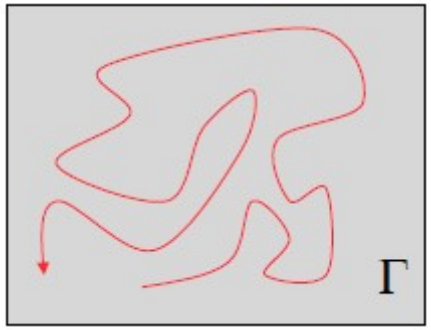
Unit III

Content

- **Classical Equilibrium Statistical Mechanics:**
  - Phase space,
  - Hamiltonian's equation,
  - macroscopic translation and rotation,
  - phase space coordinates,
  - canonical transformations,
  - applications.
- **Molecular Dynamics:**
  - Introduction, brief MD algorithm,
  - micro-canonical ensemble (NVE),
    - velocity-verlet algorithm,
    - canonical ensemble (NVT),
  - applications.

Phase Space

- Phase space
  - Full specification of microstate of the system is given by the values of all positions and all momenta of all atoms. $\Gamma \rightarrow (p^N, r^N)$
  - View positions and momenta as completely independent coordiantes
    - Connection between them through equation of motion.
- Motion through phase space
  - Dynamics as simple movement through the high dimensional phase space
    - Facilitate connection to quantum mechanics
    - Basis for theoretical treatments of dynamics
    - Understanding of integrators



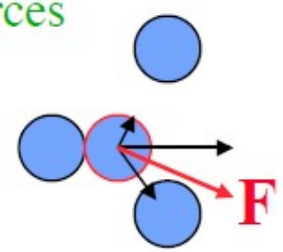
Integration Algorithms

Equations of motion in cartesian coordinates

$$\frac{d\mathbf{r}_j}{dt} = \frac{\mathbf{p}_j}{m}$$
$$\frac{d\mathbf{p}_j}{dt} = \mathbf{F}_j$$

$\mathbf{r} = (r_x, r_y)$
$\mathbf{p} = (p_x, p_y)$
} 2-dimensional space (for example)

$$\mathbf{F}_j = \sum_{\substack{i=1 \\ i \neq j}}^{N} \mathbf{F}_{ij}$$ pairwise additive forces



Desirable features of an integrator

- *minimal need to compute forces (a very expensive calculation)*
- *good stability for large time steps*
- *good accuracy*
- *conserves energy and momentum*
- *time-reversible*
- *area-preserving (symplectic)*

} More on these later

- Molecular dynamics is a technique for computer simulation of complex systems, modelled at the atomic level.
- Dynamics is displacements from average structure
- Thermodynamics is a equilibrium behaviour of structure

- MD simulations boil down to numerically integrating Newton's equations of motion
- Newton's Laws of Motion

  1. A body maintains its state of rest or of uniform motion in a straight line, unless acted upon by a force.

  2. The applied force is equal to the rate of change of momentum.

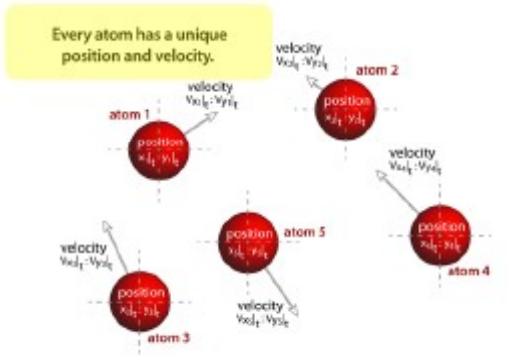
  3. For every action, there is an equal and opposite reaction

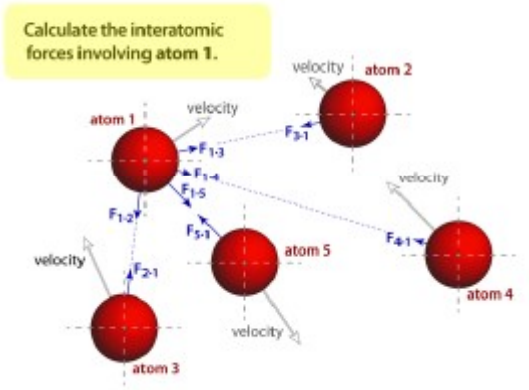
- Newtonian mechanics is used to calculate the net force with the help of acceleration experienced by each atom.
- Forces (F_i) acting on each atom,

$$\overrightarrow{F_i} = m_i a_i = -\frac{dU}{dr_i}$$

- The potential energy $U(r^N)$ where $r_N = (r_1, r_2, \ldots r_n)$ represents the complete set of 3N atomic coordinates.
- Using position and accelerations at time t_n, the new positions at time t_{n+1} is calculated.

