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Applied Computational Science II

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Brief introduction to

Molecular Dynamics

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A good reference

- **D.C. Rapaport**
The Art of Molecular Dynamics Simulation
Second Edition
Cambridge University Press, Cambridge, 2004
- The introductory material presented here is mostly from Ch. 2 of this book.

What is Molecular Dynamics (MD)?

- A catch-all name for a set of numerical techniques to **integrate the Newtonian equations of motion** for interacting many-particle systems.
- The **equations of motion (EOM)** can be simply expressed as the **kinematic equations**,

$$\mathbf{r}_i(t) = \mathbf{r}_i(0) + \int_0^t \dot{\mathbf{r}}_i(t') dt'$$

$$\dot{\mathbf{r}}_i(t) = \dot{\mathbf{r}}_i(0) + \int_0^t \ddot{\mathbf{r}}_i(t') dt'$$

with the accelerations from **Newton's Second Law**,

$$m_i \ddot{\mathbf{r}}_i(t) = \mathbf{F}_i(\mathbf{r}(t)) = - \sum_{j \neq i} \frac{\partial U(\mathbf{r}(t))}{\partial |\mathbf{r}_i(t) - \mathbf{r}_j(t)|}$$

- In **Newton's Second Law**,

$$m_i \ddot{\mathbf{r}}_i(t) = \mathbf{F}_i(\mathbf{r}(t)) = - \sum_{j \neq i} \frac{\partial U(\mathbf{r}(t))}{\partial |\mathbf{r}_i(t) - \mathbf{r}_j(t)|}$$

m_i is the mass of particle i , and $U(\mathbf{r})$ is the potential energy as a function of the set \mathbf{r} of all the N particle positions \mathbf{r}_i .

- In more complicated cases it may be advantageous to write the EOMs in the form of **Lagrange's EOMs**

$$\frac{d}{dt} \left(\frac{\partial \mathcal{L}}{\partial \dot{\mathbf{r}}_i} \right) - \frac{\partial \mathcal{L}}{\partial \mathbf{r}_i} = 0$$

where

$$\mathcal{L} = \frac{1}{2} \sum_i m_i \dot{\mathbf{r}}_i^2 - U(\mathbf{r})$$

is the **Lagrangian**, which can be generalized to include **constraints**.

