CE 530 Molecular Simulation

Lecture 3
Common Elements of a Molecular Simulation

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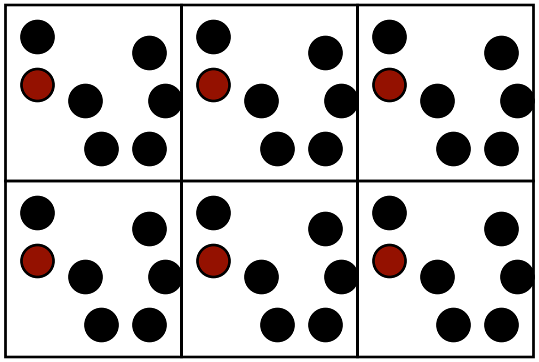
Boundary Conditions

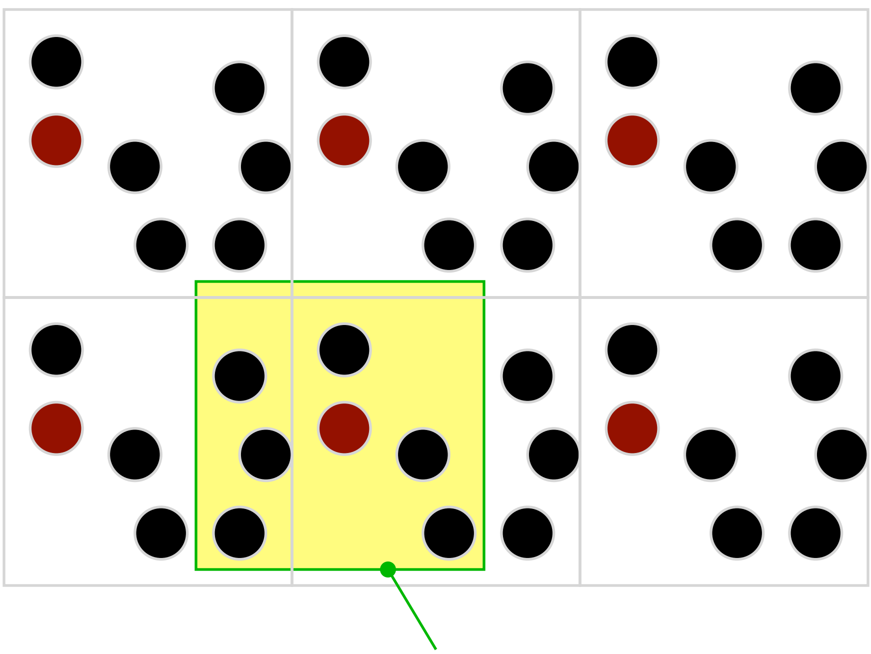
- Impractical to contain system with a real boundary
  - *Enhances finite-size effects*
  - *Artificial influence of boundary on system properties*
- Instead surround with replicas of simulated system
  - *"Periodic Boundary Conditions" (PBC)*