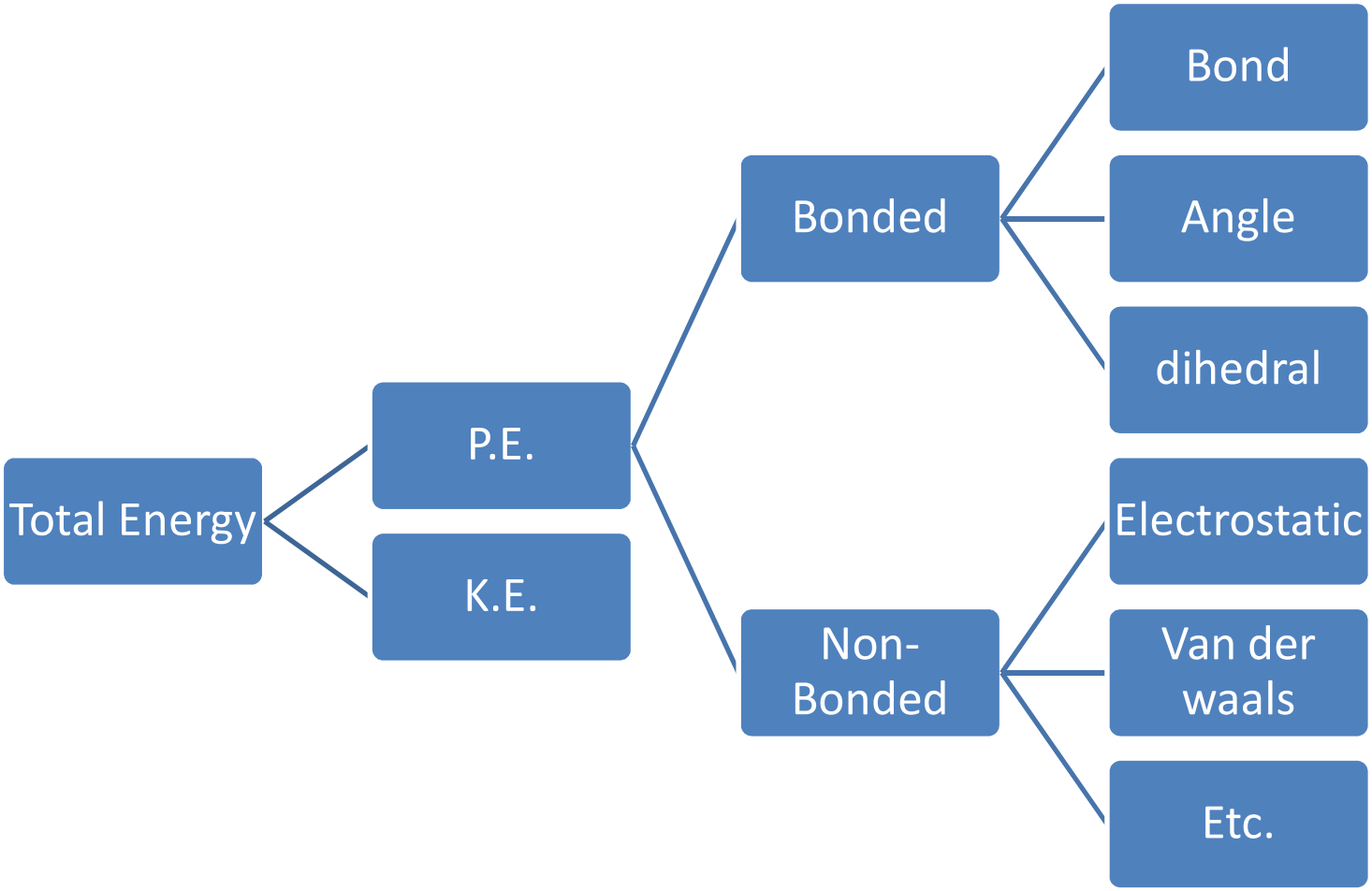
Forces are derived from inter-atomic potential functions.