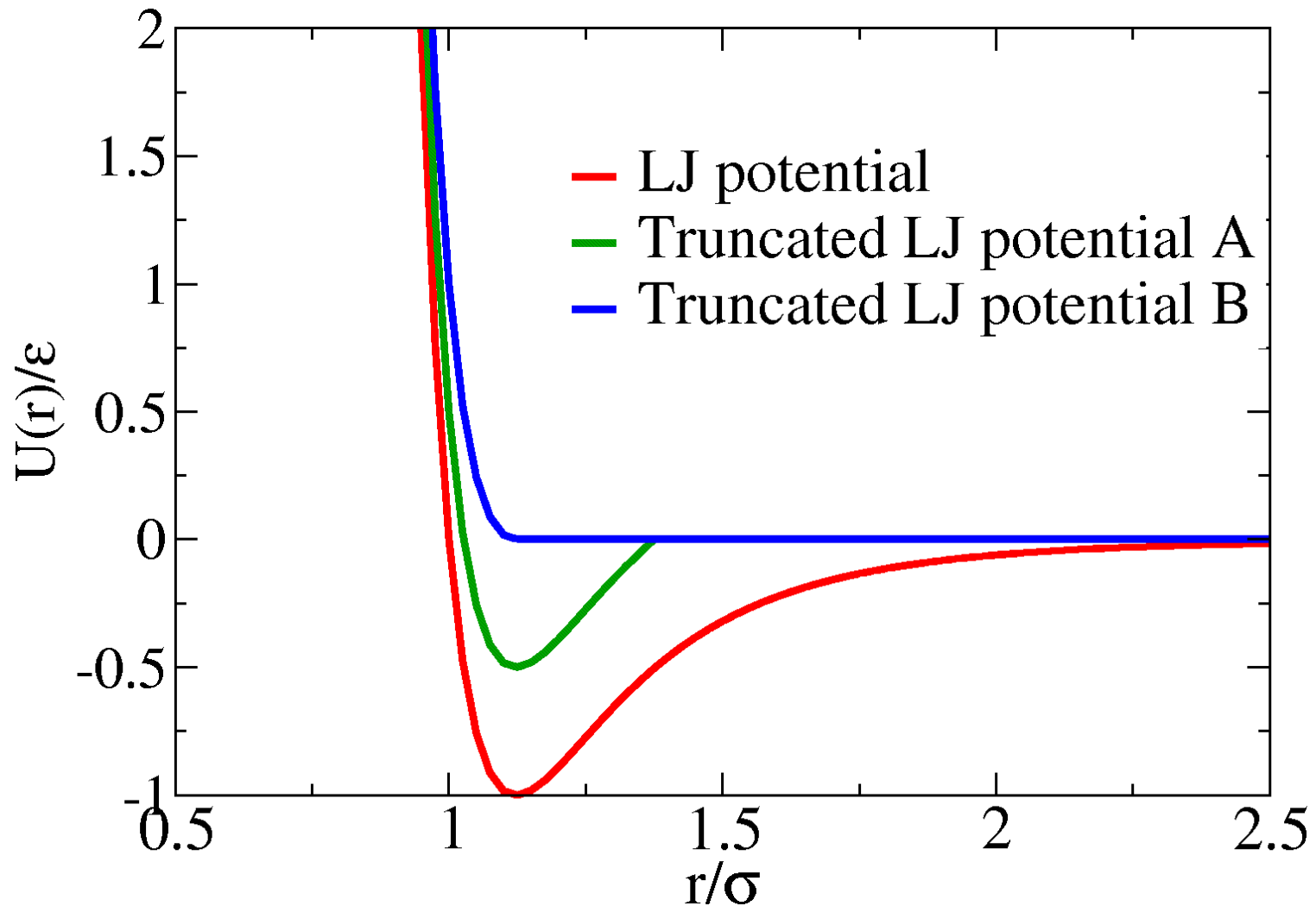
Lennard-Jones (LJ) potential

- For this introduction, let us consider the LJ potential, which is often used to model simple monatomic gases, such as Ar.

$$U(r_{ij}) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] & r_{ij} < r_c \\ 0 & r_{ij} \geq r_c \end{cases}$$

Often this is simplified as the purely repulsive

$$U(r_{ij}) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] + \epsilon & r_{ij} < r_c = 2^{1/6}\sigma \\ 0 & r_{ij} \geq r_c \end{cases}$$



The **LJ potential** and two truncated forms.
A: repulsive/attractive. **B: purely repulsive.**

Dimensionless units

- Length: $r \rightarrow r\sigma$
- Energy: $e \rightarrow e\varepsilon$
- Time: $t \rightarrow t(m\sigma^2/\varepsilon)^{1/2}$
- In these dimensionless units we have:
- EOM: $\ddot{\mathbf{r}}_i(t) = 48 \sum_{j \neq i} \left(r_{ij}^{-14} - \frac{1}{2} r_{ij}^{-8} \right) \mathbf{r}_{ij}$
- Kinetic and potential energies:

$$E_K = \frac{1}{2N} \sum_i \dot{\mathbf{r}}_i^2$$

$$E_P = \frac{4}{N} \sum_{1 \leq i < j \leq N} \left(r_{ij}^{-12} - r_{ij}^{-6} \right)$$

Boundary conditions

- If we want to study bulk conditions in a relatively small system, we should eliminate the walls of the container by using **periodic boundary conditions (pbc)**.
- In **pbc** we consider the system periodically repeated indefinitely in all d dimensions.

Integration schemes

- A large many-particle system like this is **chaotic** in the sense that **its trajectories are infinitely sensitive to the initial conditions.**
- Thus there is nothing to be gained by using higher-order integration schemes.
- The most common ones are **Leapfrog** and **Predictor-Corrector.**

- The Leapfrog scheme sketched here is usually sufficient:

$$\dot{r}_{ix}(t + h/2) = \dot{r}_{ix}(t - h/2) + h\ddot{r}_{ix}(t)$$

$$r_{ix}(t + h) = r_{ix}(t) + h\dot{r}_{ix}(t + h/2)$$

- Position and velocity are evaluated at different times. To get velocity at t we have:

$$\dot{r}_{ix}(t) = \dot{r}_{ix}(t - h/2) + (h/2)\ddot{r}_{ix}(t)$$

Here r_{ix} represents the x component of the position of the i th particle. Analogous equations apply to the components in the other coordinate directions.

- This Leapfrog scheme can be modified to give position and velocity at the **same times**:

$$\dot{r}_{ix}(t + h/2) = \dot{r}_{ix}(t) + (h/2)\ddot{r}_{ix}(t)$$

$$r_{ix}(t + h) = r_{ix}(t) + h\dot{r}_{ix}(t + h/2)$$

- Use the new coordinates to update accelerations and then update the velocities over the next half time step:

$$\dot{r}_{ix}(t + h) = \dot{r}_{ix}(t + h/2) + (h/2)\ddot{r}_{ix}(t + h)$$

Measurements

- Except for rounding errors, this basic MD scheme conserves the **total system energy**,
 $E = E_K + E_P$.
- Thermodynamic quantities like temperature T and pressure P therefore **fluctuate**.
- Their average values are given as

$$\langle T \rangle = \frac{2}{d} E_K = \frac{1}{dN} \sum_i \dot{\mathbf{r}}_i^2$$

$$\begin{aligned} \langle P \rangle V &= N \langle T \rangle + \frac{1}{d} \sum_{i < j} \mathbf{r}_{ij} \cdot \mathbf{F}_{ij} \\ &\stackrel{\text{LJ}}{=} N \langle T \rangle + \frac{48}{d} \sum_{i < j} \left(r_{ij}^{-12} - \frac{1}{2} r_{ij}^{-6} \right) \end{aligned}$$

Given T and P

- To allow simulations at constant T and P one needs to introduce **constraints** called **thermostats**, that allow the **energy** to **fluctuate**.
- This is beyond what I can cover in this brief introduction.

Some examples

- Here are some MD simulations of LJ fluids undergoing phase separation from the web:
- <http://www.chemistry.wustl.edu/~gelb/gchem/materials/lve/>