$$

Applying the Trotter-Suzuki Formula yields

$$
\begin{aligned}
x(\Delta t) &= e^{\frac{iL_1\Delta t}{2}} e^{iL_2\Delta t} x(0) \\
&= e^{\frac{iL_1\Delta t}{2}} x_{ref}(\Delta t, x(0), \mathrm{v}(0)) \\
&= x_{ref}\left(\Delta t, x(0), \mathrm{v}(0) + \frac{\Delta t}{2m}\Delta F[x(0)]\right)
\end{aligned}
$$

and

$$
\begin{aligned}
\mathrm{v}(\Delta t) &= \mathrm{v}_{ref}\left(\Delta t, x(0), \mathrm{v}(0) + \frac{\Delta t}{2m}\Delta F[x(0)]\right) \\
&+ \frac{\Delta t}{2m}\Delta F[x(\Delta t)]
\end{aligned}
$$

**This looks painful AND we need the analytical solution?**

# RESPA

How can the reference system position and velocities be generated?

$$\begin{aligned} e^{iL_{ref}\Delta t} &= \left[e^{\frac{iL_{ref}t}{n}}\right]^n \\ e^{iL_{ref}\Delta t} &= \left[e^{\frac{iL'_2\delta t}{2}} e^{iL'_1\delta t} e^{\frac{iL'_2\delta t}{2}}\right]^n + \mathcal{O}(\Delta t \delta t^2) \end{aligned}$$

with Velocity Verlet!!

That is, the inner propagator is further decomposed into

$$\begin{aligned} h'_1 &= \frac{p^2}{2m} \\ h'_2 &= \phi_{ref}(x) \end{aligned}$$

# RESPA

Therefore the approximation looks like

$$e^{iL_{approx}\Delta t} \;=\; e^{\frac{iL_2\Delta t}{2}}\left[e^{\frac{iL_1'\delta t}{2}}e^{iL_2'\delta t}e^{\frac{iL_1'\delta t}{2}}\right]^n e^{\frac{iL_2\Delta t}{2}}$$

Note, that $iL_2$ and $iL_2'$ commute and can be combined on the 1st and nth step of the procedure!

# RESPA

Specific : dti=dt/n : dt = n*dti

```
v = v + (F_del*dti*n/2m)
loop over RESPA time steps
   v = v + (F_ref*dti/2m)
   x = x + v*dti
   get_F_ref()
   v = v + (F_ref*dti/2m)
end loop over RESPA time steps
get_F_del()
v = v + (F_del*dti*n/2m)
```

# RESPA

General :using commutation relation

```
loop over RESPA time steps
   v = v + (F_use*dti/2m)
   x = x + v*dti
   get_correct_F(irespa,w)
   v = v + (F_use*dt/2m)
end loop over RESPA time steps
```

get_correct_F(irespa,w) where $w = n$

```
F_use=0
add_F_ref_to_F_use(1)
if(irespa==n)add_F_del_to_F_use(w)
```

# Comparison of Algorithms

The energy conservation as a function of time step will be used to compare the algorithms

$$\Delta E(\Delta t) = \frac{1}{N} \sum_{m=1}^{N} \mid \frac{E(m\Delta t) - E(0)}{E(0)} \mid$$

You can design other measures but I like this one.

# Applications

A) The Lennard Jones Fluid: A study of long range forces

$$
\begin{aligned}
iL_2 &= \sum_{i=1}^{N} \frac{\mathbf{F}_i^{ref}(\mathbf{r})}{m} \cdot \nabla_{\mathrm{v}_i} + \mathbf{v} \cdot \nabla_{r_i} \\
iL_1 &= \sum_{i=1}^{N} \frac{\Delta \mathbf{F}_i(\mathbf{r})}{m} \cdot \nabla_{\mathrm{v}_i}
\end{aligned}
$$

where

$$
\mathbf{F}_i^{ref}(\mathbf{r}) = \sum_{i=1}^{N} \mathbf{f}_{i,j}(\mathbf{r}) S(r_{i,j}, r_c, \lambda)
$$

and $S(r, r_c, \lambda)$ is a distance dependent switching function that sets the reference force to zero at $r_c$. The parameter $\lambda$ is the length scale of the switch.

