Molecular Dynamics Simulation: Q & A

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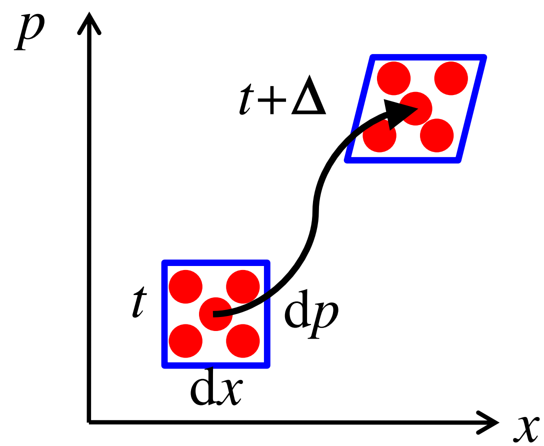
Liouville's Theorem

Q: Why is it important to preserve the phase-space volume along the molecular-dynamics trajectory?

$$\underset{t}{(x,p)} \rightarrow \underset{t+\Delta}{(x',p')}$$



$$\frac{\partial(x',p')}{\partial(x,p)} = 1$$

A: Exact phase-space-volume conservation tends to provide long-time stability, though formal analysis of long-time accuracy very hard.

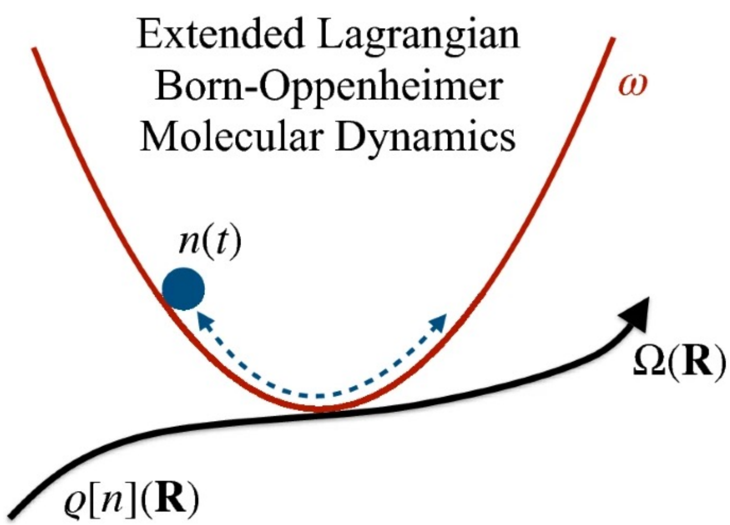
cf. **Backward error analysis**

S. Reich, *SIAM J. Numer. Anal.* **36**, 1549 ('99)

W. Hayes, *Appl. Num. Meth*. **53**, 299 ('05)

Shadow Molecular Dynamics

- **Extended-Lagrangian Born-Oppenheimer molecular dynamics (XL-BOMD), aka, shadow molecular dynamics: Instead (of approximately solving the exact equations of motion), we calculate the exact electron density, energies, and forces, but for an underlying approximate shadow Born-Oppenheimer potential energy surface. In this way, the calculated forces are conservative with respect to the approximate shadow potential & generate accurate molecular trajectories with long-term energy stabilities.**
- **Shadow MD was inspired by backward error analysis.**



