Advanced Molecular Dynamics

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Naïve approach

Velocity scaling

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

$$v_i \to v_i\sqrt{\frac{T_{\mathrm{req}}}{\mathrm{T}}}$$

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

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

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

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

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

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

$$\left\langle p^{2}\right\rangle=\int \mathrm{d}\mathrm{p}P\left(p\right)p^{2}=\left(\frac{\beta}{2\pi m}\right)^{3/2}\int \mathrm{d}p4\pi p^{4}\exp\left[-\beta p^{2}/2m\right]\;=\frac{3m}{\beta}$$

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

Fluctuations in the momentum:

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

Fluctuations in the temperature

$$\frac{\sigma_{k_BT}^{2}}{\left\langle k_BT\right\rangle^{2}}=\frac{\left\langle\left(k_BT\right)^{2}\right\rangle-\left\langle k_BT\right\rangle^{2}}{\left\langle k_BT\right\rangle^{2}}\quad=\frac{2}{3N}$$

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

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

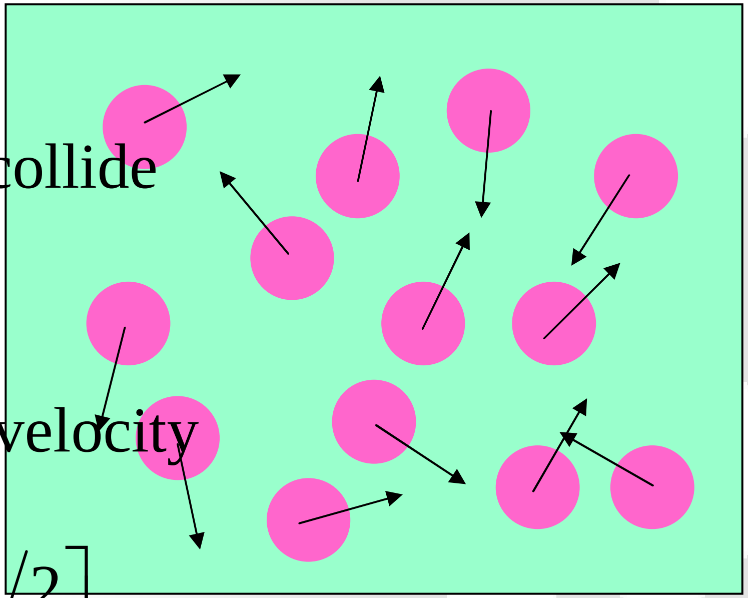
$$= \left\langle \frac{1}{\left(3mN\right)^2} \left(\sum_{i=1}^{N} p_i^4 + \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j \neq i}}^{N} p_i^2 p_j^2 \right) \right\rangle$$

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

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

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

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)

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

```
   subroutine integrate(switch,f        integrate equations of motion:
                            ,en,temp)   with Andersen thermostat
   if (switch.eq.1) then                first step velocity Verlet
      do i=1,npart
         x(i)=x(i)+dt*v(i)+             update positions current time
+          dt*dt*f(i)/2
         v(i)=v(i)+dt*f(i)/2            first update velocity
      enddo
   else if (switch.eq.2) then           second step velocity Verlet
      tempa=0
      do i=1,npart
         v(i)=v(i)+dt*f(i)/2            second update velocity
         tempa=tempa+v(i)**2
      enddo
      tempa=tempa/(s*npart)             instantaneous temperature
      sigma=sqrt(temp)                  Andersen heat bath
      do i=1,npart
        if (ranf().lt.nu*dt) then       test for collision with bath
           v(i)=gauss(sigma)            give particle Gaussian velocity
        endif
      enddo
   endif
   return
   end
```

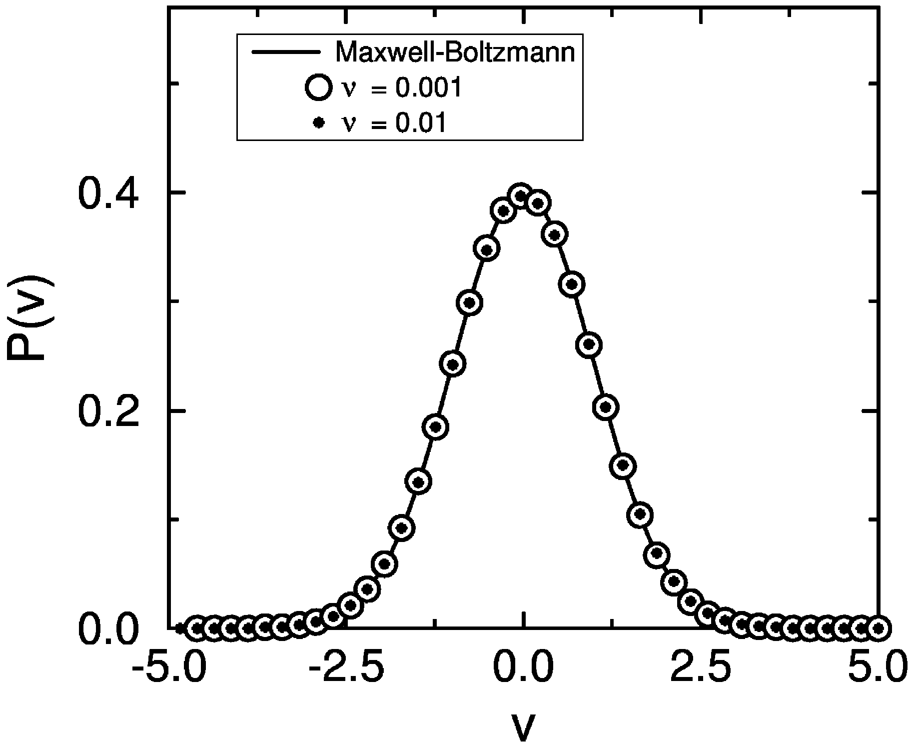
$$e^{(iL_r\Delta t)} : \mathbf{r}(t+\Delta t) \to \mathbf{r}(t) + \Delta t\,\dot{\mathbf{v}}(t+\Delta t/2)$$

