Advanced Molecular Dynamics

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Constant Temperature
Naïve approach

Velocity scaling

$$\frac{3}{2}k_B T = \frac{1}{N}\sum_{i=1}^{N}\frac{1}{2}mv_i^2$$

$$v_i \rightarrow v_i\sqrt{\frac{T_{\text{req}}}{\text{T}}}$$

Do we sample the canonical ensemble?

Partition function

$$Q_{NVT} = \frac{1}{h^{3N} N!} \int \mathrm{dp}^N \exp\left[-\beta \sum p_i^2 / 2m\right] \int \mathrm{dr}^N \exp\left[-\beta U\left(\mathrm{r}^N\right)\right]$$

Maxwell-Boltzmann velocity distribution

$$P(p) = \left(\frac{\beta}{2\pi m}\right)^{3/2} \exp\left[-\beta p^2 / 2m\right]$$

$$\left\langle p^2 \right\rangle = \int \mathrm{dp} P(p)\, p^2$$

$$= \left(\frac{\beta}{2\pi m}\right)^{3/2} \int \mathrm{d}p 4\pi p^4 \exp\left[-\beta p^2 / 2m\right]$$

$$= \frac{3m}{\beta}$$

$$P(p)=\left(\frac{\beta}{2\pi m}\right)^{3/2}\exp\left[-\beta p^2/2m\right]$$

$$\left\langle p^2\right\rangle=\int \mathrm{d}p P(p)\,p^2=\left(\frac{\beta}{2\pi m}\right)^{3/2}\int \mathrm{d}p 4\pi p^4\exp\left[-\beta p^2/2m\right]\;=\frac{3m}{\beta}$$

$$\left\langle p^4\right\rangle=\int \mathrm{d}p P(p)\,p^4=15\left(\frac{m}{\beta}\right)^2$$

Fluctuations in the momentum:

$$\frac{\sigma^2_{p^2}}{\left\langle p^2\right\rangle^2}=\frac{\left\langle p^4\right\rangle-\left\langle p^2\right\rangle^2}{\left\langle p^2\right\rangle^2}\qquad=\frac{15\left(m/\beta\right)^2-\left(3m/\beta\right)^2}{\left(3m/\beta\right)^2}=\frac{2}{3}$$

Fluctuations in the temperature

$$\frac{\sigma^2_{k_BT}}{\left\langle k_BT\right\rangle^2}=\frac{\left\langle \left(k_BT\right)^2\right\rangle-\left\langle k_BT\right\rangle^2}{\left\langle k_BT\right\rangle^2}\;=\frac{2}{3N}$$

$$\left\langle k_B T \right\rangle = \left\langle \frac{1}{3N} \sum_{i=1}^{N} p_i^2 / m \right\rangle = \frac{1}{3Nm} N \left\langle p^2 \right\rangle$$

$$\left\langle \left(k_B T\right)^2 \right\rangle = \left\langle \frac{1}{\left(3mN\right)^2} \left(\sum_{i=1}^{N} p_i^2 \right)^2 \right\rangle$$

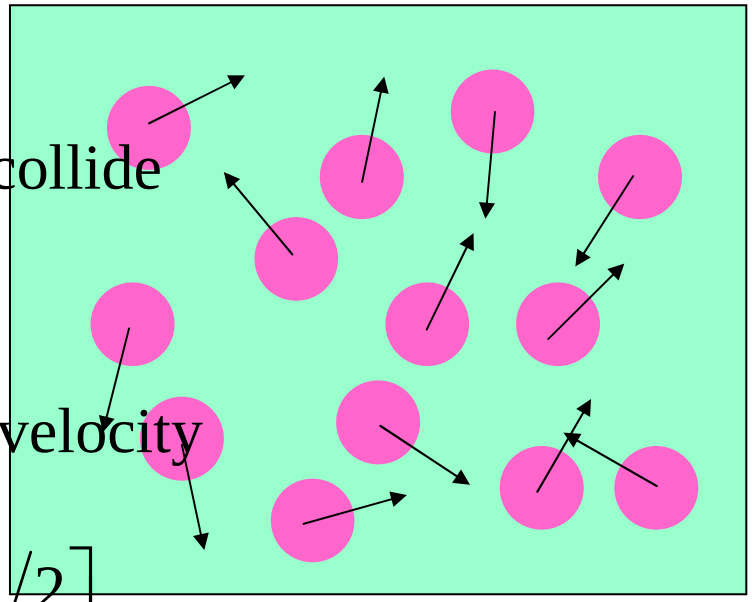
$$= \left\langle \frac{1}{\left(3mN\right)^2} \left(\sum_{i=1}^{N} p_i^4 + \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j \neq i}}^{N} p_i^2 p_j^2 \right) \right\rangle$$

$$= \frac{1}{\left(3mN\right)^2} \left(N \left\langle p^4 \right\rangle - N\left(N-1\right) \left\langle p^2 \right\rangle^2 \right)$$

$$\frac{\sigma_{k_B T}^2}{\left\langle k_B T \right\rangle^2} = \frac{N \left\langle p^4 \right\rangle - N\left(N-1\right) \left\langle p^2 \right\rangle^2 - \left(N \left\langle p^2 \right\rangle \right)^2}{\left(N \left\langle p^2 \right\rangle \right)^2}$$

$$= \frac{1}{N} \frac{\left\langle p^4 \right\rangle - \left\langle p^2 \right\rangle^2}{\left\langle p^2 \right\rangle^2} = \frac{2}{3N}$$

Andersen thermostat



Every particle has a fixed probability to collide with the Andersen demon

After collision the particle is give a new velocity

$$P(v) = \left(\frac{\beta}{2\pi m}\right)^{3/2} \exp\left[-\beta m v^2/2\right]$$

The probabilities to collide are uncorrelated (Poisson distribution)

$$P(t;\nu) = \nu \exp\left[-\nu t\right]$$

Algorithm 14 (Molecular Dynamics: Andersen Thermostat)

```
program md_Andersen                    MD at constant temperature
call init(temp)                        initialization
call force(f,en)                       determine the forces
t=0
do while (t.lt.tmax)                   MD loop
   call integrate(1,f,en,temp)         first part of the eqs. of motion
   call force(f,en)                    determine the forces
   call integrate(2,f,en,temp)         second part of eqs. of motion
   t=t+dt
   call sample                         sample averages
enddo
stop
end
```

