Lecture VI: Molecular Dynamics (cont.)

Recap and Integrators

The main idea of **Molecular Dynamics (MD)** is to move a system forward in time by numerically solving the equations of motion.

- **Euler Algorithm**: This method uses a simple Taylor expansion: $\underline{r}(t_0 + \delta t) = \underline{r}(t_0) + \underline{v}(t_0)\delta t + \frac{1}{2}\frac{\underline{F}(t_0)}{m}\delta t^2$. It has some drawbacks: it is not time-reversible, and it does not conserve energy or phase space volume.
- **Verlet Algorithm**: This algorithm has the correct physical properties. The position is updated using the formula: $\underline{r}(t + \delta t) = 2\underline{r}(t) - \underline{r}(t - \delta t) + \frac{\underline{F}(t)}{m}\delta t^2$. While it doesn't use velocities directly in the main equation, they can be calculated.
- **Velocity Verlet Algorithm**: This is a similar and equivalent method that explicitly includes velocities:
  - $\underline{r}(t + \delta t) = \underline{r}(t) + \dot{\underline{r}}(t)\delta t + \frac{\underline{F}(t)}{2m}\delta t^2$
  - $\dot{\underline{r}}(t + \delta t) = \dot{\underline{r}}(t) + \frac{\underline{F}(t+\delta t)+\underline{F}(t)}{2m}\delta t$

Lyapunov Instability

MD simulations have a characteristic called **Lyapunov instability**. This means that two simulations starting from almost identical initial points will separate exponentially over time. Because of this, MD does not reproduce the exact, true path of the system. However, this is not a problem, because the main goal is to correctly sample the thermodynamic ensemble, not to follow a single, precise trajectory.

Formal Derivation of Integrators

We can formally derive integrators like the Verlet algorithm from Liouville mechanics. These types of integrators are called symplectic, which means they are time-reversible and conserve phase space volume.

1. The time evolution of any observable property $A(p, q)$ is described by $A(t) = e^{i\hat{L}t}A(0)$, where $\hat{L}$ is the Liouville operator.
2. This operator can be split into two parts: one for position ($\hat{L}_q$) and one for momentum ($\hat{L}_p$).
3. Since these two parts do not commute, we can't simply split the exponential. Instead, we use the **Trotter theorem** to approximate the change over a small time step δt:

$$e^{i\hat{L}\delta t} \approx e^{i\hat{L}_p\frac{\delta t}{2}}e^{i\hat{L}_q\delta t}e^{i\hat{L}_p\frac{\delta t}{2}}$$

4. This sequence of operations translates to the following steps:
    - Update momenta for a half time step ($\delta t/2$).
    - Update positions for a full time step (δt).
    - Update momenta again for another half time step ($\delta t/2$).
5. This process is mathematically the same as the Velocity Verlet algorithm. This framework allows for the systematic creation of many different integrators, including those used to control temperature and pressure.

Generating the Canonical (NVT) Ensemble

Standard MD simulates the microcanonical (NVE) ensemble, where the number of particles, volume, and energy are constant. To simulate the **canonical (NVT) ensemble**, where temperature is constant instead of energy, we need to control the temperature using a **thermostat**.

There are three main types of thermostats:

1. **Velocity Rescaling Methods** (e.g., Berendsen thermostat): These methods directly rescale particle velocities to force the temperature to the desired value. They often do not generate a correct canonical ensemble.
2. **Stochastic Methods** (e.g., Langevin dynamics): These add friction and random forces to the equations, which mimics collisions with a heat bath. This correctly generates the NVT ensemble but alters the natural dynamics of the system.

3. **Extended Lagrangian Methods** (e.g., Nosé-Hoover thermostat): This is a deterministic method that adds extra, fictitious degrees of freedom to the system to represent the heat bath. The equations of motion for the real particles are modified to couple them to this thermostat. This method correctly produces the NVT ensemble. A known issue is that the original Nosé-Hoover thermostat can sometimes fail to explore the entire phase space (it's not always ergodic), but this can be fixed by using **Nosé-Hoover chains**, which link several thermostats together.

The Virial Theorem and Pressure

The **Virial theorem** connects the time-averaged kinetic energy to the forces within the system. It states:

$$\langle T \rangle = -\frac{1}{2} \left\langle \sum_{i=1}^{N} \underline{F}_i \cdot \underline{q}_i \right\rangle$$

This theorem can be used to calculate the instantaneous pressure in a simulation:

$$P = \frac{N k_B T}{V} + \frac{1}{3V} \left\langle \sum_{i=1}^{N} \underline{F}_i \cdot \underline{q}_i \right\rangle$$

The first part of the equation is the ideal gas pressure, and the second part is the contribution from the forces between particles.