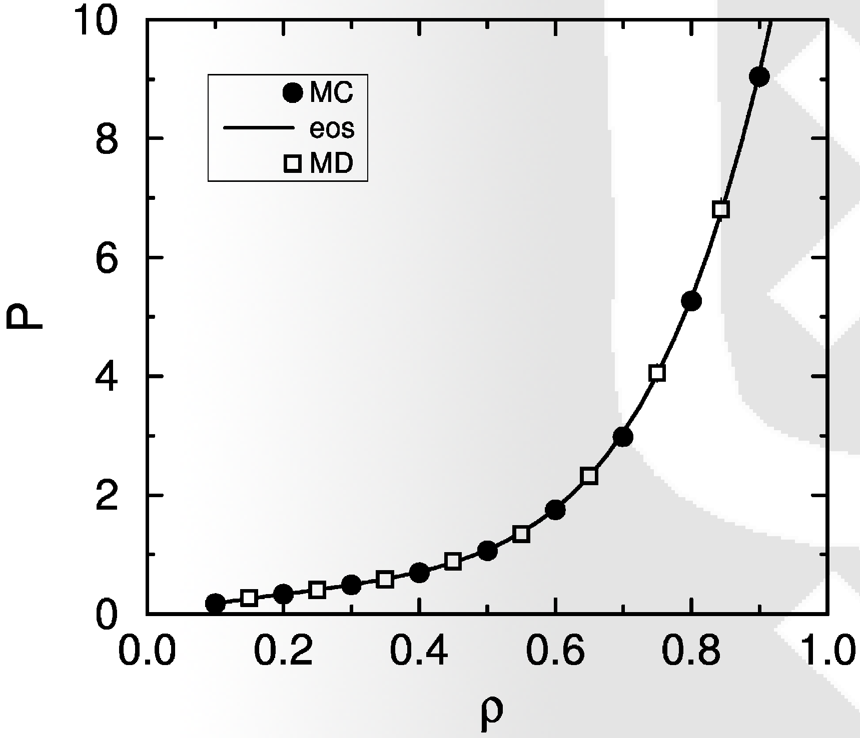
$$e^{(iL_p\Delta t/2)} : \mathbf{v}(t+\Delta t) \to \mathbf{v}(t+\Delta t/2) + \frac{\Delta t}{2m}\dot{\mathbf{f}}(t)$$

Velocity Verlet:

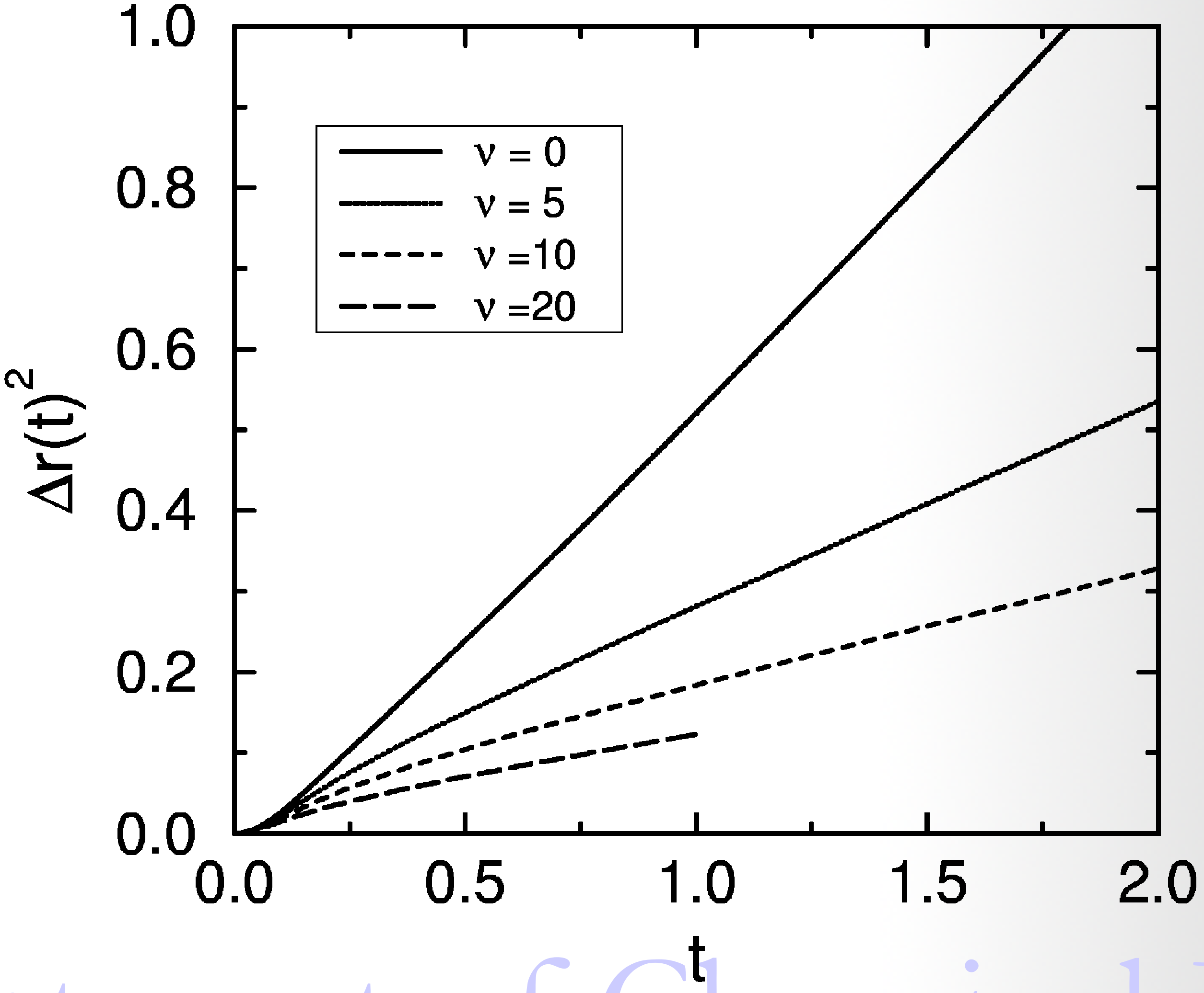
$$e^{(iL_p\Delta t/2)}e^{(iL_r\Delta t)}e^{(iL_p\Delta t/2)}$$