Algorithm 15 (Equations of Motion: Andersen Thermostat)

$$e^{(iL_p \Delta t/2)} : \mathbf{v}(t) \rightarrow \mathbf{v}(t) + \frac{\Delta t}{2m}\dot{\mathbf{f}}(0)$$

```
 subroutine integrate(switch,f
                     ,en,temp)
 if (switch.eq.1) then
    do i=1,npart
       x(i)=x(i)+dt*v(i)+
+        dt*dt*f(i)/2
       v(i)=v(i)+dt*f(i)/2
    enddo
 else if (switch.eq.2) then
    tempa=0
    do i=1,npart
       v(i)=v(i)+dt*f(i)/2
       tempa=tempa+v(i)**2
    enddo
    tempa=tempa/(s*npart)
    sigma=sqrt(temp)
    do i=1,npart
      if (ranf().lt.nu*dt) then
         v(i)=gauss(sigma)
      endif
    enddo
 endif
 return
 end
```

integrate equations of motion: with Andersen thermostat

first step velocity Verlet

update positions current time

first update velocity

second step velocity Verlet

$$e^{(iL_r \Delta t)} : \mathbf{r}(t + \Delta t) \rightarrow \mathbf{r}(t) + \Delta t \dot{\mathbf{v}}(t + \Delta t/2)$$

second update velocity

$$e^{(iL_p \Delta t/2)} : \mathbf{v}(t + \Delta t) \rightarrow \mathbf{v}(t + \Delta t/2) + \frac{\Delta t}{2m}\dot{\mathbf{f}}(t)$$

instantaneous temperature

Andersen heat bath

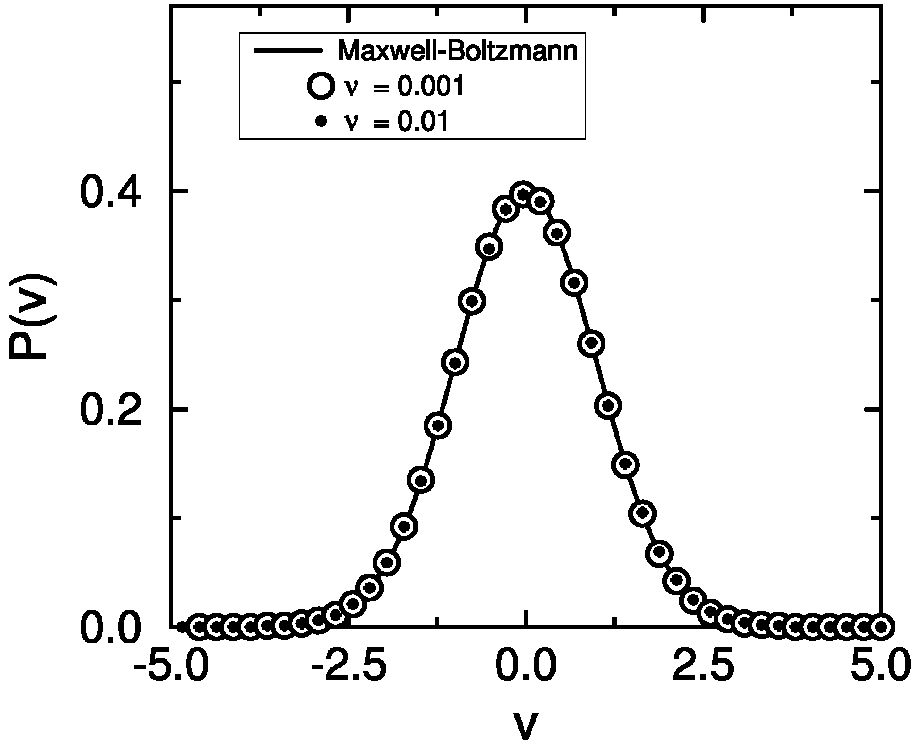
test for collision with bath

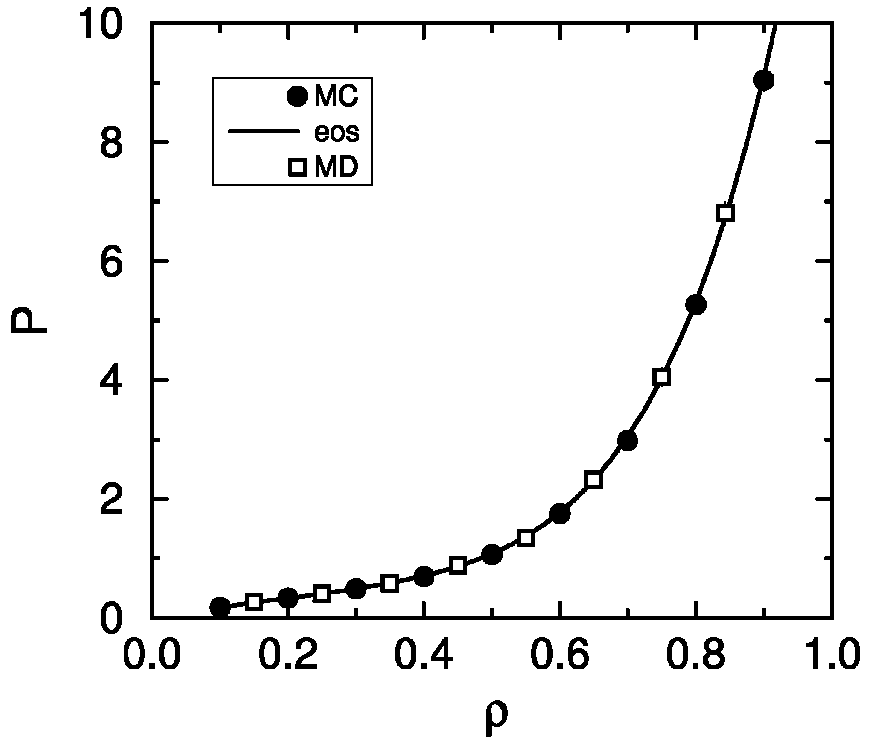
give particle Gaussian velocity

Velocity Verlet:

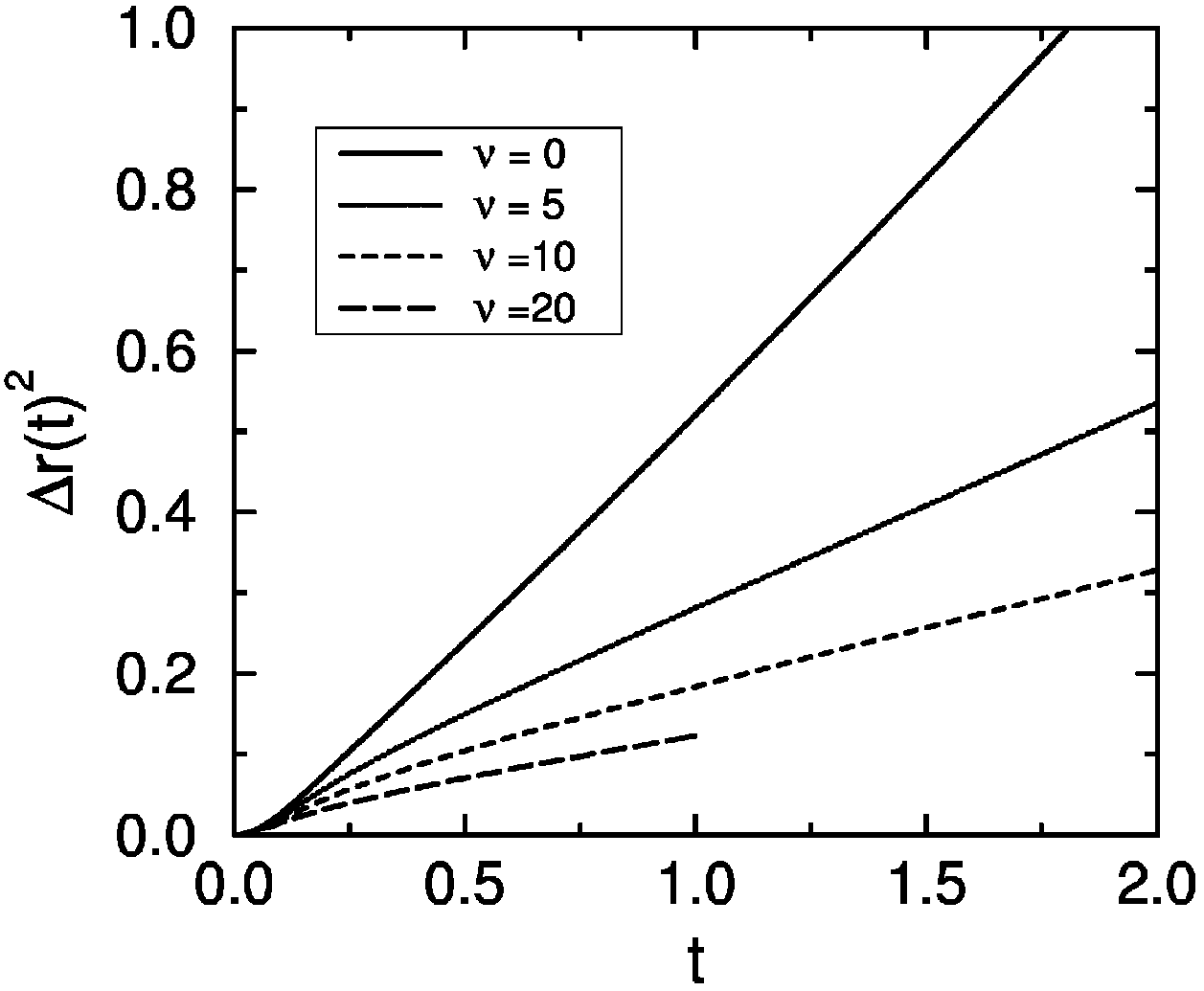
$$e^{(iL_p \Delta t/2)} e^{(iL_r \Delta t)} e^{(iL_p \Delta t/2)}$$