  - *Click here to view an applet demonstrating PBC*

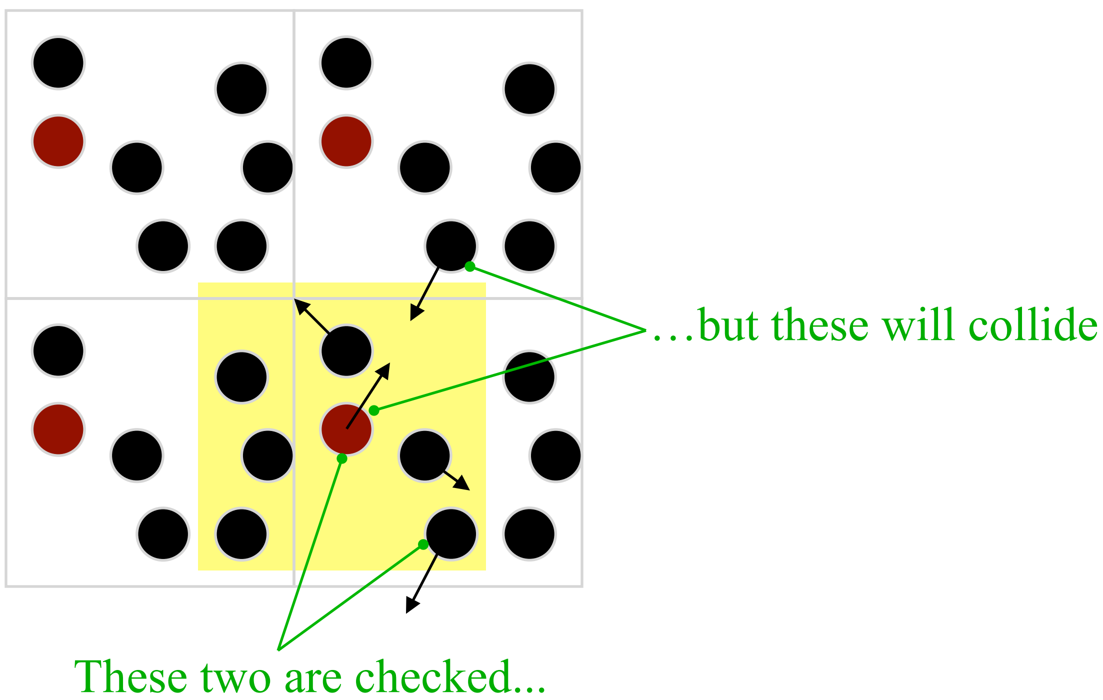
Issues with Periodic Boundary Conditions 1.

- Minimum image convention
  - *Consider only nearest image of a given particle when looking for collision partners*



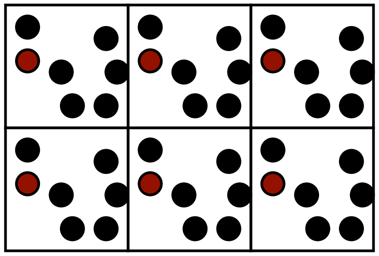
Issues with Periodic Boundary Conditions 2.

- Caution not to miss collisions
  - *click here for a bad simulation*

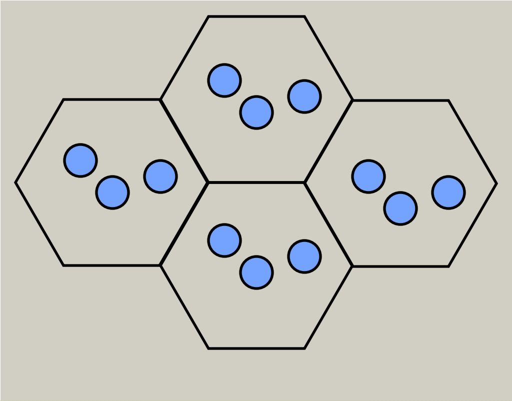


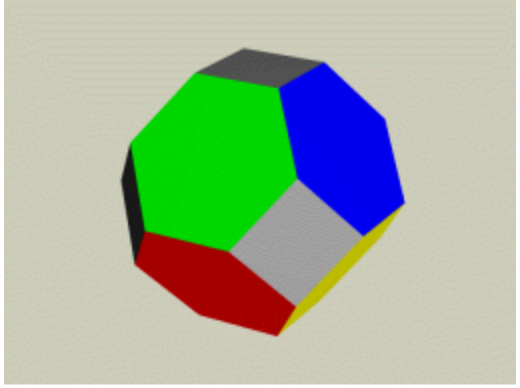
Issues with Periodic Boundary Conditions 3.