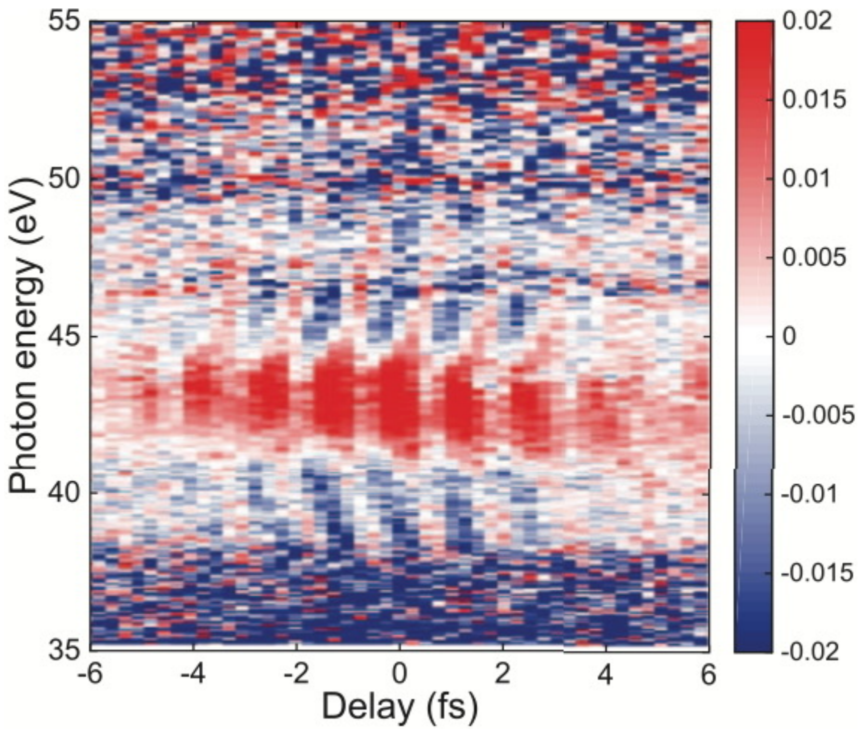
A. M. N. Niklasson, *J. Chem. Phys.* **158**, 154105 ('23)

Velocity Autocorrelation (VAC)

Q: VAC in nonsteady state?

A: Present it as a function of two time variables.

$$\langle \vec{v}_i(t) \bullet \vec{v}_i(t') \rangle = vac\left(\tau = t - t', \underbrace{T = \frac{t+t'}{2}}_{\text{No } T \text{ dependence in a steady state}}\right)$$