A force field is made up by the contributions of many terms that represent the different types of interactions between the atoms (energy function)

Classification of Energy



Lennard-Jones potential

- Mathematically simple model that approximates the interaction between to two neutral atoms or molecules.

$$v^{LJ}(r) = 4\varepsilon\left[\left(\frac{R}{r}\right)^{12} - \left(\frac{R}{r}\right)^{6}\right]$$

- R – the diameter, ε – the well depth

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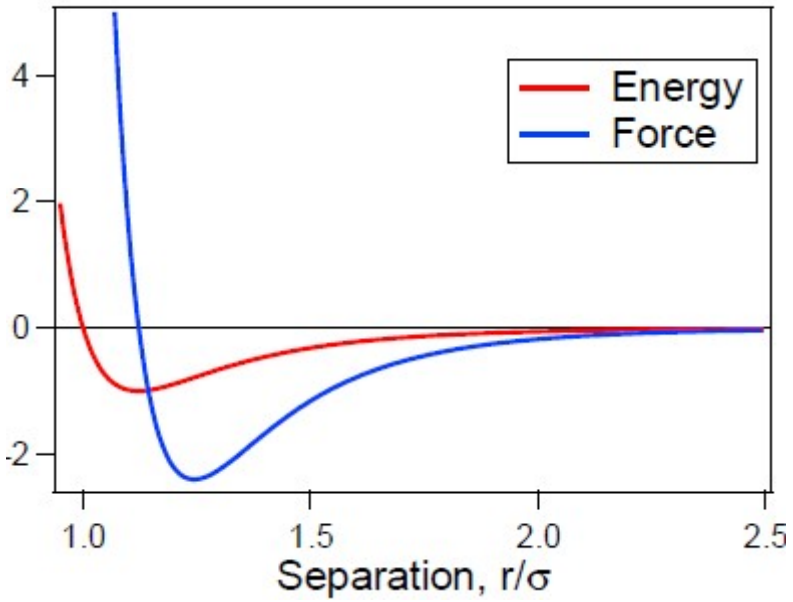


- If electrostatic charges are present, then coulomb potentials is presented by

$$v^{coulomb}(r) = \frac{q_1 q_2}{4\pi\varepsilon_o r}$$

q_1 and q_2 are charges and ε_o is permittivity of free space.

Energy Functions

$$U(\vec{R}) = \sum_{bonds} k_i^{bond}(r_i - r_0)^2 + \sum_{angles} k_i^{bond}(\theta_i - \theta_0)^2$$

$$+ \sum_{dihedrals} k_i^{bond}\left[1 + \cos(n_i\phi_i + \delta_i)\right]$$

bonded

$$+ \sum_i \sum_{j \neq i} 4\varepsilon_{ij}\left[\left(\frac{R_{ij}}{r_{ij}}\right)^{12} - \left(\frac{R_{ij}}{r_{ij}}\right)^{6}\right] + \sum_i \sum_{j \neq i} \frac{q_i q_j}{4\pi\varepsilon r_{ij}}$$

nonbond

bond= oscillations about the equilibrium bond length
angle= oscillations of 3 atoms about an equilibrium angle
dihedral= torsional rotation of 4 atoms about a central bond
nonbond= non-bonded energy terms (electrostatics and Lenard-Jones)

Molecular Dynamics Ensembles

- Constant energy, constant number of particles (NE)
- Constant energy, constant volume (NVE)
- Constant temperature, constant volume (NVT)
- Constant temperature, constant pressure (NPT)

Choose the ensemble that best fits your system and start the simulations

MD trajectory

MD trajectory is a series of atoms positions in time. To obtain the trajectory we need to:

- Build the molecules – find the (x,y,z) position of all atoms
- Chose the force field (or create it)
- Find the optimal structure (energy minimization)
- Calculate the trajectory = solve the newton's equations of motions of all atoms in the force field at each time moment. (timestep)
- Analyze the trajectory obtained, make or verify hypothesis