# Applications

B) An oscillator embedded in a L.J. Fluid: A study of separation of time scales.

$$
\begin{aligned}
iL_2 &= \sum_{i=1}^{N} \mathbf{v} \cdot \nabla_{r_i} + \mathbf{f}_1(\mathbf{r}_{12}) \cdot \nabla_{\mathrm{v}_1} + \mathbf{f}_2(\mathbf{r}_{12}) \cdot \nabla_{\mathrm{v}_2} \\
iL_1 &= \sum_{i=1}^{N} \frac{\Delta \mathbf{F}_i(\mathbf{r})}{m} \cdot \nabla_{\mathrm{v}_i}
\end{aligned}
$$

The equation of motion for particles 1 and 2

$$
\begin{aligned}
\mathbf{r}_i(\Delta t) &= \mathbf{r}^i_{ref}\left(\Delta t, \mathbf{r}_i(0), \mathbf{v}(0) + \frac{\Delta t}{2m}\Delta F[\mathbf{r}(0)]\right) \\
\mathbf{v}(\Delta t) &= \mathbf{v}_{ref}\left(\Delta t, \mathbf{r}(0), \mathbf{v}(0) + \frac{\Delta t}{2m}\Delta F[x(0)]\right)
\end{aligned}
$$

the rest are integrated with velocity Verlet.

# Limitation of RESPA

- The RESPA shadow conserved quantity possesses instablities at $\omega_{max}\Delta t = \pi$. Thus the largest time step is controlled by the highest frequency in the problem.
- Long range/short range decompositions for water don't yield enormous increases in computational efficiency.
- Other than NAMD, few simulation codes use it although you can get 2.5x increases in efficiency.

# Extended System Methods

**Outline:**

1. Nosé-Hoover canonical dynamics: Potential difficulties, Numerical studies.
2. Nosé-Hoover chain canonical dynamics: Potential improvements, Numerical studies.
3. Andersen-Hoover isothermal-isobaric dynamics: Equations of motion, Virial theorems, Numerical studies.
4. Parinello-Rahman-Hoover isothermal-isobaric dynamics: Virial theorems, Equations of motion, Numerical studies.

# Extended System Methods

## Nosé-Hoover dynamics: Theory

1. Nosé-Hoover equations of motion:

$$\begin{aligned}
\dot{\mathbf{r}}_i &= \frac{\mathbf{p}_i}{m_i} \\
\dot{\mathbf{p}}_i &= \mathbf{F}_i - \frac{p_\xi}{Q}\mathbf{p}_i \\
\dot{\xi} &= \frac{p_\xi}{Q} \\
\dot{p}_\xi &= \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{m_i} - N_f kT
\end{aligned}$$

   where $N_f$ is the number of degrees of freedom and $\xi$ is the "thermostat".

2. Conserved Quantity:

$$\begin{aligned}
H' &= \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} + \frac{p_\xi^2}{2Q} + \phi(\mathbf{r}, V) + N_f kT\xi \\
\frac{dH'}{dt} &= \sum_{i=1}^{N} \left[\nabla_{\mathbf{p}_i} H' \cdot \dot{\mathbf{p}}_i + \nabla_{\mathbf{r}_i} H' \cdot \dot{\mathbf{r}}_i\right] + \frac{\partial H'}{\partial p_\xi}\dot{p}_\xi + \frac{\partial H'}{\partial \xi}\dot{\xi} = 0
\end{aligned}$$