Andersen thermostat: static properties





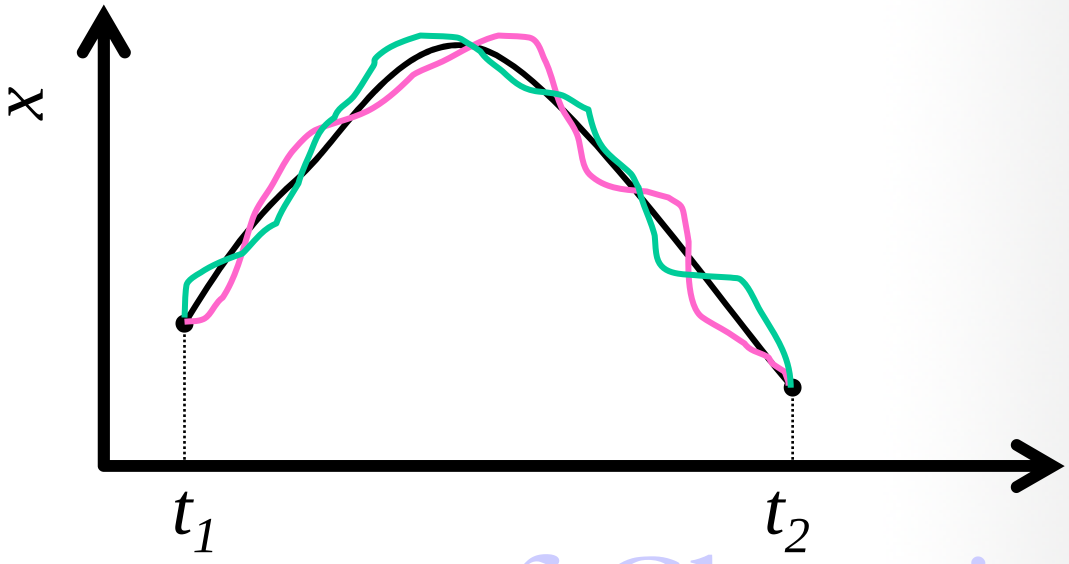
Andersen thermostat: dynamic properties



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:

$$U_p = 0$$

$$U_k = \frac{1}{2} m v^2$$

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

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

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

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

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

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

η(t)=0 for all t

Always > 0!!

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

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

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

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

Lagrangian

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

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

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

Should be 0 for all paths

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

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

Equations of motion

Lagrangian equations of motion

Conjugate momentum

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

Newton?

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

Valid in any coordinate system: Cartesian

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

Conjugate momentum

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

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

Lagrangian dynamics

With these variables we can do statistical thermodynamics

We have:

2nd order differential equation

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

Two 1st order differential equations

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

Change dependence:

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

Hamiltonian

$$L\left(q,\dot{q}\right) \qquad \left(q,\dot{q}\right)\rightarrow\left(q,p\right)$$

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

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

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

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

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

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

$$\begin{cases}\dot{q}=\dfrac{\partial H}{\partial p}\\[2ex]\dot{p}=-\dfrac{\partial H}{\partial q}\end{cases}$$

Hamilton’s equations of motion

Newton?

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

Conjugate momentum

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

Hamiltonian

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

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

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

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

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

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

$$p' = p/s$$

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

Nosé and thermodynamics

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

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

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

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

Gaussian integral

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

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

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

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

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

Conjugate momenta

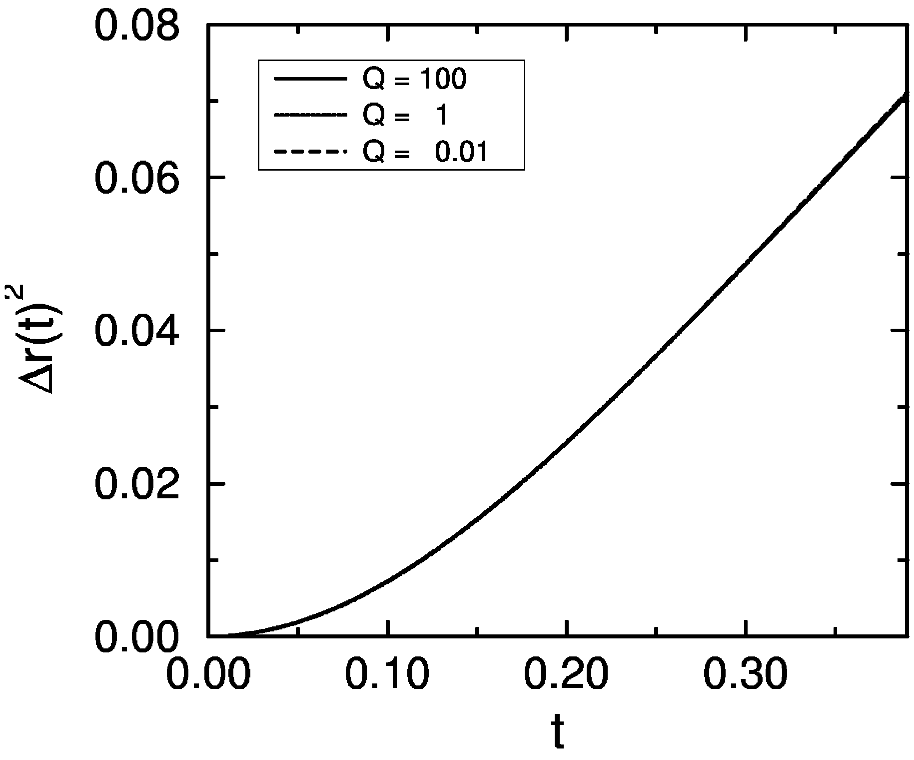
$$p_i = \frac{\partial L}{\partial \dot{r}_i} = m s^2 \dot{r}_i \qquad p_s = \frac{\partial L}{\partial \dot{s}} = Q \dot{s}$$

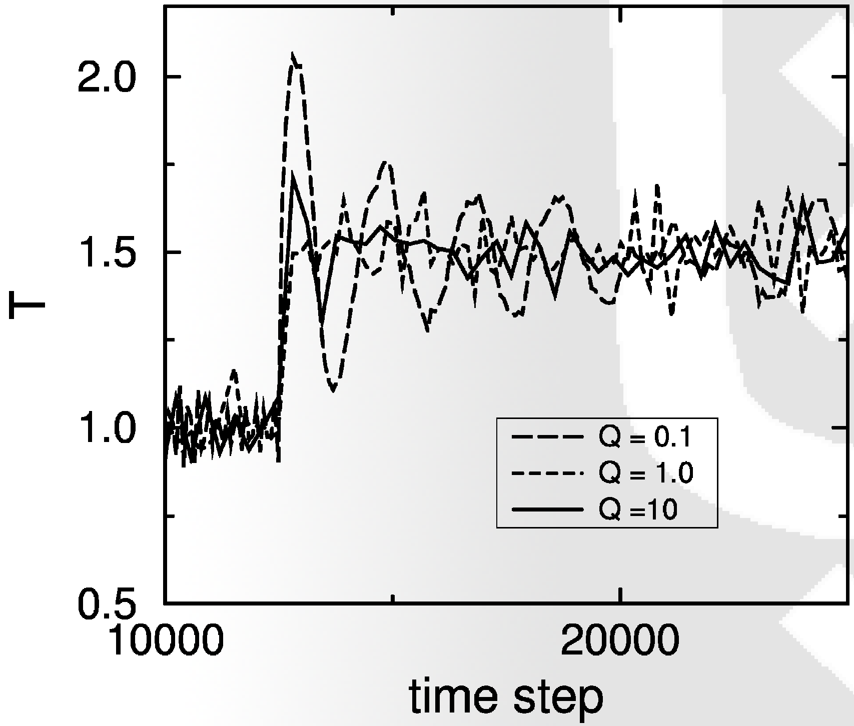
Equations of motion:

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

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

Nosé Hoover

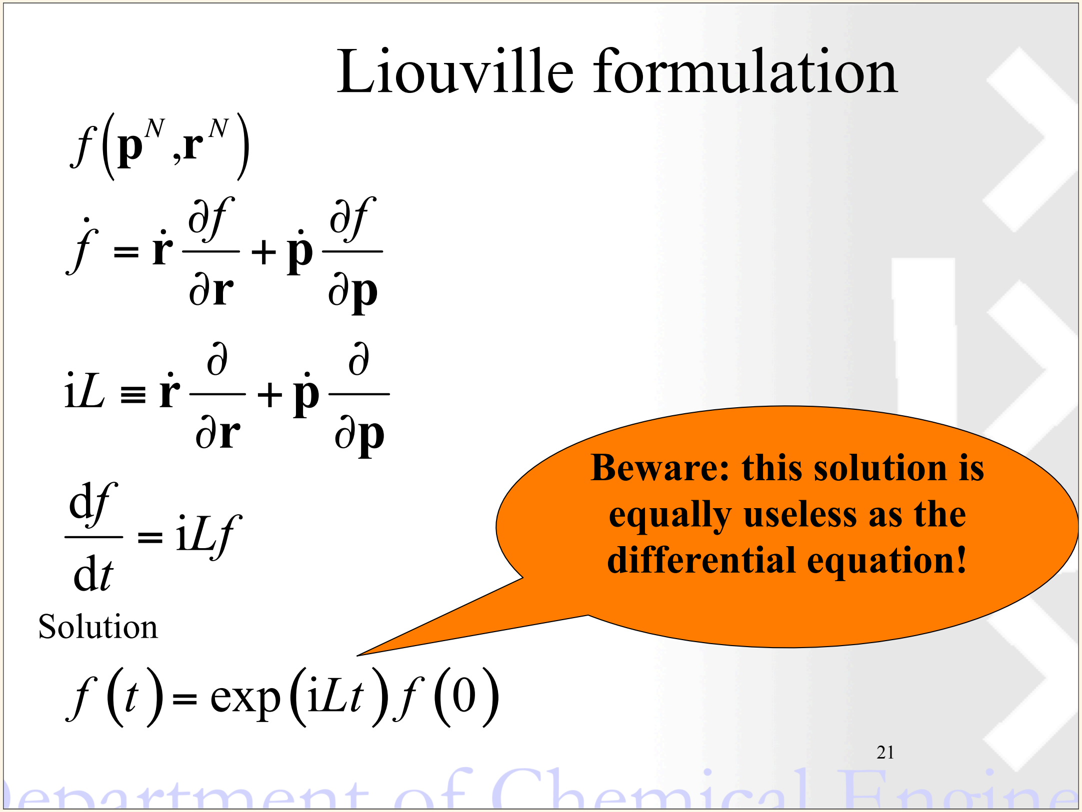

Q = 100
Q = 1
Q = 0.01
$\Delta r(t)^2$
0.08
0.06
0.04
0.02
0.00
0.00
0.10
0.20
0.30
t


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

Multiple Timesteps

Time evolution

$f\left(\mathbf{r}^N, \mathbf{p}^N\right)$: phase space probability density distribution



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

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

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

Time evolution

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

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

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

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

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

Shift of coordinates

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

Time evolution

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

$$\begin{aligned} f(t) &= \exp(i\mathcal{L}_r t) f(0) \\ &= \exp\left(\dot{\mathbf{r}}(0)t\frac{\partial}{\partial \mathbf{r}} f(0)\right) \\ &= \sum_{n=0}^{\infty} \frac{(\dot{\mathbf{r}}(0)t)^n}{n!}\frac{\partial^n}{\partial \mathbf{r}^n} f(0) \\ &= f\left(\mathbf{p}^N(0), (\mathbf{r}(0)+\dot{\mathbf{r}}(\mathbf{0})t)^N\right) \end{aligned}$$

$$\begin{aligned} f(t) &= \exp(i\mathcal{L}_p t) f(0) \\ &= \exp\left(\dot{\mathbf{p}}(0)t\frac{\partial}{\partial \mathbf{p}} f(0)\right) \\ &= \sum_{n=0}^{\infty} \frac{(\dot{\mathbf{p}}(0)t)^n}{n!}\frac{\partial^n}{\partial \mathbf{p}^n} f(0) \\ &= f\left((\mathbf{p}(0)+\dot{\mathbf{p}}(\mathbf{0})t)^N, \mathbf{r}^N(0)\right) \end{aligned}$$