Andersen thermostat: static properties





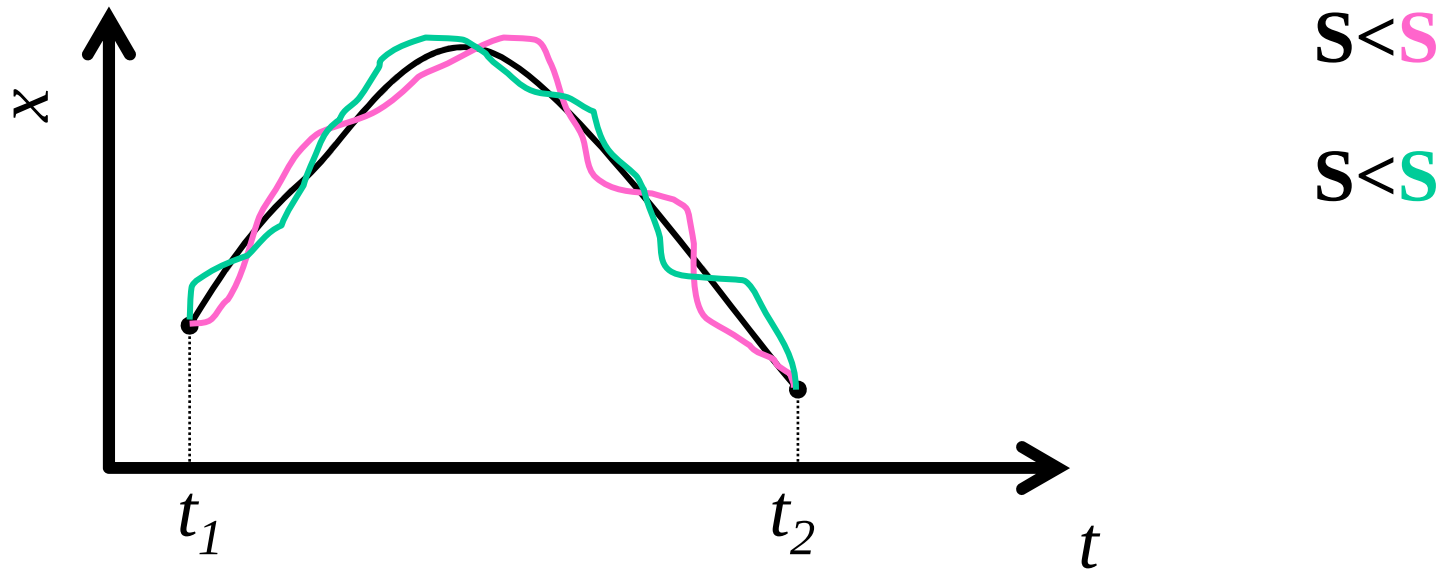
Andersen thermostat: dynamic properties



Hamiltonian & Lagrangian

The equations of motion give the path that starts at t_1 at position $x(t_1)$ and end at t_2 at position $x(t_2)$ for which the action (S) is the minimum

$$S = \int_{t_1}^{t_2} \mathrm{d}t \left[U_k - U_p \right]$$



S<S

S<S

Example: free particle

Consider a particle in vacuum:

$$U_p = 0$$

$$U_k = \frac{1}{2}mv^2$$

v(t)=v$_{av}$

$$S = \int_{t_1}^{t_2} \mathrm{d}t \left[U_k - U_p \right] = \int_{t_1}^{t_2} \mathrm{d}t \left[\frac{1}{2}mv^2 \right]$$

$$v(t) = v_{av} + \eta(t)$$

$$S = \frac{1}{2}m\int_{t_1}^{t_2} \mathrm{d}t \left[v_{av} + \eta(t) \right]^2$$

$$= S_{av} + m\int_{t_1}^{t_2} \mathrm{d}t v_{av}\eta(t) + \frac{1}{2}m\int_{t_1}^{t_2} \mathrm{d}t \left[\eta(t) \right]^2$$

$$= S_{av} + \frac{1}{2}m\int_{t_1}^{t_2} \mathrm{d}t \left[\eta(t) \right]^2$$

$$v_{av} \equiv \int_{t_1}^{t_2} \mathrm{d}t v(t) \Big/ \int_{t_1}^{t_2} \mathrm{d}t$$

$$= \frac{1}{t_2 - t_1}\int_{t_1}^{t_2} \mathrm{d}t \left[v_{av} + \eta(t) \right]$$

$$v_{av} = v_{av} + \frac{1}{t_2 - t_1}\int_{t_1}^{t_2} \mathrm{d}t \eta(t)$$

$$\int_{t_1}^{t_2} \mathrm{d}t \eta(t) = 0$$

η(t)=0 for all t

Always > 0!!

Lagrangian

Cartesian coordinates $(x, \dot{x})$ (Newton) $\rightarrow$

Generalized coordinates $(q, \dot{q})$ (?)