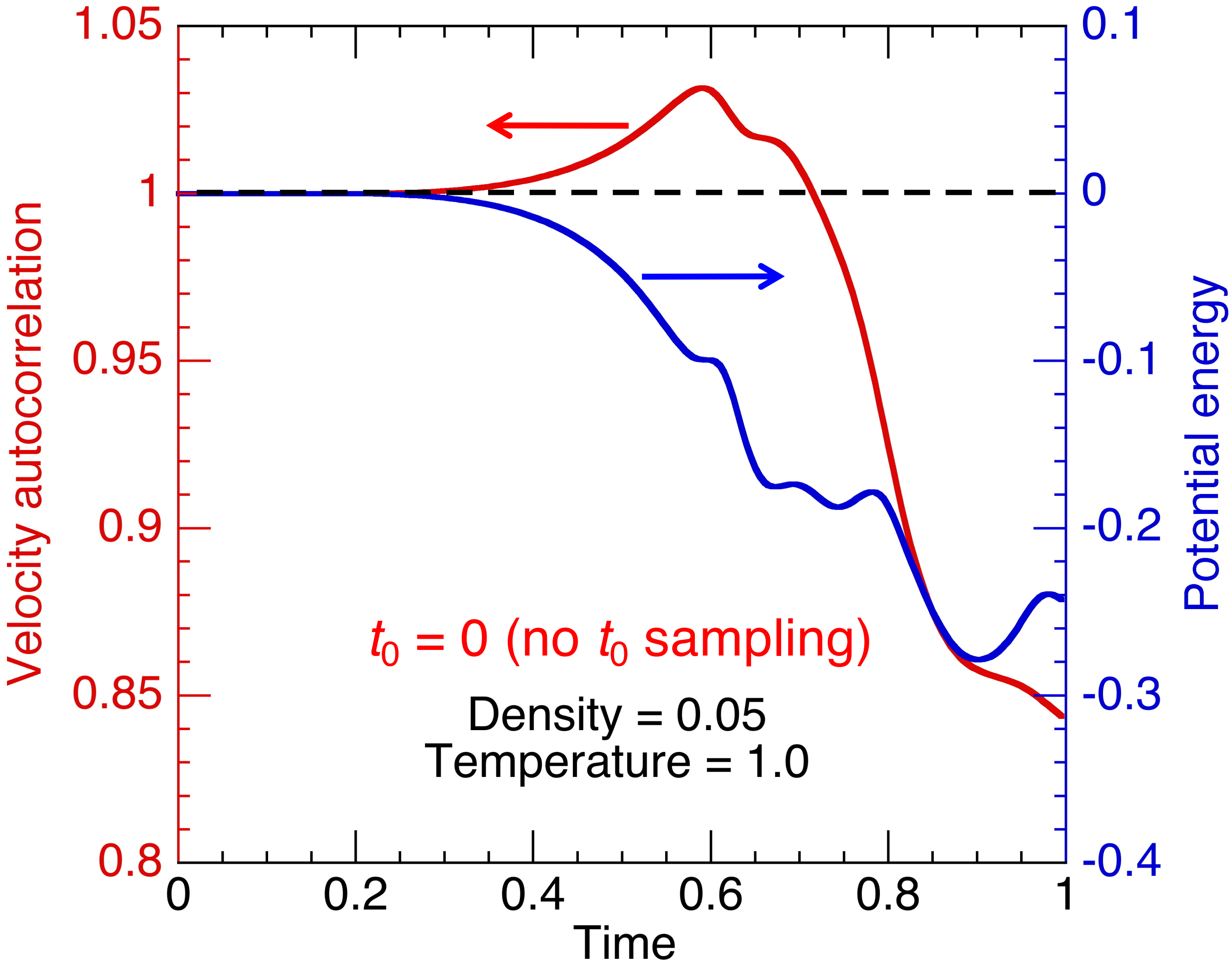


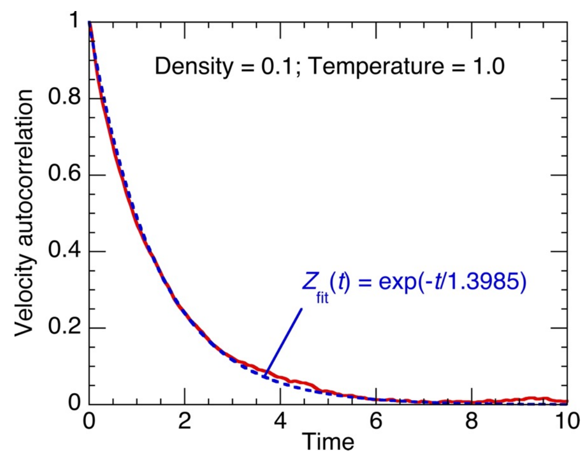
cf. **Transient photoabsorption spectrum: Note the atomic-unit energy, 27.2116 eV = *h*/(0.024 fs); *h* is Planck's constant**

M. Lucchini *et al.*, *Science* **353**, 916 ('16)

Velocity Autocorrelation > 1?