# Extended System Methods

## Nosé-Hoover dynamics: Theory

3. Dynamical Jacobian and phase space metric tensor

$$
\begin{aligned}
\frac{dJ(t)}{dt} &= -J(t)\left[\frac{d\dot{\xi}}{d\xi} + \frac{d\dot{p}_\xi}{dp_\xi} + \sum_{i=1}^{N}\left(\nabla_{\mathbf{p}_i}\dot{\mathbf{p}}_i + \nabla_{\mathbf{r}_i}\dot{\mathbf{r}}_i\right)\right] \\
J(t) &= \exp[N_f\xi(t) - N_f\xi(0)] \\
d\Gamma_0 &= J(t)d\Gamma_t \\
d\Gamma_0 &= \exp[N_f\xi(t) - N_f\xi(0)]d\Gamma_t \\
\exp[N_f\xi(0)]d\Gamma_0 &= \exp[N_f\xi(t)]d\Gamma_t \\
\sqrt{g}_0 d\Gamma_0 &= \sqrt{g}_t d\Gamma_t \\
\sqrt{g} &= \exp[N_f\xi]
\end{aligned}
$$

4. Phase space volume: Using the Generalize Liouville theorm

$$
\begin{aligned}
Q &= \int d\Gamma\sqrt{g}\prod_k \delta\left(C_k(\Gamma) - C_k^{(0)}\right) \\
Q &= \int dp_\xi \int d\xi \int d\mathbf{r} \int d\mathbf{p}\exp[N_f\xi]\delta(H' - E) \\
Q &= \frac{\exp\left[\frac{E}{kT}\right]}{N_f kT}\int dp_\xi \int d\mathbf{r} \int d\mathbf{p}\exp\left[-\frac{H''}{kT}\right] \\
H'' &= \sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{2m_i} + \frac{p_\xi^2}{2Q} + \phi(\mathbf{r}, V)
\end{aligned}
$$

The canonical phase space volume is correctly generated (within a constant).

# Extended System Methods

## Nosé-Hoover dynamics: Free particle

1. Explore behavior on 1D free particle.

$$\begin{aligned}\dot{x} &= \frac{p}{m}, \quad \dot{p} = \frac{p_\xi}{Q} p \\ \dot{\xi} &= \frac{p_\xi}{Q}, \quad \dot{p_\xi} = \frac{p^2}{m} - kT \\ H' &= \frac{p^2}{2m} + \frac{p_\xi^2}{2Q} + kT\xi \\ J &= \exp[\xi]\end{aligned}$$

   Note, $p(t) = p(0)\exp[\xi(t)]$ or $\xi = \log[p/p_0]$.

2. This constraint must be taken into account:

$$\begin{aligned}Q &= \int dp_\xi \int d\xi \int dp \exp[\xi]\delta(H'(p, p_\xi, \xi) - E)\delta(\xi - \log[p/p_0]) \\ Q &= \int dp_\xi \int dp \left(\frac{p}{p_0}\right) \delta(H''(p, p_\xi) - E) \\ H'' &= \frac{p^2}{2m} + \frac{p_\xi^2}{2Q} + kT \log[p/p_0]\end{aligned}$$

   and the canonical ensemble is **not** generated.

# Extended System Methods

## Nosé-Hoover dynamics: Numerical Studies

1. Study the free particle numerically. How bad is it?
2. Look at the 1D harmonic oscillator numerically: $\phi(x) = m\omega^2 x^2/2$.
3. Potential problems:
   (a) Few extended system degrees of freedom.
   (b) Free particle suggests $\xi$ can be slaved to $p$.
   (c) Does "Q" matter?

# Extended System Methods

## Nosé-Hoover dynamics: Improvements

1. Introduce more extended system degrees of freedom.
2. Shake up $\xi$ which can get "locked".
3. Well, $p_\xi$ is a momentum, too. Why not thermostat $p_\xi$? Why not thermostat $p_\xi$'s thermostat ... Hey, lets make a chain!!!