Lagrangian

$$L\ (x, \dot{x}) = U_k(\dot{x}) - U_p(x)$$

$$L\ (q, \dot{q}) = U_k(\dot{q}) - U_p(q)$$

Action

$$S = \int_{t_1}^{t_2} \mathrm{d}t L\ (x, \dot{x}) = \int_{t_1}^{t_2} \mathrm{d}t L\ (q, \dot{q})$$

The true path plus deviation

$$q(t) = \underline{q}(t) + \eta(t) \longrightarrow$$

$$S[q+\eta] = S[q] + \int_{t_1}^{t_2} \mathrm{d}t \left[-\frac{d}{dt} \frac{\partial L\ (q, \dot{q})}{\partial \dot{q}} + \frac{\partial L\ (q, \dot{q})}{\partial q} \right] \eta(t)$$

Should be 0 for all paths

$$S[q+\eta] = S[q] + \int_{t_1}^{t_2} \mathrm{d}t \left[-\frac{d}{dt}\frac{\partial L\ (q,\dot{q})}{\partial \dot{q}} + \frac{\partial L\ (q,\dot{q})}{\partial q} \right] \eta(t)$$

$$\frac{d}{dt}\frac{\partial L\ (q,\dot{q})}{\partial \dot{q}} = \frac{\partial L\ (q,\dot{q})}{\partial q}$$

Equations of motion

Lagrangian equations of motion

Conjugate momentum

$$p_q = \frac{\partial L\ (q,\dot{q})}{\partial \dot{q}} \qquad \dot{p}_q = \frac{\partial L\ (q,\dot{q})}{\partial q}$$

Newton?

$$L\left(q,\dot{q}\right)=U_k\left(\dot{q}\right)-U_p\left(q\right) \qquad \frac{d}{dt}\frac{\partial L\left(q,\dot{q}\right)}{\partial\dot{q}}=\frac{\partial L\left(q,\dot{q}\right)}{\partial q}$$

Valid in any coordinate system: Cartesian

$$L\left(x,\dot{x}\right)=\frac{1}{2}m\dot{x}^2-U_p\left(x\right)$$

Conjugate momentum

$$p_x=\frac{\partial L\left(x,\dot{x}\right)}{\partial\dot{x}}=m\dot{x}$$

$$\dot{p}_x=\frac{\partial L\left(x,\dot{x}\right)}{\partial x}=-\frac{\partial U_p\left(x\right)}{\partial x}=F$$

Lagrangian dynamics

We have:

With these variables we can do statistical thermodynamics

2^{nd} order differential equation

$$(q, \dot{q}) \rightarrow \ddot{q} = \cdots$$

Two 1^{st} order differential equations

$$(q, p) \rightarrow \dot{q} = \cdots \wedge \dot{p} = \cdots$$

Change dependence:

$$(q, \dot{q}) \rightarrow (q, p)$$

Hamiltonian

$$L\ (q,\dot{q}) \qquad (q,\dot{q}) \to (q,p)$$

$$p = \frac{\partial L\ (q,\dot{q})}{\partial \dot{q}} \qquad \dot{p} = \frac{\partial L\ (q,\dot{q})}{\partial q}$$

$$H(q,p) = \dot{q}p - L\ (q,\dot{q})$$

$$\mathrm{d}H(q,p) = \mathrm{d}(qp) - \mathrm{d}L\ (q,\dot{q})$$

$$= \dot{q}\mathrm{d}(p) + p\mathrm{d}(\dot{q}) - \left[\frac{\partial L\ (q,\dot{q})}{\partial q}\mathrm{d}q + \frac{\partial L\ (q,\dot{q})}{\partial \dot{q}}\mathrm{d}\dot{q}\right]$$

$$= -\dot{p}\mathrm{d}q + \dot{q}\mathrm{d}(p)$$

$$\mathrm{d}H(q,p) = \left(\frac{\partial H}{\partial q}\right)\mathrm{d}q + \left(\frac{\partial H}{\partial p}\right)\mathrm{d}p$$

$$\begin{cases} \dot{q} = \dfrac{\partial H}{\partial p} \\ \dot{p} = -\dfrac{\partial H}{\partial q} \end{cases}$$

Hamilton's equations of motion

Newton?

$$L\left(x,\dot{x}\right)=\frac{1}{2}m\dot{x}^2-U_p\left(x\right)$$

Conjugate momentum

$$p=\frac{\partial L\left(x,\dot{x}\right)}{\partial\dot{x}}=m\dot{x}$$

Hamiltonian

$$\begin{aligned}H\left(x,p\right)&=\dot{x}p-L\left(x,\dot{x}\right)\\&=\frac{p^2}{m}-\left[\frac{1}{2}m\dot{x}^2-U_p\left(x\right)\right]\\&=\frac{1}{2}\frac{p^2}{m}+U_p\left(x\right)\end{aligned}$$

$$\dot{x}=\frac{\partial H}{\partial p}=\frac{p}{m}$$

$$\dot{p}=-\frac{\partial H}{\partial x}=-\frac{\partial U_p\left(x\right)}{\partial x}$$

Nosé thermostat

Lagrangian

$$L_{\text{Nose}} = \sum_{i=1}^{N} \frac{1}{2} m s^2 \dot{r}_i^2 - U\left(r^N\right) - \frac{1}{2} Q \dot{s}^2 - \frac{g}{\beta} \ln s$$

Extended system 3N+1 variables

Associated mass

Hamiltonian

$$H_{\text{Nose}} = \sum_{i=1}^{N} \dot{r}_i p_i + \dot{s} p_s - L\left(x, \dot{x}\right)$$

Conjugate momentum

$$p_i = \frac{\partial L}{\partial \dot{r}_i} = m s^2 \dot{r}_i \qquad p_s = \frac{\partial L}{\partial \dot{s}} = Q \dot{s}$$

$$H_{\text{Nose}} = \sum_{i=1}^{N} \frac{p_i^2}{2 m s^2} + \frac{p_s}{2Q} + U\left(r^N\right) + \frac{g}{\beta} \ln s$$

$$p' = p / s$$

$$= H_{\text{Nose}}\left(p', r\right) + \frac{p_s}{2Q} + \frac{g}{\beta} \ln s$$

Nosé and thermodynamics

$$H_{\text{Nose}} = H_{\text{Nose}}(p',r) + \frac{p_s^{\,2}}{2Q} + \frac{L}{\beta}\ln s$$

$$Q_{\text{Nose}} = \frac{1}{N!}\int \mathrm{d}p_s \int \mathrm{d}p^N \int \mathrm{d}r^N \int \mathrm{d}s\,\delta\left(H_{\text{Nose}} - E\right)$$

$$= \frac{1}{N!}\int \mathrm{d}p_s \int \mathrm{d}p'^N \int \mathrm{d}r^N \int \mathrm{d}s\, s^{3N}\,\delta\left(H(p',r) + \frac{p_s^{\,2}}{2Q} + \frac{L}{\beta}\ln s - E\right)$$

$$= \frac{1}{N!}\int \mathrm{d}p_s \int \mathrm{d}p'^N \int \mathrm{d}r^N \int \mathrm{d}s\,\frac{\beta s^{3N+1}}{L}\,\delta\left(s - e^{\frac{\beta}{L}\left[E - H(p',r) - \frac{p_s}{2Q}\right]}\right)$$