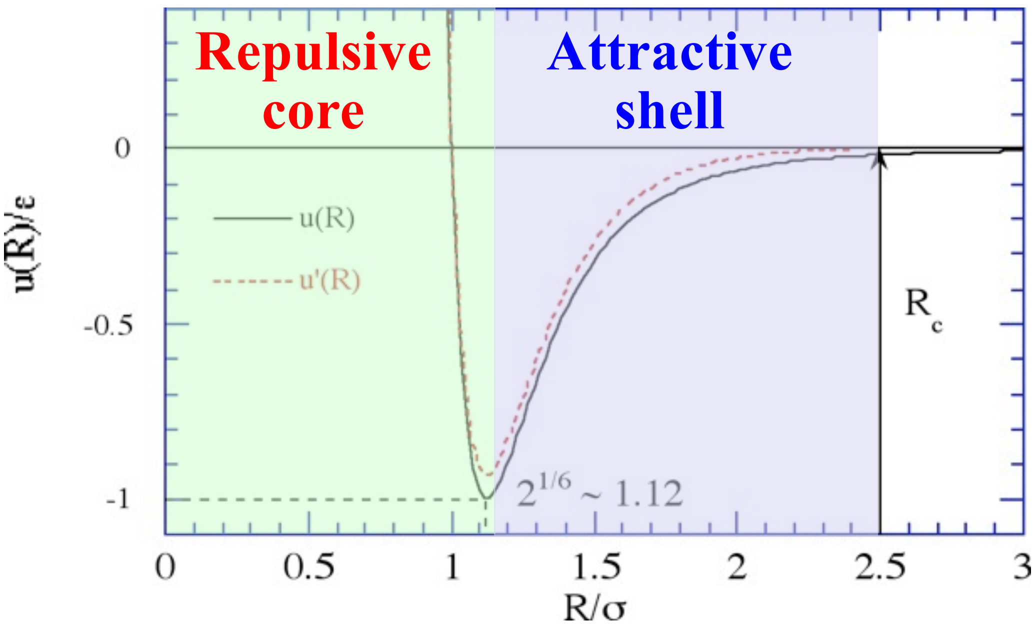
- Yes, in a gas phase just when starting from an FCC lattice