Shift of coordinates

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

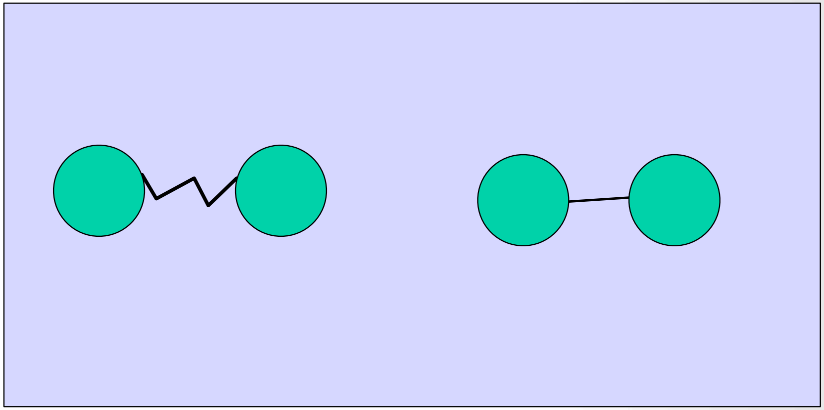
Shift of momenta

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

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

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

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

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

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

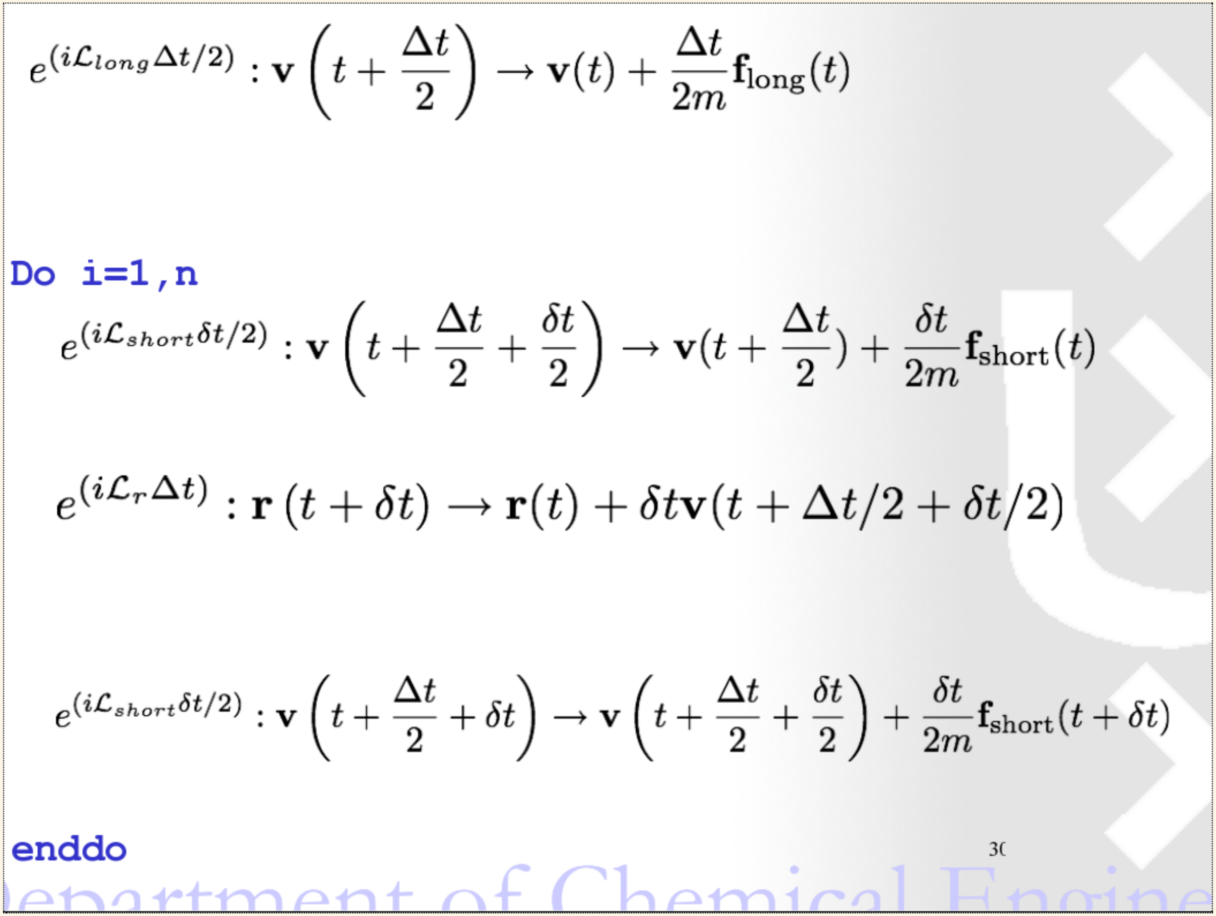
Trotter expansion:

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

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

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

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

Time evolution

- **System**:

$$N \text{ particles: } \mathbf{R}^N, \dot{\mathbf{R}}^N, \mathbf{P}_I = M_I \dot{\mathbf{R}}$$

- **Lagrangian**:

$$\mathcal{L}(\mathbf{R}^N, \dot{\mathbf{R}}^N) = \mathcal{K}(\dot{\mathbf{R}}^N) - \mathcal{V}(\mathbf{R}^N)$$

- **Equation of Motion**:

$$\frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{\mathbf{R}}_I} - \frac{\partial \mathcal{L}}{\partial \mathbf{R}_I} = 0 \quad \longrightarrow \quad M_I \ddot{\mathbf{R}} = -\frac{\partial}{\partial \mathbf{R}_I} \mathcal{V}(\mathbf{R}^{\mathcal{N}})$$

- **Molecular Dynamics trajectory**:

  Numerical time propagation with discrete time step

  Issues: constants of motion, ergodicity, thermostats, barostats, …

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

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

$$\begin{aligned} M_I \ddot{\mathbf{R}}_I &= -\frac{\partial E^{\mathrm{KS}}}{\partial \mathbf{R}_I} + \sum_{ij} \Lambda_{ij} \frac{\partial}{\partial \mathbf{R}_I} \langle \psi_i \mid \psi_j \rangle \\ \mu \mid \ddot{\psi}_i \rangle &= -\frac{\delta E^{\mathrm{KS}}}{\delta \langle \psi_i \mid} + \sum_j \Lambda_{ij} \mid \psi_j \rangle \end{aligned}$$

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 $\sim$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?

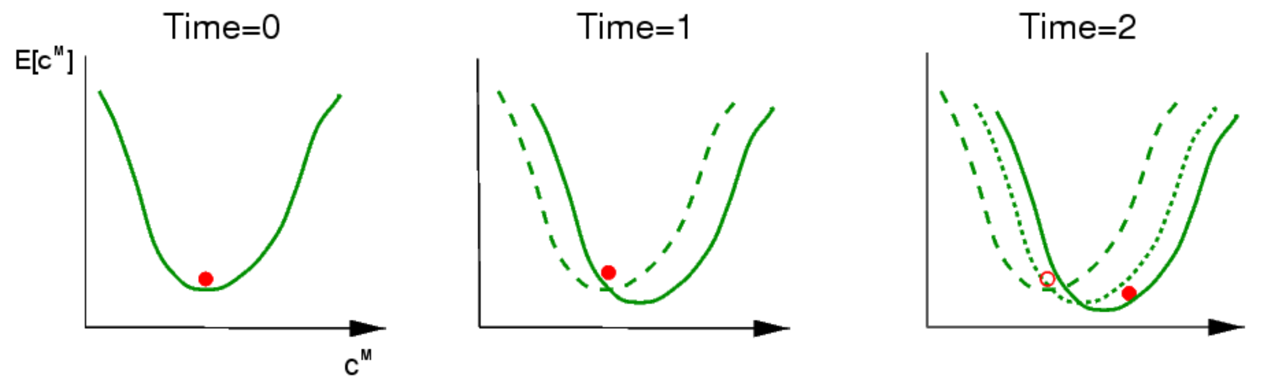
- Adiabatic decoupling

  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.

