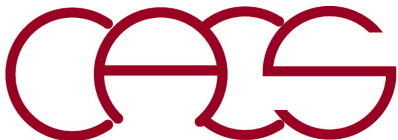


Molecular Dynamics Simulation: Q & A

Aiichiro Nakano

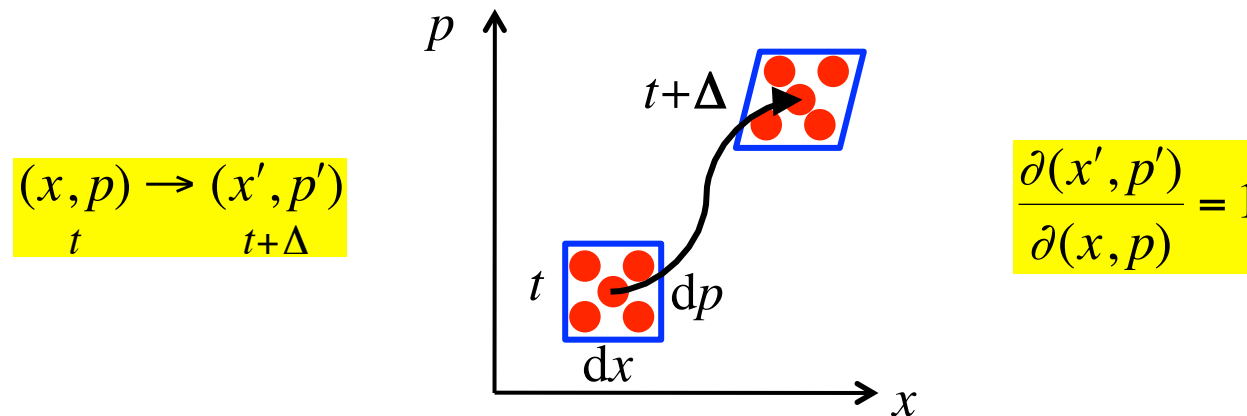
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Liouville's Theorem

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



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)

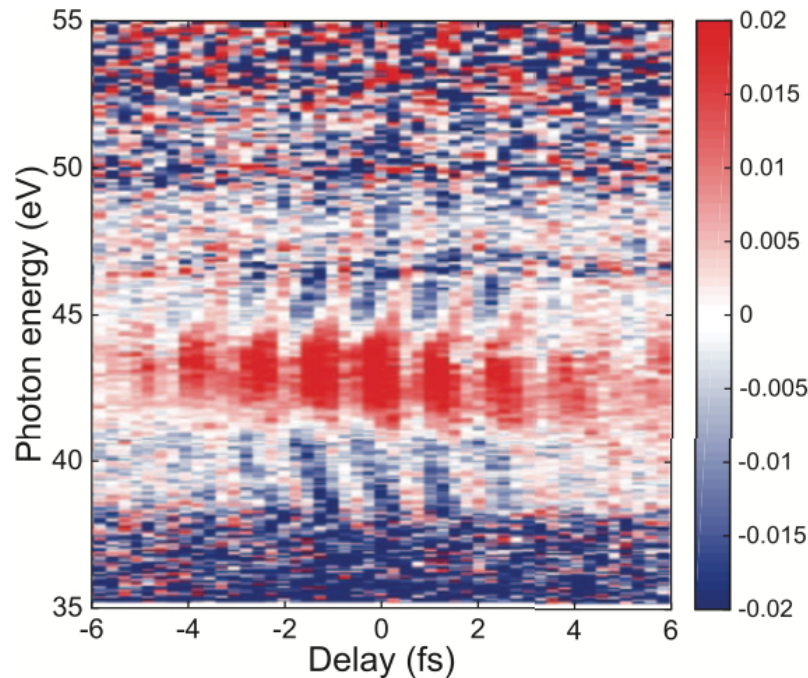
Velocity Autocorrelation (VAC)

Q: VAC in nonsteady state?

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

$$\langle \vec{v}_i(t) \cdot \vec{v}_i(t') \rangle = vac \left(\tau = t - t', T = \underbrace{\frac{t + t'}{2}} \right)$$