# Extended System Methods

## Nosé-Hoover chain dynamics: Derivation

1. Equations of motion:

$$
\begin{aligned}
\dot{\mathbf{r}}_i &= \frac{\mathbf{p}_i}{m_i} \\
\dot{\mathbf{p}}_i &= -\mathbf{F}_i - p_i \frac{p_{\xi_1}}{Q_1} \\
\dot{\xi}_i &= \frac{p_{\xi_i}}{Q_i} \\
\dot{p}_{\xi_1} &= \left[ \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{m_i} - N_f kT \right] - p_{\xi_1} \frac{p_{\xi_2}}{Q_2} \\
\dot{p}_{\xi_j} &= \left[ \frac{p_{\xi_{j-1}}^2}{Q_{j-1}} - kT \right] - p_{\xi_j} \frac{p_{\xi_{j+1}}}{Q_{j+1}} \\
\dot{p}_{\xi_M} &= \left[ \frac{p_{\xi_{M-1}}^2}{Q_{M-1}} - kT \right].
\end{aligned}
$$

2. Conversed quantity:

$$
H' = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} + \sum_{k=1}^{M} \frac{p_{\xi_k}^2}{2Q_k} + N_f kT \xi_1 + \sum_{k=2}^{M} kT \xi_k + \phi(\mathbf{r}, V)
$$

# Extended System Methods

## Nosé-Hoover chain dynamics: Derivation

3. Dynamical Jacobian:

$$
\begin{aligned}
\frac{dJ(t)}{dt} &= -J(t)\left[\sum_{k=2}^{M}\left(\frac{d\dot{\xi}_k}{d\xi_k}+\frac{d\dot{p}_{\xi_k}}{dp_{\xi_k}}\right)+\sum_{i=1}^{N}\left(\nabla_{\mathbf{p}_i}\dot{\mathbf{p}}_i+\nabla_{\mathbf{r}_i}\dot{\mathbf{r}}_i\right)\right] \\
J(t) &= \exp[N_f(\xi_1(t)-\xi_1(0))+\sum_{k=2}^{M}\xi_k(t)-\xi_k(0)] \\
\sqrt{g} &= \exp[N_f\xi_1+\sum_{k=2}^{M}\xi_k]
\end{aligned}
$$

4. Phase Space volume:

$$
\begin{aligned}
Q &= \int dp_{\xi_1}\ldots p_{\xi_M}\int d\xi_1\ldots d\xi_M\int d\mathbf{r}\int d\mathbf{p} \\
&\times\ \exp[N_f\xi_1+\sum_{k=2}^{M}\xi_k]\delta(H'-E) \\
Q &\propto \int dp_{\xi_1}\ldots p_{\xi_M}\int d\mathbf{r}\int d\mathbf{p}\exp\left[-\frac{H''}{kT}\right] \\
H'' &= \sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{2m_i}+\sum_{k=1}^{M}\frac{p_{\xi_k}^2}{2Q_k}+\phi(\mathbf{r},V)
\end{aligned}
$$

The canonical phase space volume is correctly generated (within a constant).

# Extended System Methods

**Nosé-Hoover chain dynamics:**

1. Formal Problems with the Free particle overcome.
2. Numerical examples: Free particle and Harmonic oscillator
3. Multidimensional problems: Need one Nosé-Hoover chain per degree of freedom to ensure egodicity (smooth energy landscape). The derivation for multiple thermostats follows straightforwardly.

# Extended System Methods : Numerical Integration

The equations of motion are not Hamiltonian. Althought new theoretical work has demonstracted that a Generalized Symplectic Property can be formulated, a generalized decomposition theorem has not yet been developed to ensure that a shadow conserved quantity is generated by a properly developed integetor.

The best that one can presently do is to ensure that the metric factor, $\sqrt{g}$, the square root of the determinent of the metric tensor, $\mathbf{g}$, is properly generated by the integator.