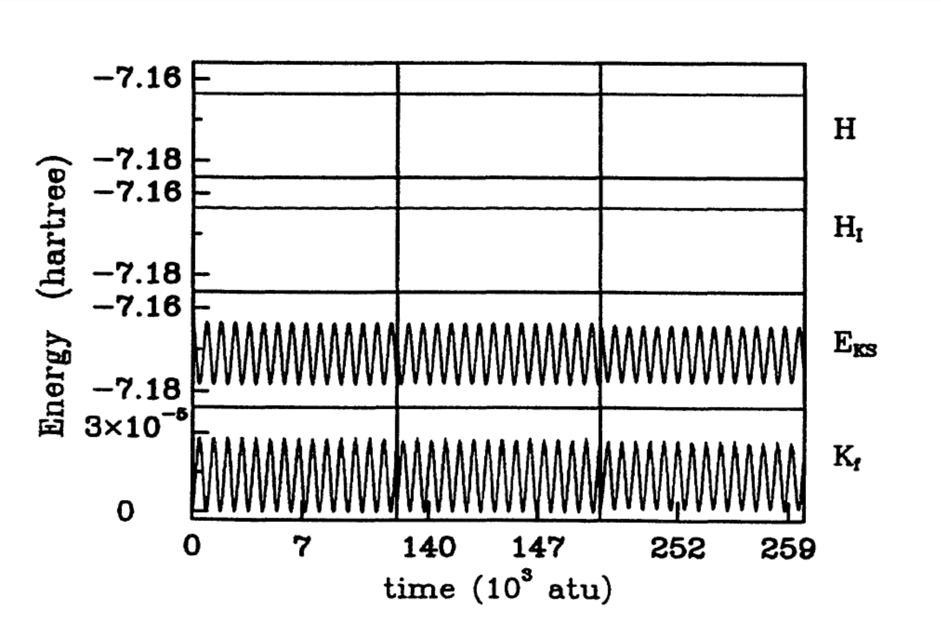
- Pictorial view



Example*: Conservation of Energy

[a]

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



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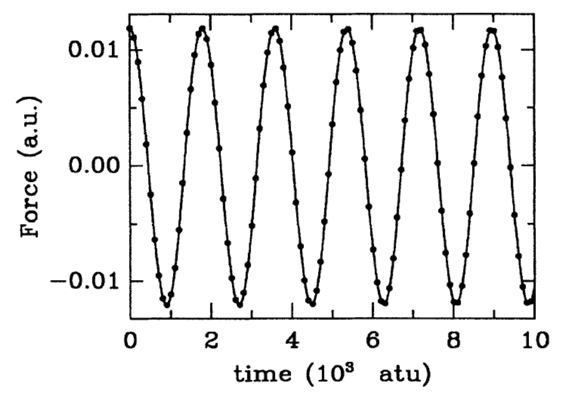
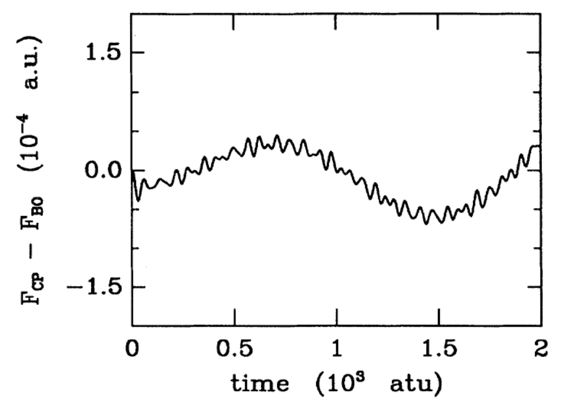
[a] *Pastore, Smargiassi, and Buda, Phys.Rev. A**44** (1991)

Example*: Deviation of BO surface

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

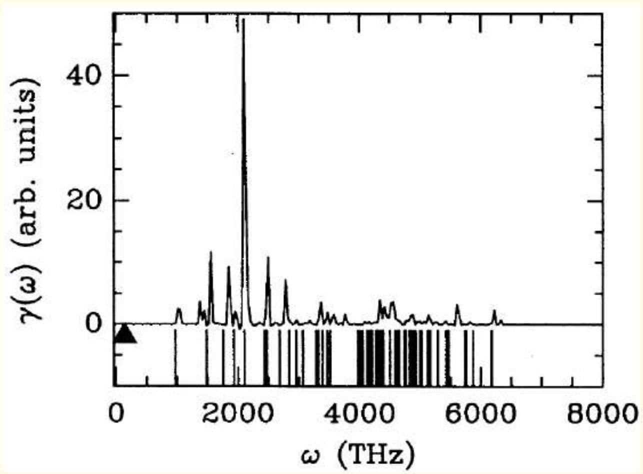




Example*: Adiabatic Separation

Adiabatic decoupling is achieved by non-overlapping frequency spectra of the ions and the orbitals.

Spectrum of Si-Crystal



$$f\left(\omega\right)=\int_{t=0}^{\infty}\cos\left(\omega t\right)\sum_{i}\left\langle\dot{\psi}_i(t)\dot{\psi}_i\left(0\right)\right\rangle\,dt$$

Controlling adiabacity (I)

What determines the frequency spectrum of the “orbital motion”

- In harmonic approximation, with ϵ_i (ϵ_j) the eigenvalues of the occupied (unoccupied) orbitals (μ is fictitious electronic mass):

$$\omega_{ij}^{e} = \sqrt{\frac{2\left(\varepsilon_i - \varepsilon_j\right)}{\mu}}$$

- Lowest frequency

$$\omega_{\mathrm{min}}^{e} \propto \sqrt{\frac{E_{\mathrm{gap}}}{\mu}}$$

- Highest frequency

$$\omega_{\mathrm{max}}^{e} \propto \sqrt{\frac{E_{\mathrm{cut}}}{\mu}}$$

Controlling adiabacity (II)