MD algorithm

1. Prepare molecule
   - Read in pdb and psffile
2. Minimization
   - Reconcile observed structure with force field used (T = 0).
3. Heating
   - Raise temperature of the system
4. Equilibration
   - Ensure system is stable
5. Dynamics
   - Simulate under desired conditions (NVE, NPT, etc)
   - Collect your data
6. Analysis
   - Collect your data
   - Evaluate observables (macroscopic level pro

Energy Minimization

- Energy minimization methods are used to compute the equilibrium configuration of molecules. Stable states of molecules correspond to global and local minima on their potential energy surface. Starting from non-equilibrium geometry the mathematical procedure of optimization moves atoms to find the lowest energy configuration .
- Energy minimization does not include the temperature. From physical point of view the final state of the system corresponds to the configuration of atoms in zero kelvin.
- Potential energy surface – multidimensional surface with atomic positions as variables. During the minimization procedure we change atoms coordinates to the global minima.

The Velocity Verlet Algorithm

- The Velocity Verlet algorithm is a numerical method used to integrate Newton's equations of motion.
  - Fast and accurate
  - Linear and angular momentum preserved
  - Time reversible
  - Requires only on force evaluation for each time step
  - The algorithms is simple (long-time stable)

The velocity verlet algorithm generates a sequence of snapshots for the particle coordinates and velocities at all intermediate times Δt.

Verlet Algorithm

- Very simple, very good, very popular algorithm
- Consider expansion of coordinate forward and backward in time

$$\mathbf{r}(t+\delta t) = \mathbf{r}(t) + \frac{1}{m}\mathbf{p}(t)\delta t + \frac{1}{2m}\mathbf{F}(t)\delta t^2 + \frac{1}{3!}\dddot{\mathbf{r}}(t)\delta t^3 + O(\delta t^4)$$

$$\mathbf{r}(t-\delta t) = \mathbf{r}(t) - \frac{1}{m}\mathbf{p}(t)\delta t + \frac{1}{2m}\mathbf{F}(t)\delta t^2 - \frac{1}{3!}\dddot{\mathbf{r}}(t)\delta t^3 + O(\delta t^4)$$

- Add these together

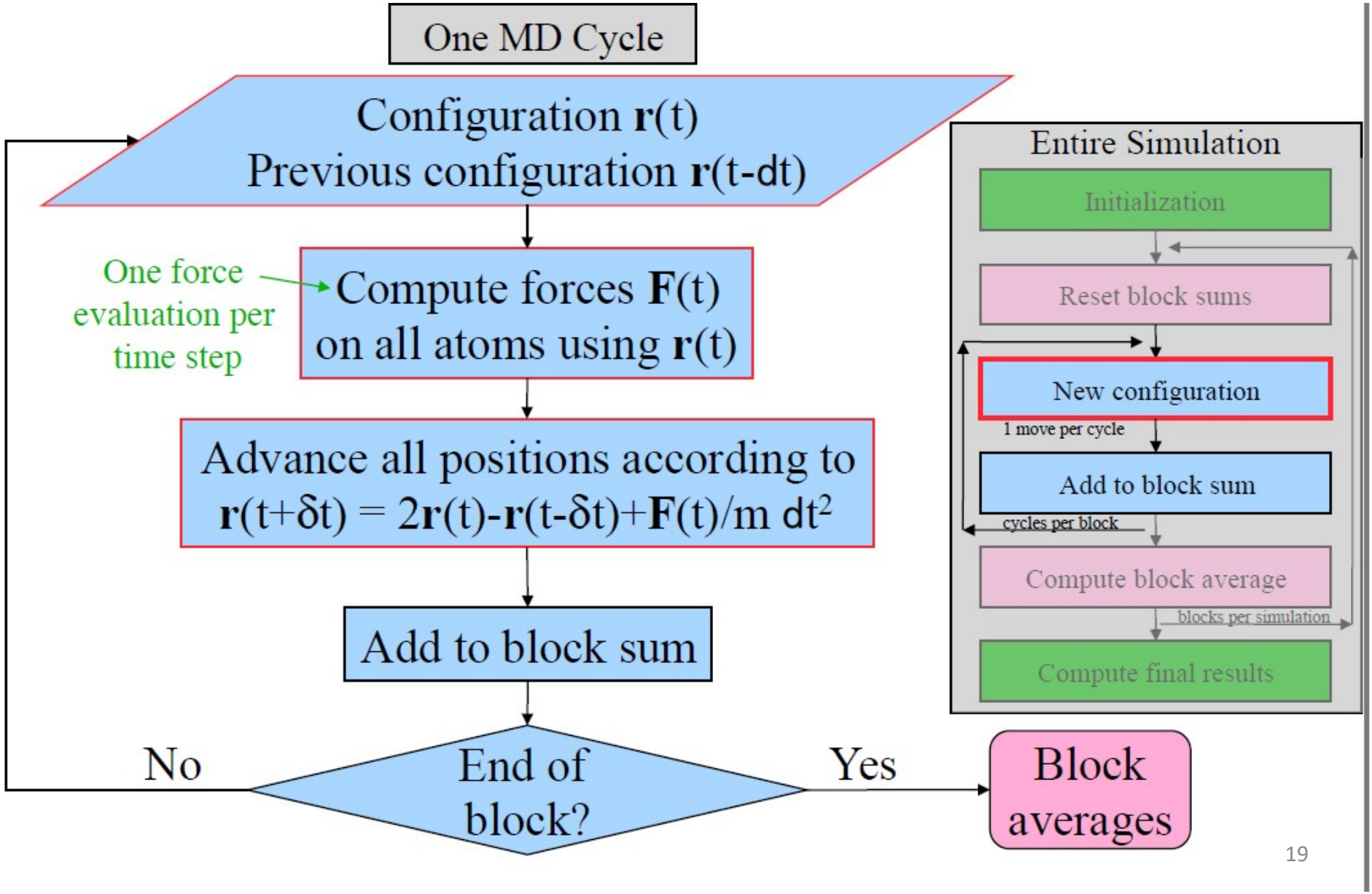
$$\mathbf{r}(t+\delta t) + \mathbf{r}(t-\delta t) = 2\mathbf{r}(t) + \frac{1}{m}\mathbf{F}(t)\delta t^2 + O(\delta t^4)$$