# Extended System Methods : Numerical Integration

An effective decomposition for the NHC method is given in *Mol. Phys.* (1995). Briefly, one takes the Hamiltonian part of the Liouville operator and sandwhiches it between the non-Hamiltonian NHC evolution. The decomposition of the NHC evolution is designed to preserve the metric factor, $\sqrt{g}$.

$$iL = iL_{Hamiltonian} + iL_{NHC}$$

```
loop over RESPA time steps
   integrate_NHC(dti,v,xnhc,vnhc);
   v = v + (F_use*dti/2m)
   x = x + v*dti
   get_correct_F(irespa,w)
   v = v + (F_use*dt/2m)
   integrate_NHC(dti,v,xnhc,vnhc)
end loop over RESPA time steps
```

Cool new extended system method that avoids resonance artifacts and allows 100fs time steps to be used: *Phys. Rev. Lett.* (2004).

# Extended System Methods : Useful Appendices

Information about Constant Temperature and Constant PRessure methods is provided.

# Extended System Methods : Appendix A

## Nosé-Hoover chain dynamics: Masses

1. Find second order equations for $\dot{\xi}_j$

$$
\begin{aligned}
\frac{d^2\dot{\xi}_1}{dt^2} &= \left\{\frac{2}{Q_1}\left[\sum_{i=1}^{N} \mathbf{F}_i \frac{\mathbf{p}_i}{m_i}\right] - \frac{\dot{\xi}_2}{Q_1}\left[\sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{m_i} - N_f kT\right]\right\} \\
&- \dot{\xi}_1 \left\{\sum_{i=1}^{N} \frac{p_i^2}{m_i} - \dot{\xi}_2^2 + \dot{\xi}_2 \dot{\xi}_3 + \frac{1}{Q_2}\left[Q_1 \dot{\xi}_1^2 - kT\right]\right\} \\
\frac{d^2\dot{\xi}_2}{dt^2} &= \left\{\frac{2\dot{\xi}_1}{Q_2}\left[\sum_{i=1}^{N} \frac{p_i^2}{m_i} - NkT\right] - \frac{\dot{\xi}_3}{Q_2}\left[Q_1 \dot{\xi}_1^2 - kT\right]\right\} \\
&- \dot{\xi}_2 \left\{\frac{2\dot{\xi}_1^2 Q_1}{Q_2} - \dot{\xi}_3^2 + \frac{1}{Q_3}\left[Q_2 \dot{\xi}_2^2 - kT\right] - \dot{\xi}_3 \dot{\xi}_4\right\} \\
\frac{d^2\dot{\xi}_j}{dt^2} &= \left\{\frac{2\dot{\xi}_{j-1}}{Q_{j-1}}\left[Q_{j-2} \dot{\xi}_{j-2}^2 - kT\right] - \frac{\dot{\xi}_{j+1}}{Q_j}\left[Q_{j-1} \dot{\xi}_{j-1}^2 - kT\right]\right\} \\
&- \dot{\xi}_j \left\{\frac{2\dot{\xi}_{j-1}^2 Q_{j-1}}{Q_j} - \dot{\xi}_{j+1}^2 + \frac{1}{Q_{j+1}}\left[Q_j \dot{\xi}_j^2 - kT\right] - \dot{\xi}_{j+1} \dot{\xi}_{j+2}\right\} \\
\frac{d^2\dot{\xi}_{M-1}}{dt^2} &= \left\{\frac{2\dot{\xi}_{M-2}}{Q_{M-1}}\left[Q_{M-3} \dot{\xi}_{M-3}^2 - kT\right] - \frac{\dot{\xi}_M}{Q_{M-1}}\left[Q_{M-2} \dot{\xi}_{M-2}^2 - kT\right]\right\} \\
&- \dot{\xi}_{M-1} \left\{\frac{2\dot{\xi}_{M-2}^2 Q_{M-2}}{Q_{M-1}} - \dot{\xi}_M^2 + \frac{1}{Q_M}\left[Q_{M-1} \dot{\xi}_{M-1}^2 - kT\right]\right\} \\
\frac{d^2\dot{\xi}_M}{dt^2} &= \left\{\frac{2\dot{\xi}_{M-1}}{Q_M}\left[Q_{M-2} \dot{\xi}_{M-2}^2 - kT\right]\right\} - \dot{\xi}_M \left\{\frac{2\dot{\xi}_{M-1}^2 Q_{M-1}}{Q_M}\right\} \qquad (1)
\end{aligned}
$$