Gaussian integral

$$= \frac{1}{N!}\int \mathrm{d}p_s \int \mathrm{d}p'^N \int \mathrm{d}r^N \,\frac{\beta}{L}\, e^{\frac{\beta(3N+1)}{L}\left[E - H(p',r) - \frac{p_s}{2Q}\right]}$$

$$= \frac{C}{N!}\int \mathrm{d}p'^N \int \mathrm{d}r^N e^{-\frac{\beta(3N+1)}{L}H(p',r)} \qquad L = 3N+1$$

$$= \frac{C}{N!}\int \mathrm{d}p'^N \int \mathrm{d}r^N e^{-\beta H(p',r)}$$

Constant plays no role in thermodynamics

Recall

MD $$Q_{NVE} = \frac{1}{N!}\int \mathrm{d}p^N \int \mathrm{d}r^N \delta\left(E - H\left(r^N, p^N\right)\right)$$

MC $$Q_{NVT} = \frac{1}{N!}\int \mathrm{d}p^N \int \mathrm{d}r^N \exp\left[-\beta H\left(r^N, p^N\right)\right]$$

Delta functions

$$\int \mathrm{d}s h'(s)\delta\big(h(s)\big) = \int \mathrm{d}\big[h(s)\big]\delta\big(h(s)\big)$$

$$= \int \mathrm{d}s\,\delta(s - s_0)$$

$$h(s_0) = 0$$

$$\int \mathrm{d}s h'(s)\delta\big(h(s)\big) = \int \mathrm{d}s\,\delta(s - s_0)$$

$$\delta\big(h(s)\big) = \frac{\delta(s - s_0)}{h'(s)}$$

$$\delta\left(h(s)\right)=\frac{\delta\left(s-s_0\right)}{h'(s)}$$

$$\delta\left(H(p',r)+\frac{p_s}{2Q}+\frac{L}{\beta}\ln s-E\right)$$

$$h(s)=H(p',r)+\frac{p_s}{2Q}+\frac{L}{\beta}\ln s-E$$

$$h'(s)=\frac{g}{\beta}\frac{1}{s}\qquad s_0=\exp\left\{\frac{\beta}{L}\left[E-H(p',r)-\frac{p_s}{2Q}\right]\right\}$$

$$\frac{\beta s}{L}\delta\left(s-e^{\frac{\beta}{L}\left[E-H(p',r)-\frac{p_s}{2Q}\right]}\right)$$

Equations of Motion

Lagrangian

$$L_{\text{Nose}} = \sum_{i=1}^{N} \frac{1}{2} m s^2 \dot{r}_i^2 - U\left(r^N\right) - \frac{1}{2} Q \dot{s}^2 - \frac{g}{\beta} \ln s$$

Hamiltonian

$$H_{\text{Nose}} = \sum_{i=1}^{N} \frac{p_i^2}{2ms^2} + \frac{p_s^{\,2}}{2Q} + U\left(r^N\right) + \frac{g}{\beta} \ln s$$

Conjugate momenta

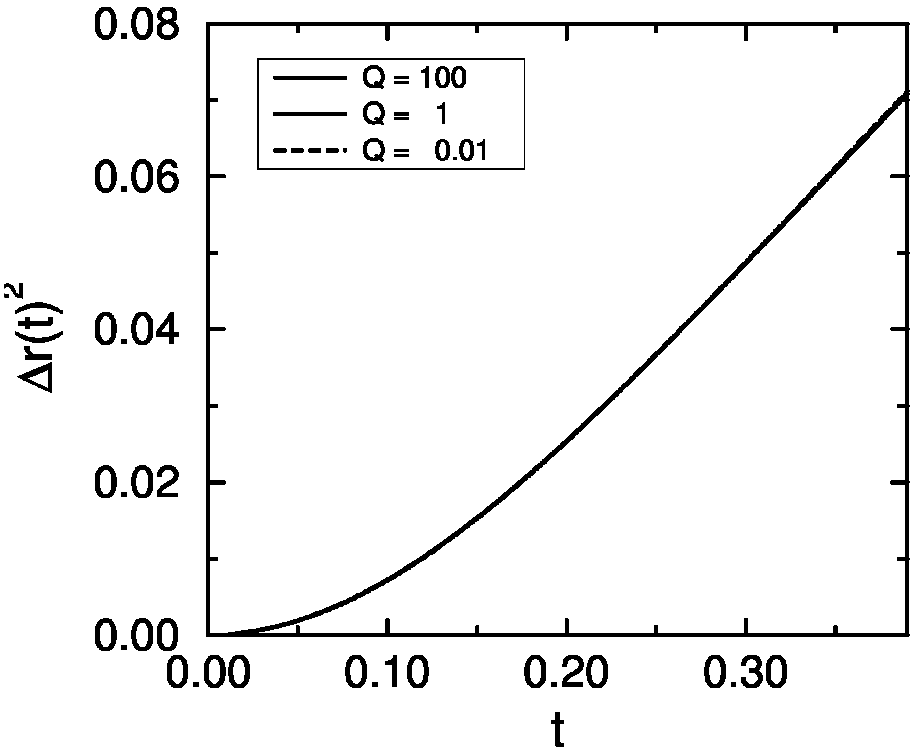
$$p_i = \frac{\partial L}{\partial \dot{r}_i} = m s^2 \dot{r}_i \qquad p_s = \frac{\partial L}{\partial \dot{s}} = Q \dot{s}$$

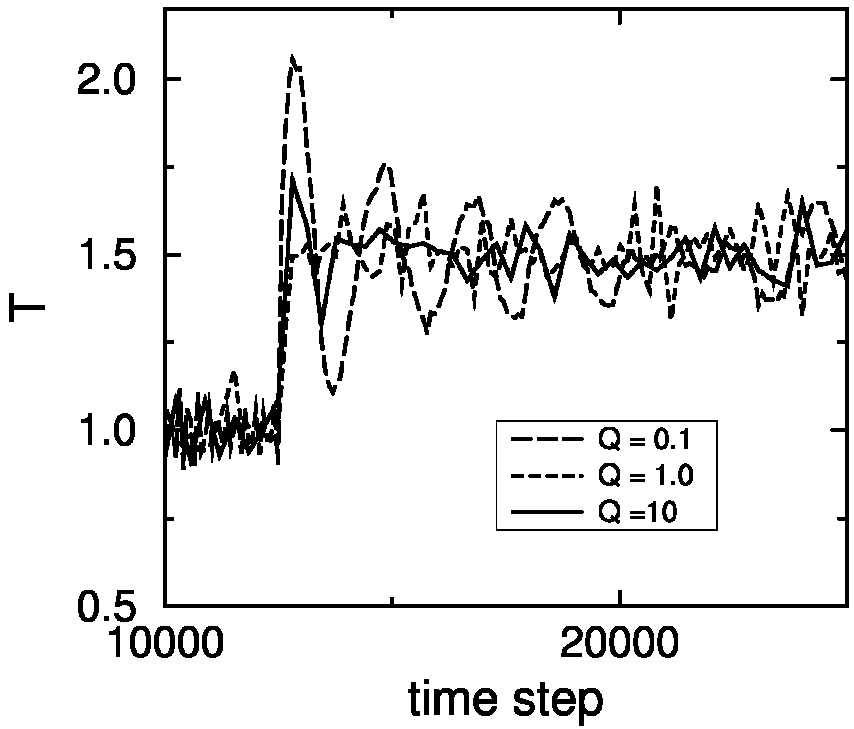
Equations of motion:

$$\frac{\mathrm{d}r_i}{\mathrm{d}t} = \frac{\partial H_{\text{Nose}}}{\partial p_i} = \frac{p_i}{ms^2} \qquad \frac{\mathrm{d}p_i}{\mathrm{d}t} = -\frac{\partial H_{\text{Nose}}}{\partial r_i} = -\frac{\partial U\left(r^N\right)}{\partial r_i}$$

$$\frac{\mathrm{d}s}{\mathrm{d}t} = \frac{\partial H_{\text{Nose}}}{\partial p_s} = \frac{p_s}{Q} \qquad \frac{\mathrm{d}p_s}{\mathrm{d}t} = -\frac{\partial H_{\text{Nose}}}{\partial s} = \frac{1}{s}\left(\sum \frac{p_i^2}{ms^2} - \frac{g}{\beta}\right)$$