- Rearrange

$$\boxed{\mathbf{r}(t+\delta t) = 2\mathbf{r}(t) - \mathbf{r}(t-\delta t) + \frac{1}{m}\mathbf{F}(t)\delta t^2} + O(\delta t^4)$$

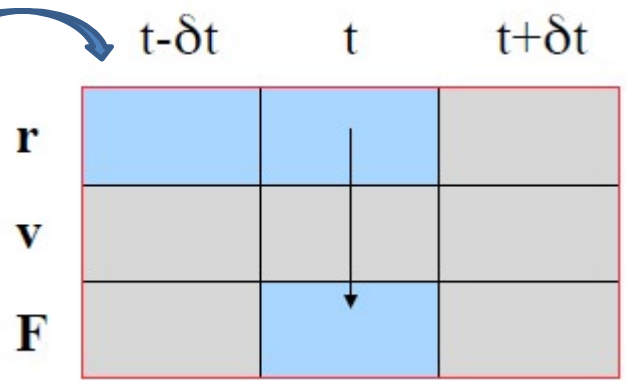
  - *update without ever consulting velocities!*

Verlet Algorithm (Flow Diagram)

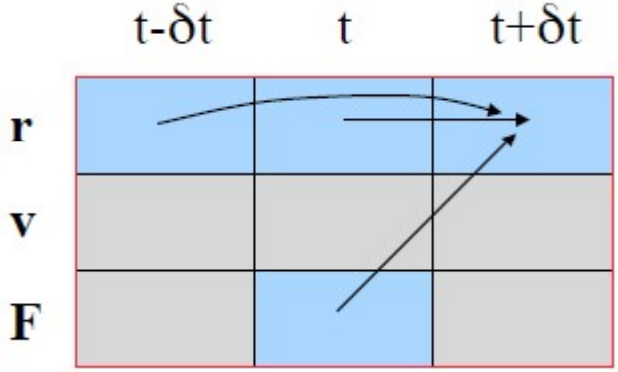


Verlet Algorithm (Flow Diagram)

Given current position and position at end of previous time step



Compute the force at the current position



Compute new position from present and previous positions, and present force

Advance to next time step, repeat