# Extended System Methods : Appendix A

**Nosé-Hoover chain dynamics: Masses**

2. Solve each equation individually by taking the phase space average of all other variables

$$
\begin{aligned}
\frac{d^2\dot{\xi}_1}{dt^2} &= -\dot{\xi}_1\left[\frac{2NkT}{Q_1} - \frac{2kT}{Q_2}\right] - \frac{Q_1}{Q_2}\dot{\xi}_1^3 \\
\frac{d^2\dot{\xi}_j}{dt^2} &= -\dot{\xi}_j\left[\frac{2kT}{Q_j} - \frac{2kT}{Q_{j+1}}\right] - \frac{Q_{j-1}}{Q_{j+1}}\dot{\xi}_j^3 \\
\frac{d^2\dot{\xi}_M}{dt^2} &= -\dot{\xi}_M\left[\frac{2kT}{Q_M}\right]
\end{aligned}
$$

3. Take $Q_1 = NkT\tau^2$ and $Q_j = kT\tau^2$ to achieve resonance where $\tau$ is the time scale on which you desire the “thermostatting” to occur.

# Extended System Methods : Appendix B

## Isotropic Constant Pressure: Virial Theorems

1. Pressure virial theorem: External and Internal Pressure balance.

$$
\begin{aligned}
\langle P_{int} - P_{ext} \rangle &= \frac{1}{\Delta} \int dV e^{-\beta P_{ext} V} \int_{D(V)} d\mathbf{p} \int d\mathbf{r} e^{-\beta H(\mathbf{p},\mathbf{r})} (P_{int} - P_{ext}) \\
\langle P_{int} - P_{ext} \rangle &= \frac{\int dV e^{-\beta P_{ext} V} Q(V) \left[ kT \frac{\partial \log[Q(V)]}{\partial V} - P_{ext} \right]}{\int dV e^{-\beta P_{ext} V} Q(V)} = 0 \\
\langle P_{int} \rangle &= P_{ext}
\end{aligned}
$$

2. Work Virial Theorem: External and Internal Work differ by $kT$, the work done by the piston.

$$
\begin{aligned}
\langle (P_{int} - P_{ext}) V \rangle &= \frac{\int dV e^{-\beta P_{ext} V} Q(V) V \left[ kT \frac{\partial \log[Q(V)]}{\partial V} - P_{ext} \right]}{\int dV e^{-\beta P_{ext} V} Q(V)} = -kT \\
\langle P_{int} V \rangle + kT &= P_{ext} \langle V \rangle
\end{aligned}
$$

# Extended System Methods: Appendix B

## Isotropic Constant Pressure: Internal Pressure

1. The canonical partition function:

$$
\begin{aligned}
Q(V) &\propto \int d\mathbf{r} \exp\left[-\beta\phi(\mathbf{r}, V)\right] \\
\mathbf{r} &= V^{1/\mathrm{d}}\mathbf{s} \\
Q(V) &\propto \int d\mathbf{s} V^N \exp\left[-\beta\phi(V^{1/\mathrm{d}}\mathbf{s}, V)\right]
\end{aligned}
$$