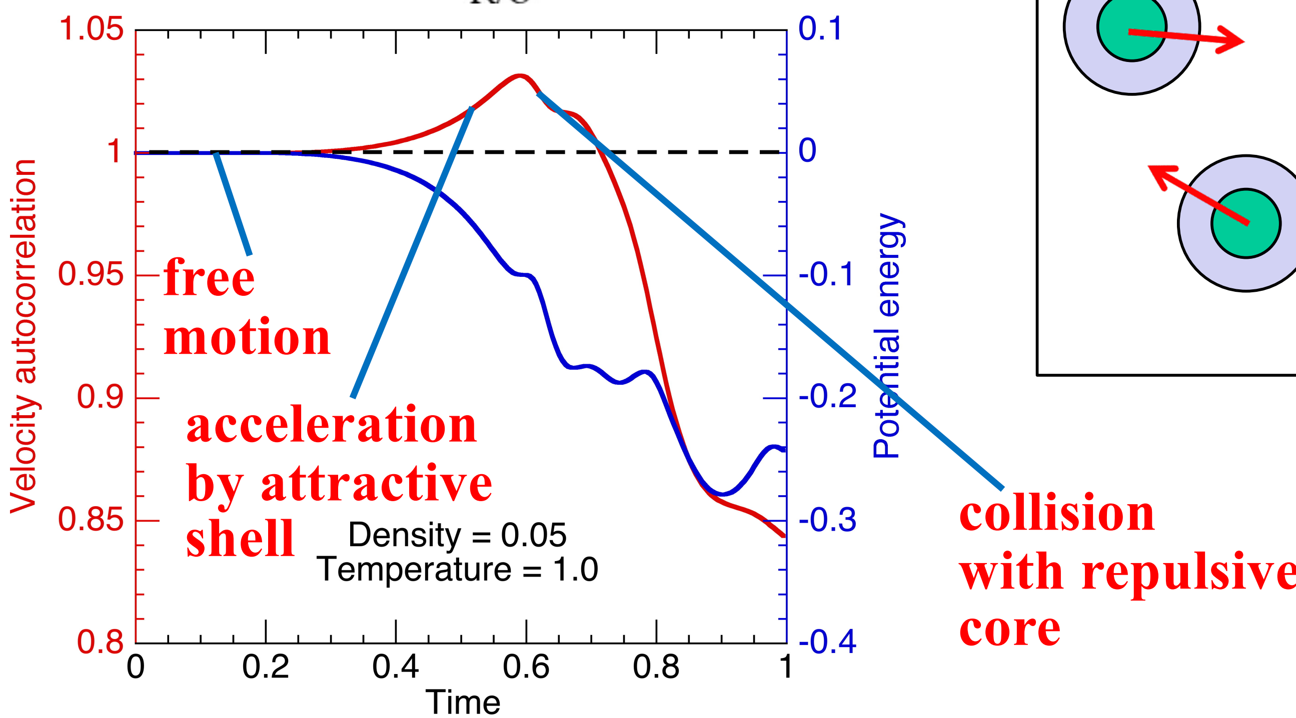


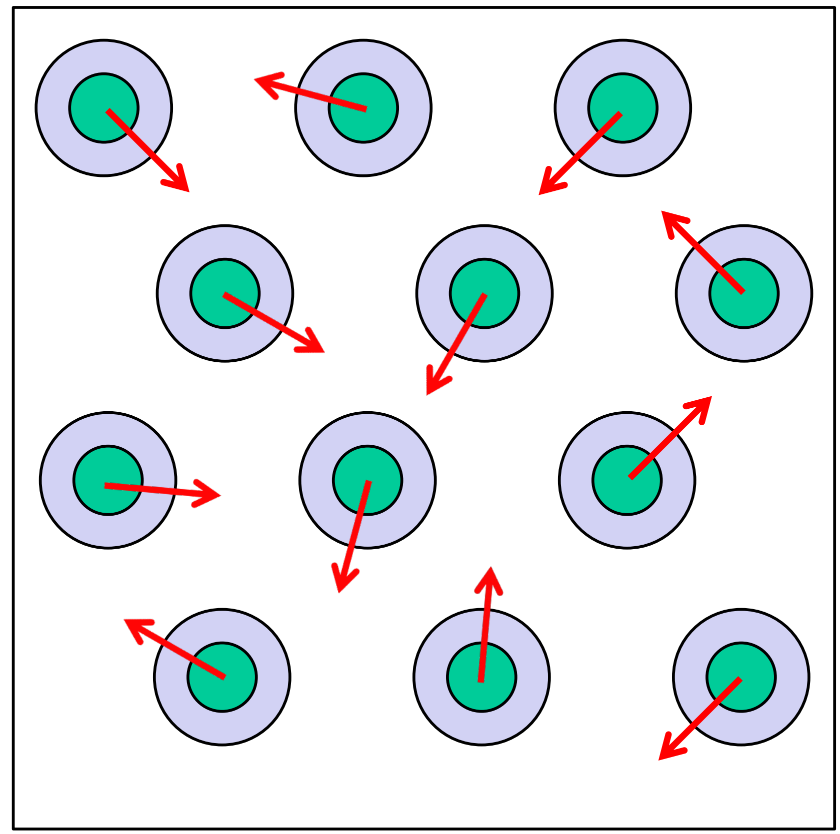


- Why? Hint = time variation of the potential energy

Finite-Range Lennard-Jones Potential







Why Taylor Expansion?

$$\frac{d}{dt}\Gamma = \hat{L}\Gamma$$

$$\Downarrow \quad \exp\left(\hat{L}t\right) \equiv \sum_{n=0}^{\infty} \frac{1}{n!}\left(\hat{L}t\right)^n$$

$$\Gamma(t) = \exp\left(\hat{L}t\right)\Gamma(0)$$

A: **Exponentiation of a differential operator is "defined" through Taylor expansion, in which the power of the operator is operationally well defined as successive applications of the operator**

$$\left(t\left(F(x)\frac{\partial}{\partial p} + \frac{p}{m}\frac{\partial}{\partial x}\right)\right)^3 f(x,p) =$$

$$t\left(F(x)\frac{\partial}{\partial p} + \frac{p}{m}\frac{\partial}{\partial x}\right)\left\{t\left(F(x)\frac{\partial}{\partial p} + \frac{p}{m}\frac{\partial}{\partial x}\right)\left[t\left(F(x)\frac{\partial}{\partial p} + \frac{p}{m}\frac{\partial}{\partial x}\right)f(x,p)\right]\right\}$$