Nosé Hoover


0.08
0.06
0.04
0.02
0.00
0.00
0.10
0.20
0.30
t
$\Delta r(t)^2$
Q = 100
Q = 1
Q = 0.01


2.0
1.5
1.0
0.5
10000
20000
time step
T
Q = 0.1
Q = 1.0
Q =10

Multiple Timesteps

Time evolution

Liouville formulation

$$f\left(\mathbf{p}^N,\mathbf{r}^N\right)$$

$$\dot{f} = \dot{\mathbf{r}}\frac{\partial f}{\partial \mathbf{r}} + \dot{\mathbf{p}}\frac{\partial f}{\partial \mathbf{p}}$$

$$\mathrm{i}L \equiv \dot{\mathbf{r}}\frac{\partial}{\partial \mathbf{r}} + \dot{\mathbf{p}}\frac{\partial}{\partial \mathbf{p}}$$

$$\frac{\mathrm{d}f}{\mathrm{d}t} = \mathrm{i}Lf$$

Solution

$$f\left(t\right) = \exp\left(\mathrm{i}Lt\right)f\left(0\right)$$

Beware: this solution is equally useless as the differential equation!

Time evolution

$$i\mathcal{L} \equiv i\mathcal{L}_r + i\mathcal{L}_p = \dot{\mathbf{r}}\frac{\partial}{\partial \mathbf{r}} + \dot{\mathbf{p}}\frac{\partial}{\partial \mathbf{p}}$$

$$f(t) = \exp(i\mathcal{L}_r t) f(0)$$

$$= \exp\left(\dot{\mathbf{r}}(0)t\frac{\partial}{\partial \mathbf{r}} f(0)\right)$$

$$= \sum_{n=0}^{\infty} \frac{(\dot{\mathbf{r}}(0)t)^n}{n!}\frac{\partial^n}{\partial \mathbf{r}^n} f(0)$$

$$= f\left(\mathbf{p}^N(0), (\mathbf{r}(0) + \dot{\mathbf{r}}(\mathbf{0})t)^N\right)$$

Shift of coordinates

$$\mathbf{r}(0) \rightarrow \mathbf{r}(0) + \dot{\mathbf{r}}(\mathbf{0})t$$

Time evolution

$$i\mathcal{L} \equiv i\mathcal{L}_r + i\mathcal{L}_p = \dot{\mathbf{r}}\frac{\partial}{\partial \mathbf{r}} + \dot{\mathbf{p}}\frac{\partial}{\partial \mathbf{p}}$$

$$f(t) = \exp(i\mathcal{L}_r t) f(0)$$

$$= \exp\left(\dot{\mathbf{r}}(0)t\frac{\partial}{\partial \mathbf{r}} f(0)\right)$$

$$= \sum_{n=0}^{\infty} \frac{(\dot{\mathbf{r}}(0)t)^n}{n!}\frac{\partial^n}{\partial \mathbf{r}^n} f(0)$$

$$= f\left(\mathbf{p}^N(0), (\mathbf{r}(0) + \dot{\mathbf{r}}(\mathbf{0})t)^N\right)$$

$$f(t) = \exp(i\mathcal{L}_p t) f(0)$$

$$= \exp\left(\dot{\mathbf{p}}(0)t\frac{\partial}{\partial \mathbf{p}} f(0)\right)$$

$$= \sum_{n=0}^{\infty} \frac{(\dot{\mathbf{p}}(0)t)^n}{n!}\frac{\partial^n}{\partial \mathbf{p}^n} f(0)$$

$$= f\left((\mathbf{p}(0) + \dot{\mathbf{p}}(\mathbf{0})t)^N, \mathbf{r}^N(0)\right)$$

Shift of coordinates

$$\mathbf{r}(0) \rightarrow \mathbf{r}(0) + \dot{\mathbf{r}}(\mathbf{0})t$$

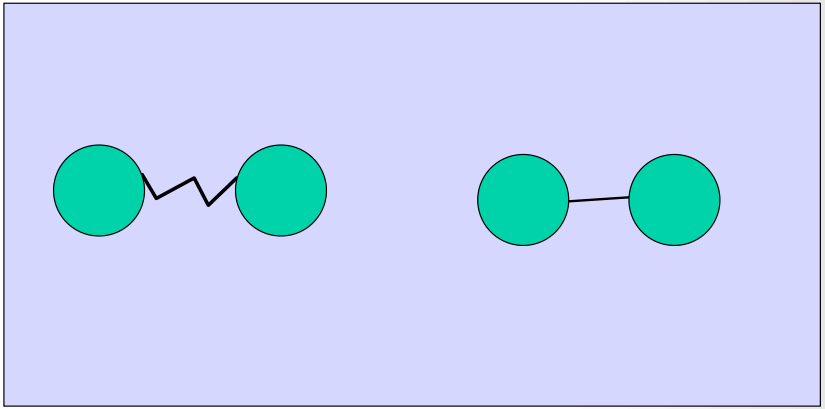
Shift of momenta

$$\mathbf{p}(0) \rightarrow \mathbf{p}(0) + \dot{\mathbf{p}}(\mathbf{0})t$$

Time evolution

Multiple time steps

- What to use for stiff potentials:



  - Fixed bond-length: constraints (Shake)
  - Very small time step

Time evolution

Multiple Time steps

$$\mathbf{F} = \mathbf{F}_{\text{short}} + \mathbf{F}_{\text{long}}$$

$$i\mathcal{L} \equiv i\mathcal{L}_r + i\mathcal{L}_p = \mathbf{v}\frac{\partial}{\partial \mathbf{r}} + \frac{\mathbf{F}}{m}\frac{\partial}{\partial \mathbf{v}}$$

$$i\mathcal{L} \equiv i\mathcal{L}_{\text{short}} + i\mathcal{L}_{\text{long}}$$

$$i\mathcal{L}_{\text{short}} = \frac{\mathbf{F}_{\text{short}}}{m}\frac{\partial}{\partial \mathbf{v}} \qquad i\mathcal{L}_{\text{long}} = \frac{\mathbf{F}_{\text{long}}}{m}\frac{\partial}{\partial \mathbf{v}}$$