No T dependence in a steady state

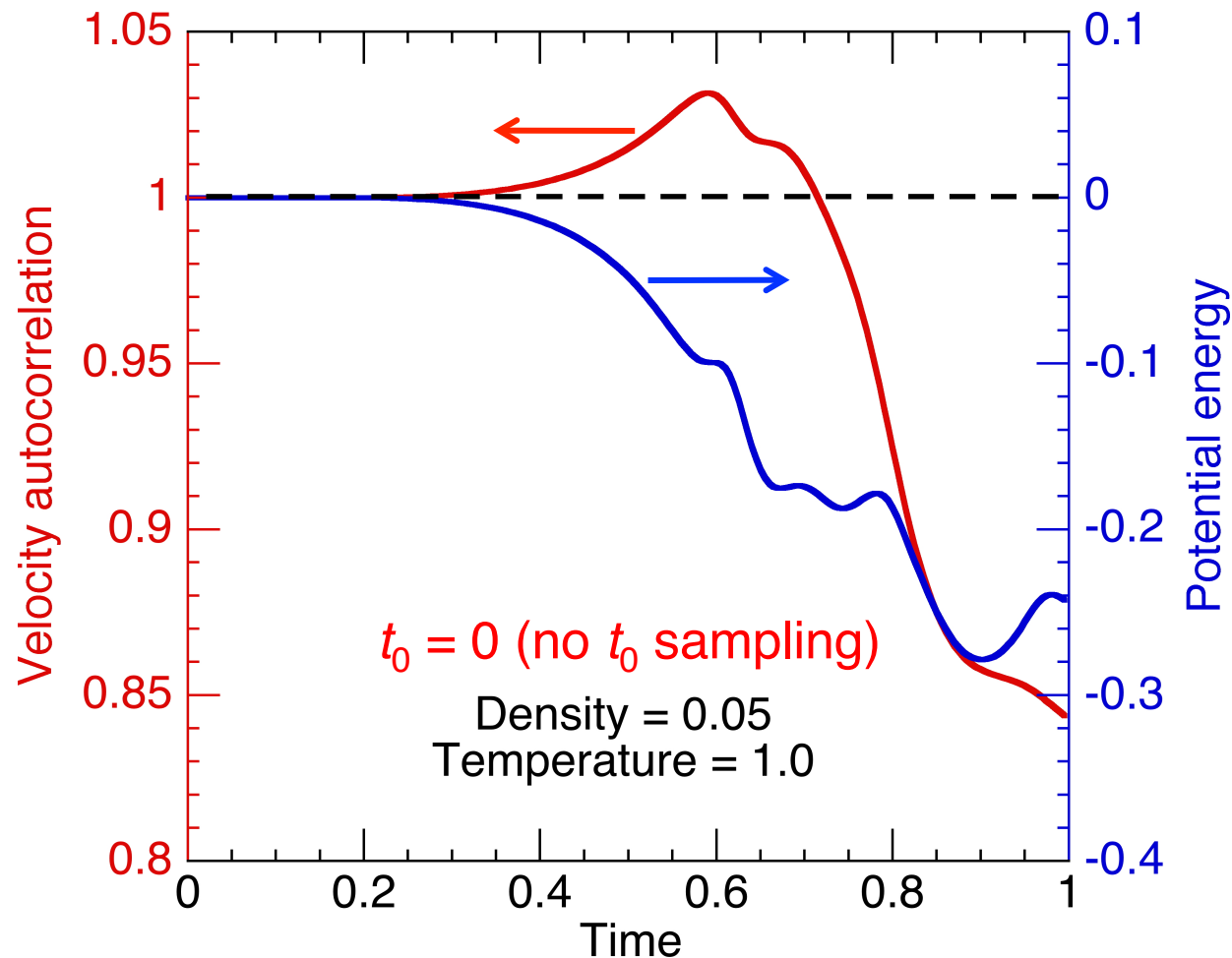


***cf.* Transient photoabsorption spectrum:**
Note the atomic-unit energy, 27.2116 eV
= $h/(0.024 \text{ fs})$; h is Planck's constant

