1. Show that the Verlet and velocity Verlet algorithms lead to identical trajectories.

Velocity Verlet: (A) $\mathbf{r}(t+\delta t)=\mathbf{r}(t)+\mathbf{v}(t)\delta t+\frac{1}{2m}\mathbf{F}(t)\delta t^2$

$$\text{(B)}\quad \mathbf{v}(t+\delta t)=\mathbf{v}(t)+\tfrac{1}{2m}\big[\mathbf{F}(t)+\mathbf{F}(t+\delta t)\big]\delta t$$

Then, from (B), evaluated for the previous time step

$$\text{(C)}\quad \mathbf{v}(t)=\mathbf{v}(t-\delta t)+\tfrac{1}{2m}\big[\mathbf{F}(t-\delta t)+\mathbf{F}(t)\big]\delta t$$

Insert (C) into (A) for **v**(t):

$$\text{(D)}\quad \mathbf{r}(t+\delta t)=\mathbf{r}(t)+\Big[\mathbf{v}(t-\delta t)+\tfrac{1}{2m}\big[\mathbf{F}(t-\delta t)+\mathbf{F}(t)\big]\delta t\Big]\delta t+\tfrac{1}{2m}\mathbf{F}(t)\delta t^2$$

$$=\mathbf{r}(t)+\mathbf{v}(t-\delta t)\delta t+\tfrac{1}{2m}\mathbf{F}(t-\delta t)\delta t^2+\tfrac{1}{m}\mathbf{F}(t)\delta t^2$$

Also, from (A), one time step previous:

$$\text{(E)}\quad \mathbf{r}(t)=\mathbf{r}(t-\delta t)+\mathbf{v}(t-\delta t)\delta t+\tfrac{1}{2m}\mathbf{F}(t-\delta t)\delta t^2$$

Subtract (E) from respective sides of (D):

$$\text{(F)}\quad \mathbf{r}(t+\delta t)-\mathbf{r}(t)=\mathbf{r}(t)+\mathbf{v}(t-\delta t)\delta t+\tfrac{1}{2m}\mathbf{F}(t-\delta t)\delta t^2+\tfrac{1}{m}\mathbf{F}(t)\delta t^2$$

$$-\Big(\mathbf{r}(t-\delta t)+\mathbf{v}(t-\delta t)\delta t+\tfrac{1}{2m}\mathbf{F}(t-\delta t)\delta t^2\Big)$$

$$\mathbf{r}(t+\delta t)-\mathbf{r}(t)=\mathbf{r}(t)-\mathbf{r}(t-\delta t)+\tfrac{1}{m}\mathbf{F}(t)\delta t^2$$

$$\mathbf{r}(t+\delta t)=2\mathbf{r}(t)-\mathbf{r}(t-\delta t)+\tfrac{1}{m}\mathbf{F}(t)\delta t^2$$

We recognize the last line as the formula for the Verlet algorithm. Q.E.D.

2. Derive the leap-frog algorithm by using Taylor expansions for $v(t+\frac{\Delta t}{2})$, $v(t-\frac{\Delta t}{2})$, $x(t+\Delta t)$, and $x(t)$.

(A) $\mathbf{v}(t+\frac{\delta t}{2}) = \mathbf{v}(t) + \frac{1}{m}\mathbf{F}(t)\frac{\delta t}{2} + O(\delta t)^2$

(B) $\mathbf{v}(t-\frac{\delta t}{2}) = \mathbf{v}(t) - \frac{1}{m}\mathbf{F}(t)\frac{\delta t}{2} + O(\delta t)^2$

(C) $\mathbf{r}(t+\delta t) = \mathbf{r}(t) + \mathbf{v}(t)\delta t + O(\delta t)^2$

(D) $\mathbf{r}(t-\delta t) = \mathbf{r}(t) - \mathbf{v}(t)\delta t + O(\delta t)^2$

(A) and (C) combine to give:

(E) $$\begin{aligned}\mathbf{r}(t+\delta t) &= \mathbf{r}(t) + \left[\mathbf{v}(t+\tfrac{\delta t}{2}) - \left(\tfrac{1}{m}\mathbf{F}(t)\tfrac{\delta t}{2} + O(\delta t)^2\right)\right]\delta t + O(\delta t)^2 \\ &= \mathbf{r}(t) + \mathbf{v}(t+\tfrac{\delta t}{2})\delta t + O(\delta t)^2\end{aligned}$$

while (B) and (D) combine to give:

(F) $$\begin{aligned}\mathbf{v}(t+\tfrac{\delta t}{2}) &= \left[\mathbf{v}(t-\tfrac{\delta t}{2}) - \left(-\tfrac{1}{m}\mathbf{F}(t)\tfrac{\delta t}{2} + O(\delta t)^2\right)\right] + \tfrac{1}{m}\mathbf{F}(t)\tfrac{\delta t}{2} + O(\delta t)^2 \\ &= \mathbf{v}(t-\tfrac{\delta t}{2}) + \tfrac{1}{m}\mathbf{F}(t)\delta t + O(\delta t)^2\end{aligned}$$

(E) and (F) when truncated at $O(\delta t)$ are the leap-frog equations. Q.E.D.

3. One should be very careful with calculation of diffusion constant via the mean squared displacement when periodic boundaries are used. Why?

The MSD requires calculation of the distance a particle has traveled at time t relative to an origin at $t = 0$. Whenever the particle undergoes the central image transformation when it leaves the box, the total net distance it traveled is no longer given by a simple difference from $\mathbf{r}(0)$. The amount it was displaced during the central image move must be added back to its current position, before taking the difference. So the total net central-image shifting done to the atom must be tracked during its trajectory.

An alternative is to not use the central-image algorithm at all, which is possible if the minimum-image is programmed to allow for this (i.e., handling transformation by more than one box length).

4. The accompanying file contains data for the trajectory of a single Lennard-Jones atom in an NVE simulation. The first three columns list the *x, y, z* coordinates of the atom at each MD step, and the last three columns are the corresponding velocity components. The time step is 0.01 (in LJ units where σ and ε/k are unity).

   Averages for temperature and pressure are 0.925 and 0.659, respectively (in Lennard-Jones units). The simulated system contains 2700 atoms at a density of 0.8.

   Compute the velocity autocorrelation function from these data, and estimate the diffusivity from this. Compare your result to the following correlation in terms of pressure and temperature.

$$\log_{10} D = 0.05 + 0.07p - \frac{1.04 + 0.1p}{T}$$

   Optional bonus question: evaluate and plot the mean-squared displacement as a function of time, and examine the limiting (long-time) slope to estimate the diffusivity from this result. Beware of the issue in problem 3.

   Note: even though there appears to be a lot of data in the file, it really is not sufficient to obtain results with good precision, so do not worry too much if your results seem less than perfect.

See Mathematica file for analysis of data.

Integration of velocity autocorrelation function gives *D* of about 0.060 (LJ units). We do not have repeated data to evaluate uncertainty.

Correlation gives 0.079.