2. The internal Pressure:

$$
\begin{aligned}
\langle P_{int} \rangle &= kT \frac{\partial \log[Q(N,V)]}{\partial V} \\
&= \frac{\int d\mathbf{s} e^{-\beta\phi(V^{1/\mathrm{d}}\mathbf{s},V)} V^N \left(\frac{1}{V}\right) \left[NkT - V \frac{d\phi(V^{1/\mathrm{d}}\mathbf{s},V)}{dV}\right]}{\int d\mathbf{s} V^N e^{-\beta\phi(V^{1/\mathrm{d}}\mathbf{s},V)}} \\
&= \frac{\int d\mathbf{r} e^{-\beta\phi(\mathbf{r},V)} \left(\frac{1}{V\mathrm{d}}\right) \left[\mathrm{d}NkT + \sum_k \mathbf{r}_k \cdot \mathbf{F}_k - (\mathrm{d}V) \frac{\partial\phi(\mathbf{r},V)}{\partial V}\right]}{\int d\mathbf{r} e^{-\beta\phi(\mathbf{r},V)}} \\
&= \frac{\int d\mathbf{p} \int d\mathbf{r} e^{-\beta H(\mathbf{r},\mathbf{p},V)} \left(\frac{1}{V\mathrm{d}}\right) \left[\sum_k \frac{\mathbf{p}_k^2}{m_k} + \sum_k \mathbf{r}_k \cdot \mathbf{F}_k - (\mathrm{d}V) \frac{\partial\phi(\mathbf{r},V)}{\partial V}\right]}{\int d\mathbf{r} \int d\mathbf{p} e^{-\beta H(\mathbf{r},\mathbf{p},V)}} \\
&= \left\langle \left(\frac{1}{\mathrm{d}V}\right) \left[\sum_k \frac{\mathbf{p}_k^2}{m_k} + \sum_k \mathbf{r}_k \cdot \mathbf{F}_k - (\mathrm{d}V) \frac{\partial\phi(\mathbf{r},V)}{\partial V}\right] \right\rangle \\
P_{int} &= \left(\frac{1}{\mathrm{d}V}\right) \left[\sum_k \frac{\mathbf{p}_k^2}{m_k} + \sum_k \mathbf{r}_k \cdot \mathbf{F}_k - (\mathrm{d}V) \frac{\partial\phi(\mathbf{r},V)}{\partial V}\right]
\end{aligned}
$$

# Extended System Methods: Appendix B

## Andersen-Hoover NPT dynamics: Derivation

1. Equations of motion: Volume is a dynamical variable!!!

$$\begin{aligned}
\dot{\mathbf{r}}_i &= \frac{\mathbf{p}_i}{m_i} + \frac{p_\epsilon}{W}\mathbf{r}_i \\
\dot{\mathbf{p}}_i &= \mathbf{F}_i - \left(1 + \frac{\mathrm{d}}{N_f}\right)\frac{p_\epsilon}{W}\mathbf{p}_i - \frac{p_\xi}{Q}\mathbf{p}_i \\
\dot{V} &= \frac{\mathrm{d}V p_\epsilon}{W} \\
\dot{p}_\epsilon &= \mathrm{d}V(P_{int} - P_{ext}) + \frac{\mathrm{d}}{N_f}\sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{m_i} - \frac{p_\xi}{Q}p_\epsilon \\
\dot{\xi} &= \frac{p_\xi}{Q} \\
\dot{p}_\xi &= \sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{m_i} + \frac{p_\epsilon^2}{W} - (N_f + 1)kT
\end{aligned}$$