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

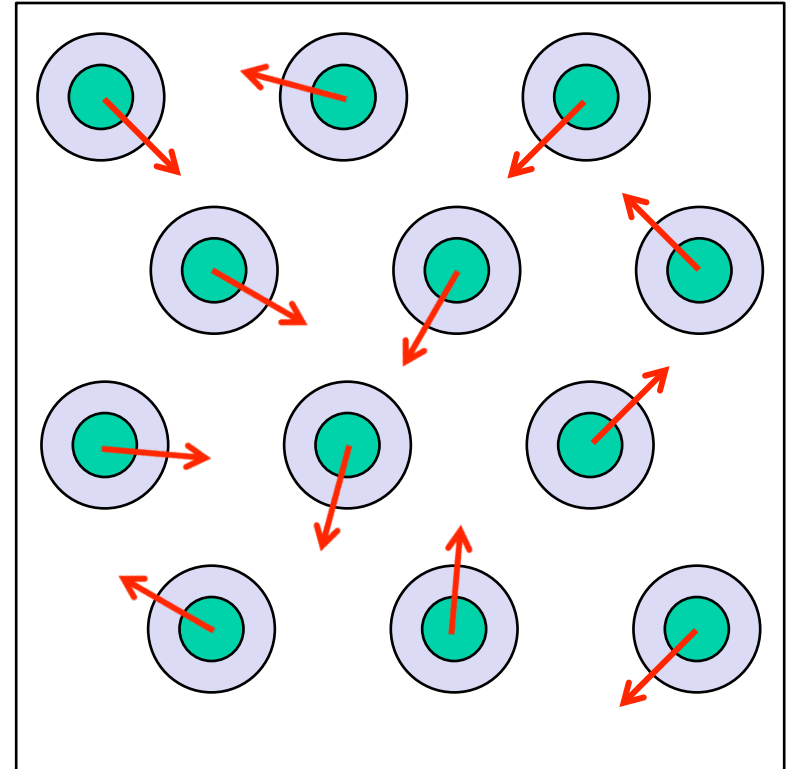
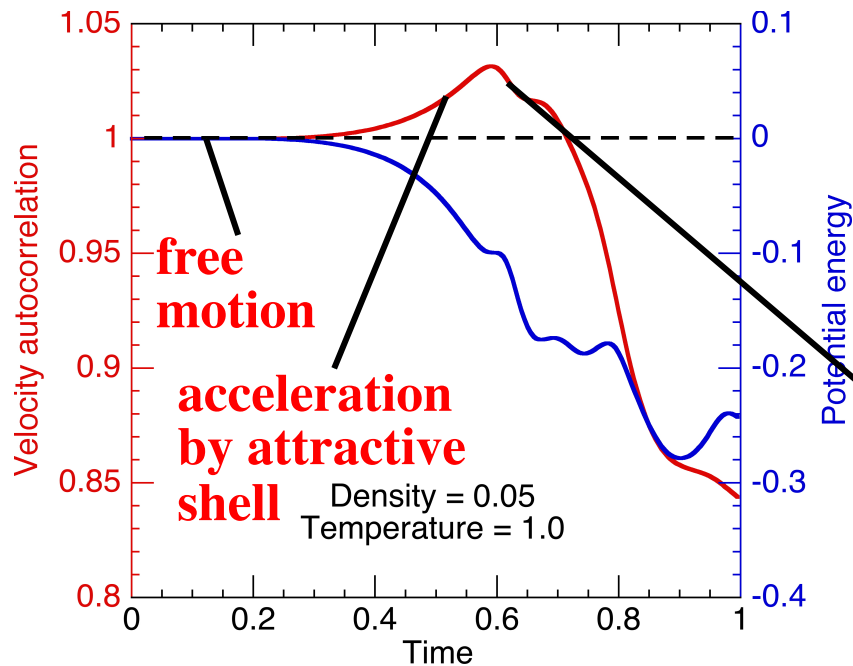
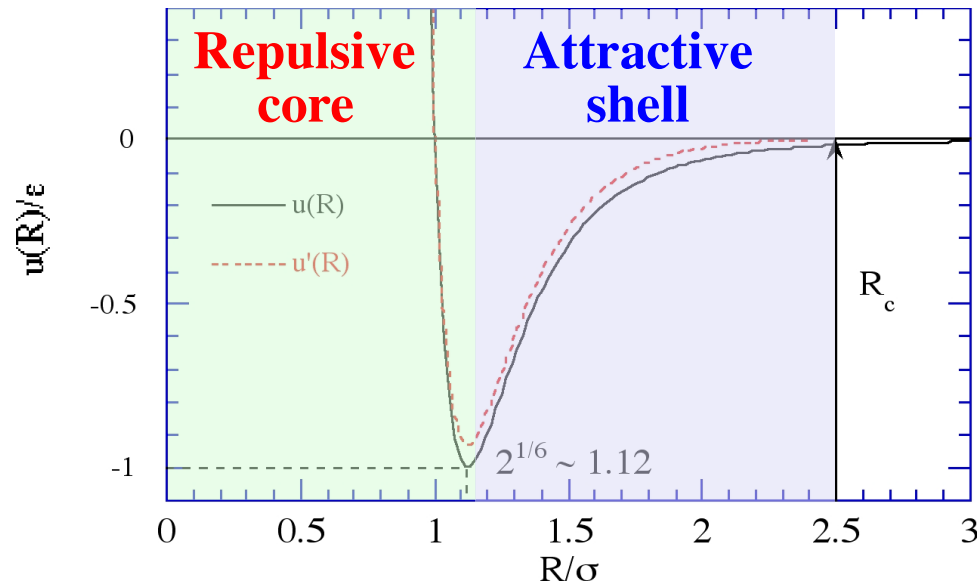
Velocity Autocorrelation > 1?

- 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?