- Lowest frequency has to be well above ionic frequencies

$$\omega^e_{\min} \propto \sqrt{\frac{E_{\text{gap}}}{\mu}}$$

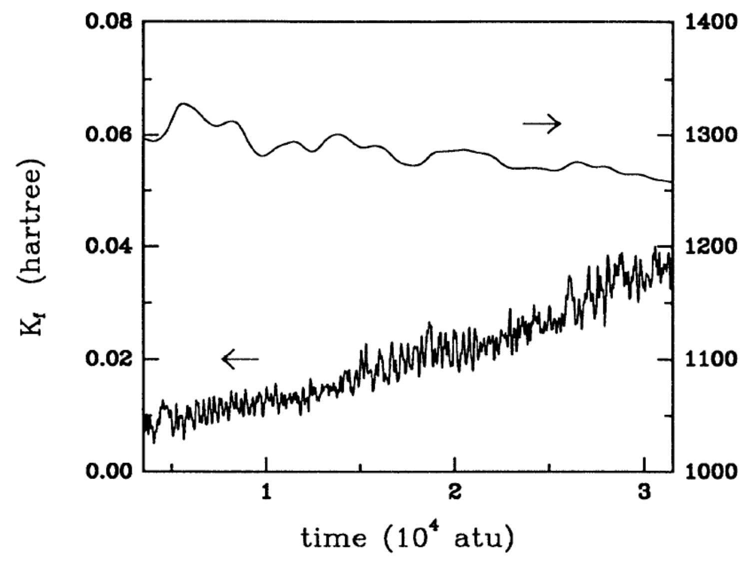
- Highest frequency set upper limit to time step

$$\omega^e_{\max} \propto \sqrt{\frac{E_{\text{cut}}}{\mu}} \qquad (\Delta t^e)_{\max} \propto \sqrt{\frac{\mu}{E_{\text{cut}}}}$$

- If Δt fixed and μ chosen
  - too small: Electronic mass too small, eventually the Δt is too large and the integration by the Verlet algorithm is not anymore correct, giving rise to a drift in the constant of motion.
  - too large: Electrons mass too large and adiabacity will be lost.

Example: Lack of sufficient adiabatic separation

Si-crystal with vacancy



Zero or small electronic gaps

Thermostat for electrons

- Perform CPMD with coupling of electronic and ionic dynamics to thermostat# [a]
- Thus electrons cannot heat up; if they try to, thermostat will adsorb the excess heat
- Target fictitious kinetic energy $E_{\mathrm{kin},0}$ instead of temperature
  - Too low: orbitals cannot follow change of ion positions
  - Too high: orbitals deviate too much from BO surface

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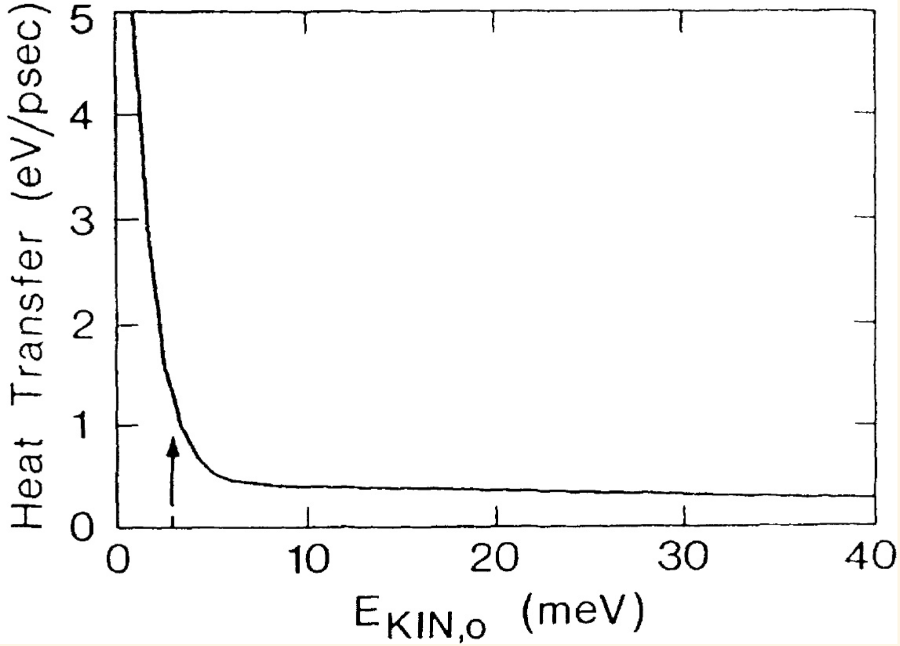
[a] #Blöchl & Parrinello, Phys.Rev.B**45** (1992)

Thermostat on electrons

Example[#]

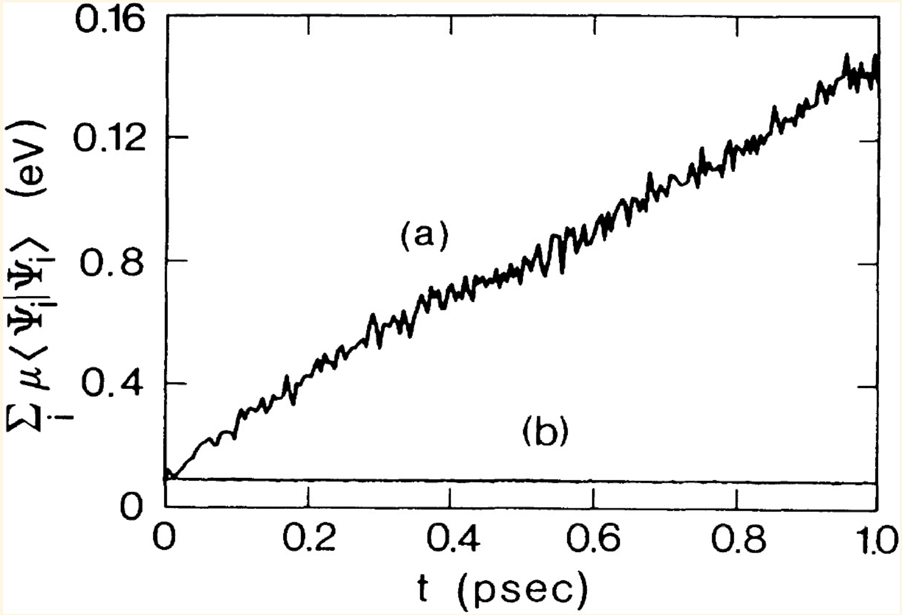
Dependence of the heat transfer on the choice of $E_{\mathrm{kin},0}$ in solid Aluminium



Thermostat on electrons

Does it help?