2. Conserved Quantity:

$$\begin{aligned}
H' &= \sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{2m_i} + \frac{p_\epsilon^2}{2W} + \frac{p_\xi^2}{2Q} + \phi(\mathbf{r}, V) + (N_f + 1)kT\xi + P_{ext}V \\
\frac{dH'}{dt} &= \sum_{i=1}^{N}\left[\nabla_{\mathbf{p}_i}H' \cdot \dot{\mathbf{p}}_i + \nabla_{\mathbf{r}_i}H' \cdot \dot{\mathbf{r}}_i\right] + \frac{\partial H'}{\partial p_\xi}\dot{p}_\xi + \frac{\partial H'}{\partial \xi}\dot{\xi} + \frac{\partial H'}{\partial p_\epsilon}\dot{p}_\epsilon \\
&+ \frac{\partial H'}{\partial V}\dot{V} = 0,
\end{aligned}$$

# Extended System Methods: Appendix B

## Andersen-Hoover NPT dynamics: Derivation

3. Dynamical Jacobian:

$$\begin{aligned} \frac{dJ(t)}{dt} &= -J(t)\left[\frac{d\dot{\xi}}{d\xi} + \frac{d\dot{p}_\xi}{dp_\xi} + \frac{d\dot{V}}{dV} + \frac{d\dot{p}_\epsilon}{dp_\epsilon} + \sum_{i=1}^{N}\left(\nabla_{\mathbf{p}_i}\dot{\mathbf{p}}_i + \nabla_{\mathbf{r}_i}\dot{\mathbf{r}}_i\right)\right] \\ J &= \exp[(N_f+1)\xi]. \end{aligned}$$

4. Phase space volume:

$$\begin{aligned} \Delta &= \int dp_\xi \int dp_\epsilon \int d\xi dV \int_{D(V)} d\mathbf{p} \int d\mathbf{r}\, \exp[(N_f+1)\xi]\delta(H'-E) \\ \Delta &= \frac{\exp\left[\frac{E}{kT}\right]}{(N_f+1)kT} \int dp_\xi \int dp_\epsilon \int dV \int_{D(V)} d\mathbf{p} \int d\mathbf{r}\, \exp\left[-\frac{H''}{kT}\right] \\ H'' &= \sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{2m_i} + \frac{p_\epsilon^2}{2W} + \frac{p_\xi^2}{2Q} + \phi(\mathbf{r},V) + P_{ext}V \end{aligned}$$

The isothermal-isobaric phase space volume is correctly generated (within a constant).

# Extended System Methods: Appendix B

## Andersen-Hoover NPT dynamics: Virial Theorems

1. Condition for equilibrium: The phase space average of the time derivitive of any pure function of the phase space variables must vanish,

$$\left\langle \frac{dA(\mathbf{r},\mathbf{p},V)}{dt} \right\rangle = \frac{d}{dt}\langle A(\mathbf{r},\mathbf{p},V)\rangle = 0$$

2. Apply the Work Virial Theorm:

$$\begin{aligned} \langle \dot{p}_\epsilon \rangle &= \left\langle \mathrm{d}V(P_{int} - P_{ext}) + \frac{\mathrm{d}}{N_f}\sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{m_i} - \frac{p_\xi}{Q}p_\epsilon \right\rangle \\ \langle \dot{p}_\epsilon \rangle &= \mathrm{d}\left\{kT + \langle V(P_{int} - P_{ext})\rangle\right\} = 0 \end{aligned}$$

# Extended System Methods: Appendix B

**Andersen-Hoover NPT dynamics: Masses**

1. For optimal performance, the variable $p_\epsilon$ should be thermostatted independently, assigned its own Nosé-Hoover chain.
2. Mass for $\epsilon = (1/\mathrm{d})\log(V)$: $W = (N_f + \mathrm{d})kT\tau^2$

# Extended System Methods: Appendix B

## Andersen-Hoover NPT dynamics: Numerical Examples

1. Free particle: $\phi(\mathbf{r}, V) = 0$
2. Cosine potential:

$$\phi(x, V) = \frac{m\omega^2 V^2}{4\pi^2}\left[1 - \cos\left(\frac{2\pi x}{V}\right)\right]$$

with $m = 1, \omega = 1, Q = 1, Q_W = 9, W = 18, kT = 1, P_{ext} = 1$