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

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

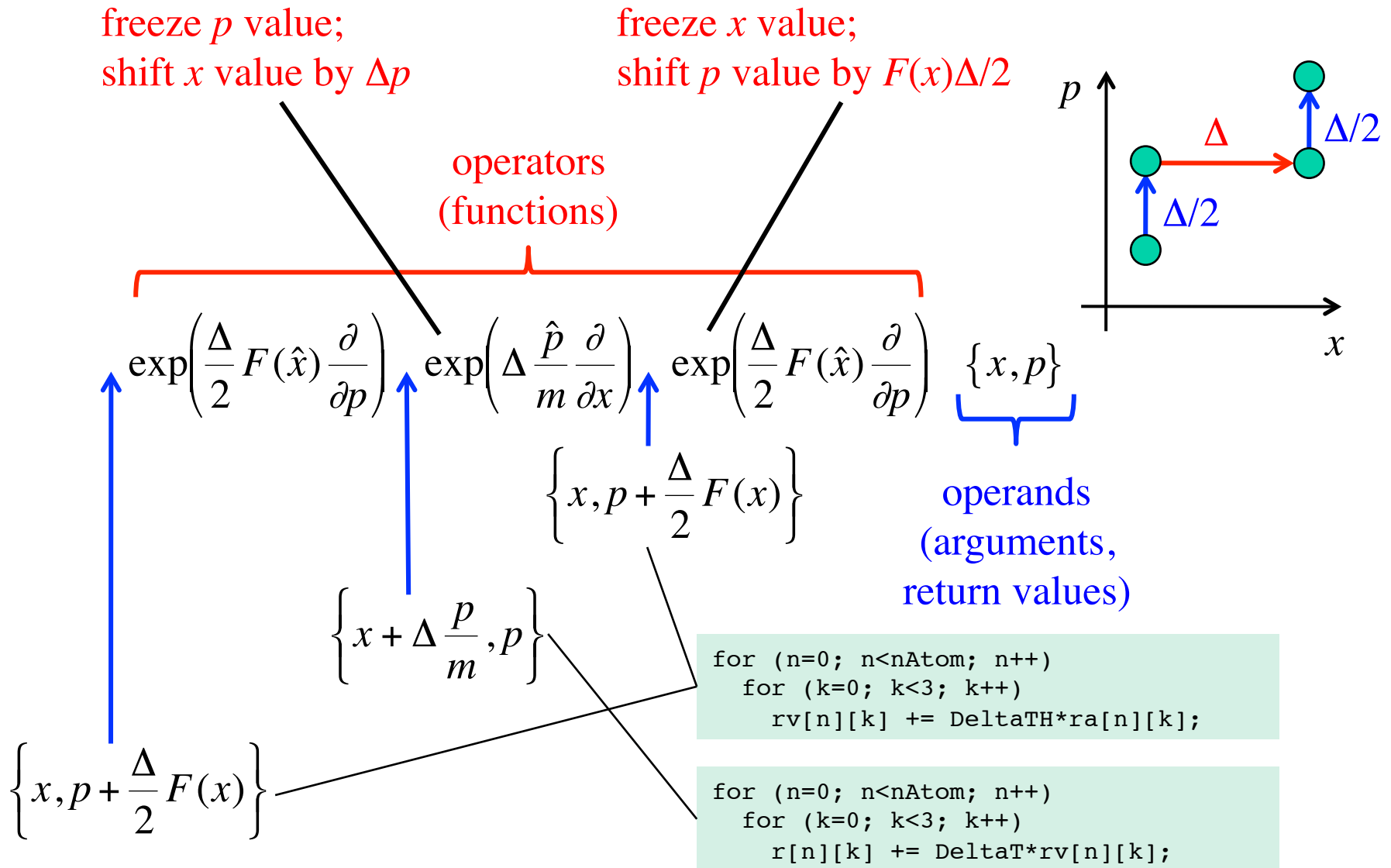
$$\Gamma(t) = \exp(\hat{L}t) \Gamma(0)$$

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

Velocity Verlet Time Propagator?

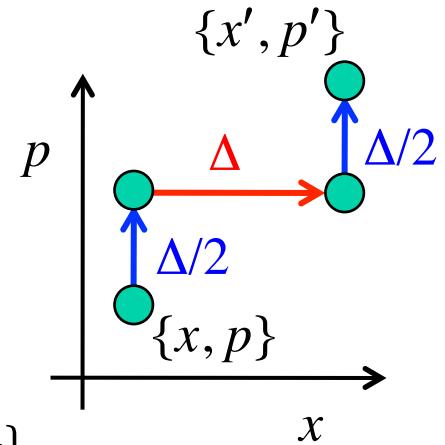


Explicit Form of Mapping?

keep p value constant;
shift x value by Δp

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

operators
(functions)



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

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

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

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