24-623/12-623: Important formulas from Lecture 4

## 1. Hamiltonian Equations of Motion

The Hamiltonian, $H$, is the sum of the total system potential energy, $U$, and the total system kinetic energy, $K$. The Hamiltonian is thus equivalent to the total energy in the system, $E$. This equivalence is only true in a classical system. In a quantum system, the Hamiltonian is an operator. The potential energy is only a function of the atomic positions and the kinetic energy is only a function of the atomic momenta, so that

$$H(\mathbf{r}, \mathbf{p}) = U(\mathbf{r}) + K(\mathbf{p}), \tag{1}$$

where $\mathbf{r}$ and $\mathbf{p}$ represent all the positions and momenta. The total kinetic energy is related to the momenta of the particles by

$$K = \sum_i \frac{|\mathbf{p}_i|^2}{2m_i}. \tag{2}$$

The Hamiltonian equations of motion for a coordinate $i$ are:

$$\dot{\mathbf{r}}_i = \frac{\partial H}{\partial \mathbf{p}_i} \tag{3}$$

$$\dot{\mathbf{p}}_i = -\frac{\partial H}{\partial \mathbf{r}_i}, \tag{4}$$

which lead to

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} \tag{5}$$

$$\dot{\mathbf{p}}_i = -\frac{\partial U}{\partial \mathbf{r}_i}, \tag{6}$$

which can be combined to give

$$m_i \ddot{\mathbf{r}}_i = -\frac{\partial U}{\partial \mathbf{r}_i}. \tag{7}$$

This expression is Newton's 2nd law, if we interpret the right hand side as the force on particle $i$. That is,

$$\mathbf{F}_i = -\frac{\partial U}{\partial \mathbf{r}_i}. \tag{8}$$

Note that we can write these equations for the scalar coordinates as well.

## 2. Velocity Verlet Integration Scheme

To perform an MD simulation, we need to integrate Eqs. (5) and (6) for all of the $N$ particles in the system. The integration is done by breaking the first-order equations down into their $x$-, $y$-, and $z$- components and working with these $6N$ scalar equations.

The Verlet scheme we will use in this class, for particle $i$ in the $x$-direction, is

$$1.\, v_{i,x}(t + \Delta t/2) = v_{i,x}(t) + F_{i,x}(t)\Delta t/(2m_i) \tag{9}$$

$$2.\, r_{i,x}(t + \Delta t) = r_{i,x}(t) + v_{i,x}(t + \Delta t/2)\Delta t \tag{10}$$

$$3.\, v_{i,x}(t + \Delta t) = v_{i,x}(t + \Delta t/2) + F_{i,x}(t + \Delta t)\Delta t/(2m_i) \tag{11}$$

## 3. System Potential Energy from a Pair Potential

The vector connecting particles $i$ and $j$ is defined by

$$\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j \tag{12}$$

Note that $\mathbf{r}_{ij} = -\mathbf{r}_{ji}$. We denote the magnitude of $\mathbf{r}_{ij}$ by $r_{ij}$.

We will be focusing our attention in this course on pair potentials. In a pair potential, the energy of an atom and the force acting on it are related to independent interactions with the other atoms in the system. We denote the potential energy function (the interatomic potential) between two atoms separated by a distance $r$ by $u(r)$. Each atom in an interaction gets half of this potential energy. Thus, the total potential energy of one atom will be given by

$$U_i = \frac{1}{2}\sum_{j \neq i} u(r_{ij}), \tag{13}$$

and the total potential energy will be

$$U = \sum_i U_i = \frac{1}{2}\sum_i \sum_{j \neq i} u(r_{ij}) = \sum_i \sum_{j > i} u(r_{ij}). \tag{14}$$

## 4. Lennard-Jones Potential

The Lennard-Jones (LJ) potential is given by

$$u(r) = 4\epsilon \left[ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right],$$

where $\epsilon$ and $\sigma$ are specific to a material. In an MD code, it is best to implement the potential in dimensionless form as

$$u^*(r^*) = 4 \left[ \left(\frac{1}{r^*}\right)^{12} - \left(\frac{1}{r^*}\right)^{6} \right],$$

where $u^* = u/\epsilon$ and $r^* = r/\sigma$.