But, it is very hard to obtain a closed form

$$\{?\,,?\} = \exp\left[t\left(F(x)\frac{\partial}{\partial p} + \frac{p}{m}\frac{\partial}{\partial x}\right)\right]\{x,p\}$$

Velocity Verlet Time Propagator?

freeze p value;
shift x value by Δp

freeze x value;
shift p value by $F(x)\Delta/2$

operators
(functions)

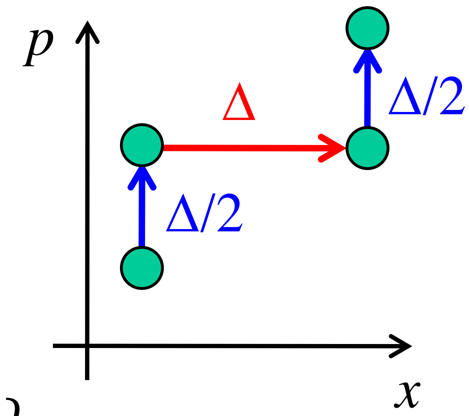
$$\exp\left(\frac{\Delta}{2}F(\hat{x})\frac{\partial}{\partial p}\right)\exp\left(\Delta\frac{\hat{p}}{m}\frac{\partial}{\partial x}\right)\exp\left(\frac{\Delta}{2}F(\hat{x})\frac{\partial}{\partial p}\right)\{x,p\}$$

operands
(arguments,
return values)

$$\left\{x, p+\frac{\Delta}{2}F(x)\right\}$$

$$\left\{x+\Delta\frac{p}{m}, p\right\}$$

$$\left\{x, p+\frac{\Delta}{2}F(x)\right\}$$




```
for (n=0; n<nAtom; n++)
  for (k=0; k<3; k++)
    rv[n][k] += DeltaTH*ra[n][k];
```

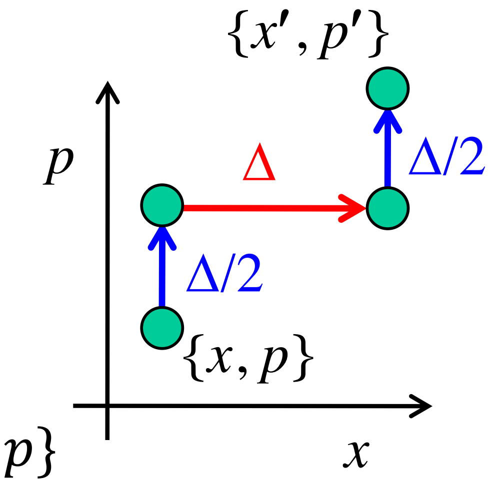
```
for (n=0; n<nAtom; n++)
  for (k=0; k<3; k++)
    r[n][k] += DeltaT*rv[n][k];
```

It's shift operation!

Explicit Form of Mapping?

keep p value constant;
shift x value by Δp

keep x value constant;
shift p value by $F(x)\Delta/2$



$$\overbrace{\exp\left(\frac{\Delta}{2}F(\hat{x})\frac{\partial}{\partial p}\right)\exp\left(\Delta\frac{\hat{p}}{m}\frac{\partial}{\partial x}\right)\exp\left(\frac{\Delta}{2}F(\hat{x})\frac{\partial}{\partial p}\right)}^{\text{operators (functions)}}\underbrace{\{x,p\}}_{\text{operands (arguments, return values)}}$$

$$\left\{x, p+\frac{\Delta}{2}F(x)\right\}$$

$$\left\{x+\frac{\Delta}{m}\left(p+\frac{\Delta}{2}F(x)\right), p+\frac{\Delta}{2}F(x)\right\}$$

$$\left\{x+\frac{\Delta}{m}\left(p+\frac{\Delta}{2}F(x)\right), p+\frac{\Delta}{2}F(x)+\frac{\Delta}{2}F\left(x+\frac{\Delta}{m}\left(p+\frac{\Delta}{2}F(x)\right)\right)\right\}=\{x',p'\}$$