Trotter expansion:

$$e^{i(\mathcal{L}_{\text{long}}+\mathcal{L}_{\text{short}}+\mathcal{L}_r)\Delta t} \approx e^{i\mathcal{L}_{\text{long}}\Delta t/2} e^{i(\mathcal{L}_{\text{short}}+\mathcal{L}_r)\Delta t} e^{i\mathcal{L}_{\text{long}}\Delta t/2}$$

Introduce: $\delta t = \Delta t/n$

$$\approx e^{i\mathcal{L}_{\text{long}}\Delta t/2}\left[e^{i\mathcal{L}_{\text{short}}\delta t/2} e^{i\mathcal{L}_r \delta t} e^{i\mathcal{L}_{\text{short}}\delta t/2}\right]^n e^{i\mathcal{L}_{\text{long}}\Delta t/2}$$

Time evolution

$$e^{(i\mathcal{L}_{long}\Delta t/2)} : \mathbf{v}\left(t+\frac{\Delta t}{2}\right) \rightarrow \mathbf{v}(t) + \frac{\Delta t}{2m}\mathbf{f}_{\text{long}}(t)$$

Do i=1,n

$$e^{(i\mathcal{L}_{short}\delta t/2)} : \mathbf{v}\left(t+\frac{\Delta t}{2}+\frac{\delta t}{2}\right) \rightarrow \mathbf{v}(t+\frac{\Delta t}{2}) + \frac{\delta t}{2m}\mathbf{f}_{\text{short}}(t)$$

$$e^{(i\mathcal{L}_{r}\Delta t)} : \mathbf{r}\,(t+\delta t) \rightarrow \mathbf{r}(t) + \delta t\mathbf{v}(t+\Delta t/2+\delta t/2)$$

$$e^{(i\mathcal{L}_{short}\delta t/2)} : \mathbf{v}\left(t+\frac{\Delta t}{2}+\delta t\right) \rightarrow \mathbf{v}\left(t+\frac{\Delta t}{2}+\frac{\delta t}{2}\right) + \frac{\delta t}{2m}\mathbf{f}_{\text{short}}(t+\delta t)$$

enddo

Car-Parrinello Molecular Dynamics

Another Extended Lagrangian Method

Ab Initio Molecular Dynamics

Born-Oppenheimer

- Instantaneous relaxation to electronic ground state
- No coupling ionic and true electronic dynamics

$$M_I \ddot{\mathbf{R}}_I = -\frac{\partial}{\partial \mathbf{R}_I}\left[E(\mathbf{R}^N) + \mathcal{V}_{nn}(\mathbf{R}^N)\right]$$

- Ionic forces from electronic structure calculation
- Knowledge of electronic properties and its time evolution
- Electronic structure methods:
  - DFT
  - Hartree Fock, MCSCF
  - Tight binding, semi-emperical

Beyond Born-Oppenheimer

- Surface hopping
- Time dependent DFT

Born Oppenheimer Molecular Dynamics (DFT)

- Kohn-Sham expression for electronic energy

$$E(\mathbf{R}^N) = \min_n E^{KS}[n(\mathbf{r}), \mathbf{R}^N]$$

1 Determine E^{KS} by direct minimization or self-consistent diagonalization of $\mathcal{H}^{KS}$

2 Evaluate force in ground state using Hellman-Feynman theorem*

$$n(\mathbf{r}) = n_o(\mathbf{r}) = \sum_{i=1}^{\mathcal{N}} \langle \psi_{i,0} | \psi_{i,0} \rangle$$

$$-\frac{\partial}{\partial \mathbf{R}_I} E(\mathbf{R}^N) = \int_\Omega d\mathbf{r}\, n_0(\mathbf{r}) \frac{\partial}{\partial \mathbf{R}_I} \mathcal{V}_{ext}(\mathbf{r}, \mathbf{R}^N)$$

3 Propagate in time

4 Repeat from 1 on

- Verify that dynamics is performed properly by checking constants of motion (Energy).

Born-Oppenheimer MD issues

- Preserving constant of motion requires high accuracy of E_{KS}
- Competition between accuracy and computational cost

Car–Parrinello MD

Define dynamical system with both nuclei and Kohn-Sham orbitals as degrees of freedom.

Car-Parrinello Lagrangian $\mathcal{L}_{CP}$

$$\mathcal{L}_{CP}(\mathbf{R}^N, \dot{\mathbf{R}^N}, \psi^{\mathcal{N}}, \dot{\psi}^{\mathcal{N}}) =$$
$$\sum_I \tfrac{1}{2} M_I \dot{\mathbf{R}}_I^2 + \sum_i \mu \langle \dot{\psi}_i | \dot{\psi}_i \rangle - E_{KS}[n, \mathbf{R}^N] - \sum_{ij} \Lambda_{ij} (\langle \psi_i | \psi_i \rangle - \delta_{ij})$$
$$n(\mathbf{r}) = \sum_{i=1}^{\mathcal{N}} \langle \psi_i | \psi_i \rangle$$

Equations of motion

$$\frac{d}{dt} \frac{\partial \mathcal{L}_{\rm CP}}{\partial \dot{\mathbf{R}}_I} = \frac{\partial \mathcal{L}_{\rm CP}}{\partial \mathbf{R}_I} \qquad \frac{d}{dt} \frac{\delta \mathcal{L}_{\rm CP}}{\delta \langle \dot{\psi}_i \mid} = \frac{\delta \mathcal{L}_{\rm CP}}{\delta \langle \psi_i \mid}$$

$$M_I \ddot{\mathbf{R}}_I = -\frac{\partial E^{\rm KS}}{\partial \mathbf{R}_I} + \sum_{ij} \Lambda_{ij} \frac{\partial}{\partial \mathbf{R}_I} \langle \psi_i \mid \psi_j \rangle$$

$$\mu \mid \ddot{\psi}_i \rangle = -\frac{\delta E^{\rm KS}}{\delta \langle \psi_i \mid} + \sum_j \Lambda_{ij} \mid \psi_j \rangle$$

Car–Parrinello MD: Characteristics

$$\mathcal{L}_{CP}(\mathbf{R}^N, \dot{\mathbf{R}}^N, \psi^{\mathcal{N}}, \dot{\psi}^{\mathcal{N}}) =$$
$$\sum_I \tfrac{1}{2} M_I \dot{\mathbf{R}}_I^2 + \sum_i \mu \langle \dot{\psi}_i | \dot{\psi}_i \rangle - E_{KS}[n, \mathbf{R}^N] - \sum_{ij} \Lambda_{ij} (\langle \psi_i | \psi_i \rangle - \delta_{ij}) =$$
$$\mathcal{K}_n \quad + \quad \mathcal{K}_e \quad - \quad E_{KS} \quad - \quad \text{constraints.}$$

- μ fictitious "electronic mass"
- Λ_{ij} Lagrange multipliers to ensure orthonormality of orbitals
- Time propogation of ionic positions and orbitals simulateously (in BOMD subsequently).
- System not exactly in the ground state -> E_{KS} not ground state energy
- $\mathcal{H}_{CP} = \mathcal{K}_n + \mathcal{K}_e + E_{KS}$ is constant of motion
- if $\mathcal{K}_e$ is ∼constant, $\mathcal{K}_n$+E_{KS} is approximately constant.
- if $\mathcal{K}_e$ is small, $H = \mathcal{K}_n$+E_{KS} is near to BO surface:
  "low electronic temperature" or "cold electrons".