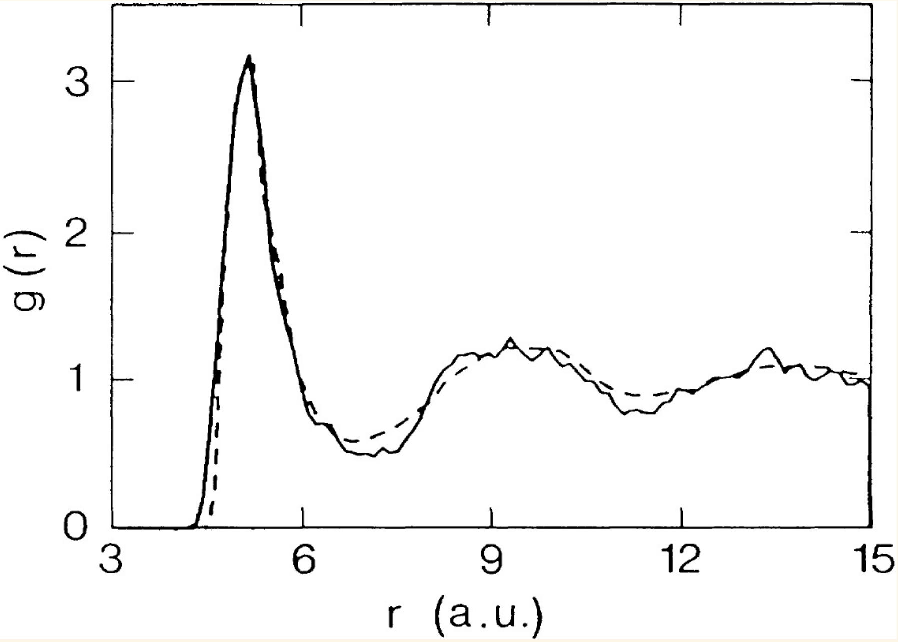
- 64 atoms of molten aluminium
- (a): Without thermostat
- (b): With thermostat



Thermostat on electrons

Does it work?

- Check: Radial pair correlation function
  - Solid line: CP-MD with thermostat
  - Dashed line: Calculations by Jacucci et al.



CPMD for Structure Optimization

Simulated annealing

- In larger molecules or crystals the structural optimisation might be difficult, especially the closer to the minimum one is
- CPMD can be used to perform the optimisation by simulated annealing: Rescaling the (atomic and possibly also electronic) velocities:

  $$\dot{\mathbf{R}}'_I = \alpha \dot{\mathbf{R}}_I$$

  Easy to incorporate into the velocity Verlet algorithm
- Optimized structure when all velocities (temperature) are ≈ 0
  Check by calculating the ionic forces
- The ionic masses are “unphysical”: Select to “flatten” the vibrational spectrum (e.g. high mass on hydrogens)
- Faster convergence due to the “global” optimisation

CP *vs* BO Molecular Dynamics

Born-Oppenheimer MD	Car-Parrinello MD
Exactly on BO surface. In principle more accurate	Always slightly off BO surface
$\Delta t \approx$ ionic time scales, maximum time step possible	$\Delta t \ll$ ionic time scales, (much) shorter time step necessary
Expensive minimization at each MD step	Time propagation and orthogonalisation, less expensive per MD step
Not stable against deviations from BO surface $\Rightarrow$ Energy/temperature drift, thermostatting of ions necessary	Stable against deviations from BO surface
Equal procedure in zero-gap systems	Thermostatting of electrons to prevent energy exchange
Most applications in solids	Applications in liquids, thermodynamics.

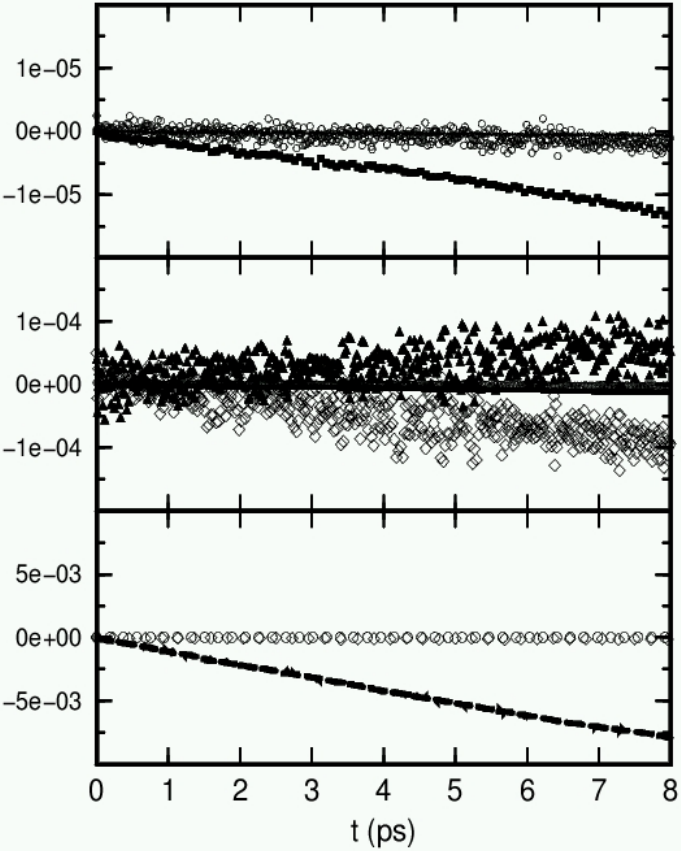
STABILITY OF BO AND CP MD COMPARED

CPMD results for the **8 Si atom model** system

Timings in cpu seconds and energy conservation in a.u. / ps for CP and BO Molecular dynamics simulations for 1 ps of trajectory on an IBM RS6000 / model 390 (Power2) workstation

Method	Time step	Convergence	Conservation (au/ps)	Time (s)
CP	5	—	6×10^{-8}	3230
CP	7	—	1×10^{-7}	2310
CP	10	—	3×10^{-7}	1610
BO	10	10^{-6}	1×10^{-6}	16590
BO	50	10^{-6}	1×10^{-6}	4130
BO	100	10^{-6}	6×10^{-6}	2250
BO	100	10^{-5}	1×10^{-5}	1660
BO	100	10^{-4}	1×10^{-3}	1060

STABILITY OF BO AND CP MD COMPARED (cont'ed)



	Δt, convergence
Top:	
solid line	: CP, 5 a.u.;
open circ.	: CP, 10 a.u.;
filled squar.	: BO, 10 a.u., 10^{-6}.
Middle:	
open circl.	: CP, 10 a.u.;
filled squar.	: BO, 10 a.u., 10^{-6};
filled trian.	: BO, 100 a.u., 10^{-6};
open diam.	: BO, 100 a.u., 10^{-5}.
Bottom:	
open circ.	: CP, 10 a.u.;
open diam.	: BO, 100 a.u., 10^{-5};
dashed line	: BO, 100 a.u., 10^{-4}

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)