CPMD: Conservation of Energy

Car-Parrinello Total energy rigorlously conserved by construction

- Forces on nuclei

$$\frac{\partial \mathcal{L}}{\partial \mathbf{R}_I} = -\frac{\partial E_{KS}}{\partial \mathbf{R}_I}$$

- Forces on electrons

$$\frac{\delta \mathcal{L}}{\delta \psi_i^*} = -H_{KS}\psi_i$$

- Imposing constraints

So Car-Parrinello total energy $\mathcal{H}_{CP}$ conserved provided the time propagation algorithm is accurate

Does Car-Parrinello MD work?

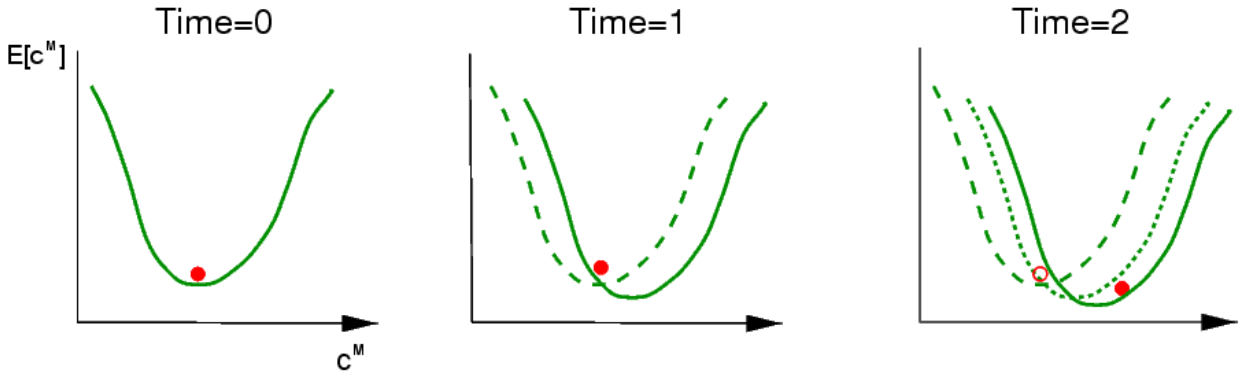
- Adiabatic decoupling

  Imposing "cold electrons" and $\mathcal{K}_e$ is $\sim$constant decoupling of the dynamics of the ions and the orbitals (electrons).

  There is no net energy transfer from ions to "kinetic energy" of orbitals.

  Adiabatic decoupling achieved by non-overlap of frequency spectrum of ionic and orbital motion.

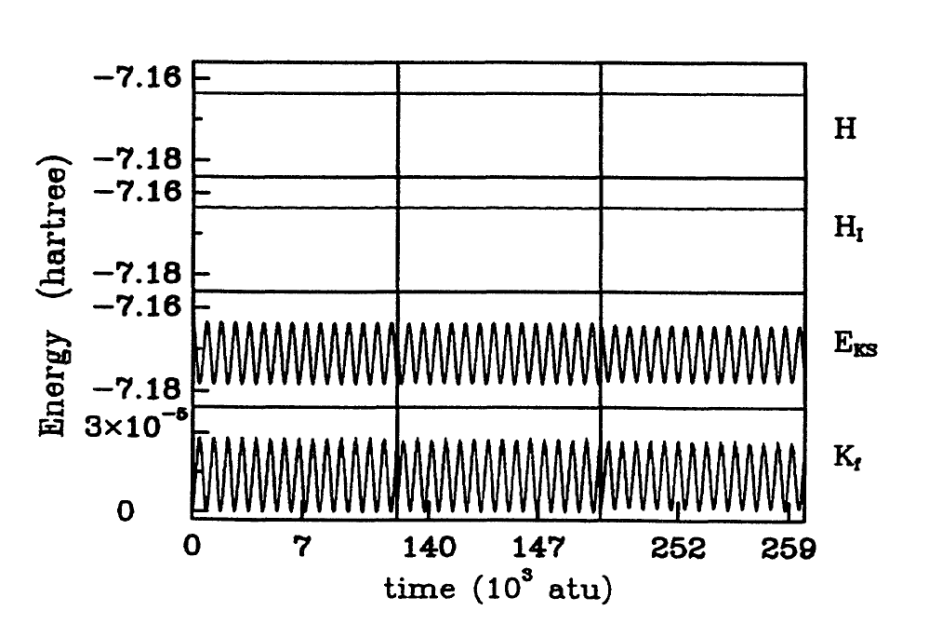
- Pictorial view



Example*: Conservation of Energy

a

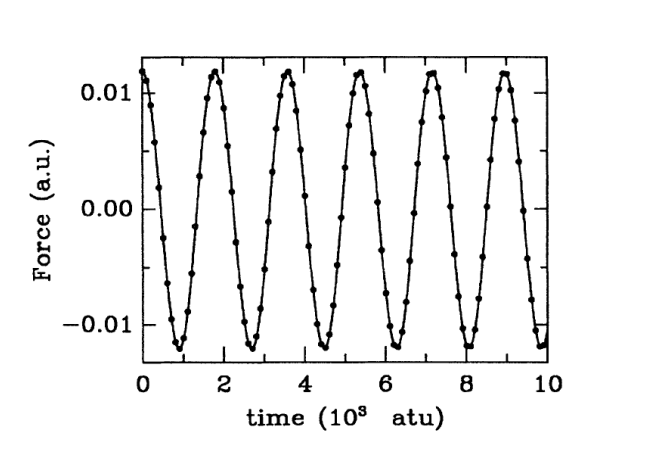
Si-crystal: Time evolution of various components of the energy

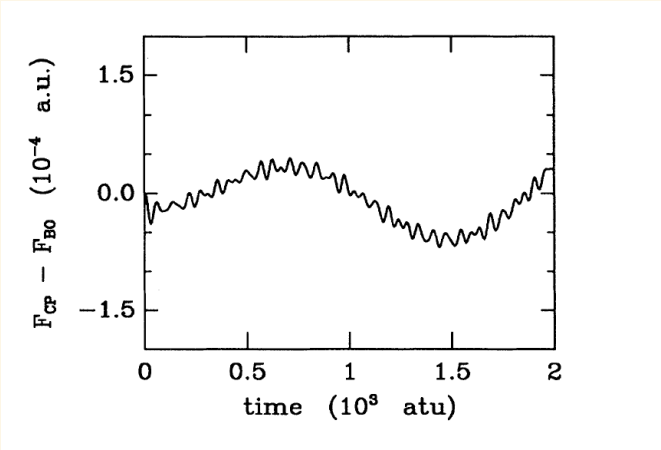


[a]*Pastore, Smargiassi, and Buda, Phys.Rev. A**44** (1991)

Example*: Deviation of BO surface

Si-crystal: Deviations of forces of BO surface are small and oscillating





Car-Parrinello Method: Summary

- Car-Parrinello method can yield very stable dynamical trajectories, provided the electrons and ions are adiabatically decoupled
- The method is best suited for e.g. liquids and large molecules with an electronic gap
- The speed of the method is comparable or faster than using Born-Oppenheimer dynamics — and still more accurate (i.e. stable)