- Correlations
  - *new artificial correlations*
  - *supressed long-range correlations*



- Other issues arise when dealing with longer-range potentials
  - *accounting for long-range interactions*
  - *nearest image not always most energetic*
  - *splitting of molecules (charges)*
  - *discuss details later*
- Other geometries possible
  - *any space-filling unit cell*
    - hexagonal in 2D
    - truncated octahedron in 3D
    - rhombic dodecahedron in 3D
  - *surface of a (hyper)sphere*
  - *variable aspect ratio useful for solids*
    - relieves artificial stresses





Implementing Cubic Periodic Boundaries 1.

- Details vary with representation of coordinates
  - *Box size*

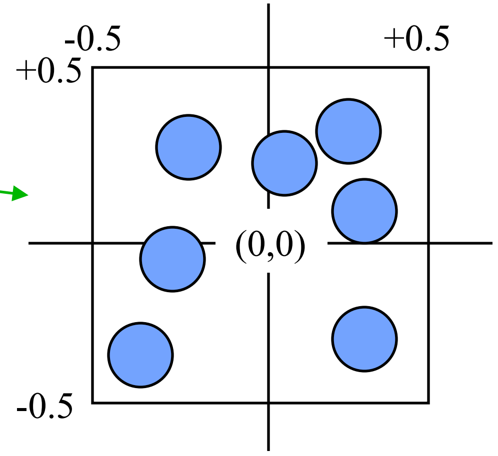
    unit box, coordinates scaled by edge length

    ```
    dr.x = dimensions.x * (r1.x - r2.x);  //difference in x coordinates
    ```

    full-size box, coordinates represent actual values
  - *Box origin*

    center of box, coordinates range from *-L/2* to *+L/2*

    corner of box, coordinates range from 0 to *L*



- Two approaches
  - *decision based ("if" statements)*
  - *function based (rounding (nint), truncation, modulo)*
  - *relative speed of each approach may vary substantially from one computer platform to another*

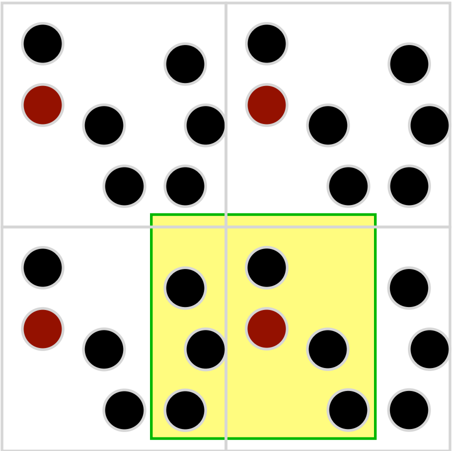
Implementing Cubic Periodic Boundaries 2. Central-image codes

- Involved in most time-consuming part of simulation
- (0,1) coordinates, decision based
  - ```
    r.x -= (r.x > 0.0) ? Math.floor(r.x) : Math.ceil(r.x-1.0); //Java syntax
    ```
  - *examples: -0.2 → +0.8; -1.4 → +0.6; +0.4 → +0.4; +0.6 → +0.6; +1.5 → +0.5*
- (0,L) coordinates, decision based
  - ```
    r.x -= dimensions.x * ((r.x > 0.0) ? Math.floor(r.x/dimensions.x) :
                                          Math.ceil(r.x/dimensions.x-1.0));
    ```
- (-1/2, 1/2), decision based
  - ```
    if(r.x > 0.5) r.x -= 1.0; if(r.x < -0.5) r.x += 1.0;  //only first shell
    ```
  - *examples: -0.2 → -0.2; -1.4 → -0.4; +0.4 → +0.4; +0.6 → -0.4; +1.5 →f +0.5*
- (-1/2, 1/2), function based
  - ```
    r.x -= Math.round(r.x);//nearest integer (r.x must be float, not double)
    ```
- (0,L), function based
  - ```
    r.x %= dimensions.x; if(r.x < 0.0) r.x += dimensions.x;//modulo operator
    ```

N.B. Most code segments are untested
    ```

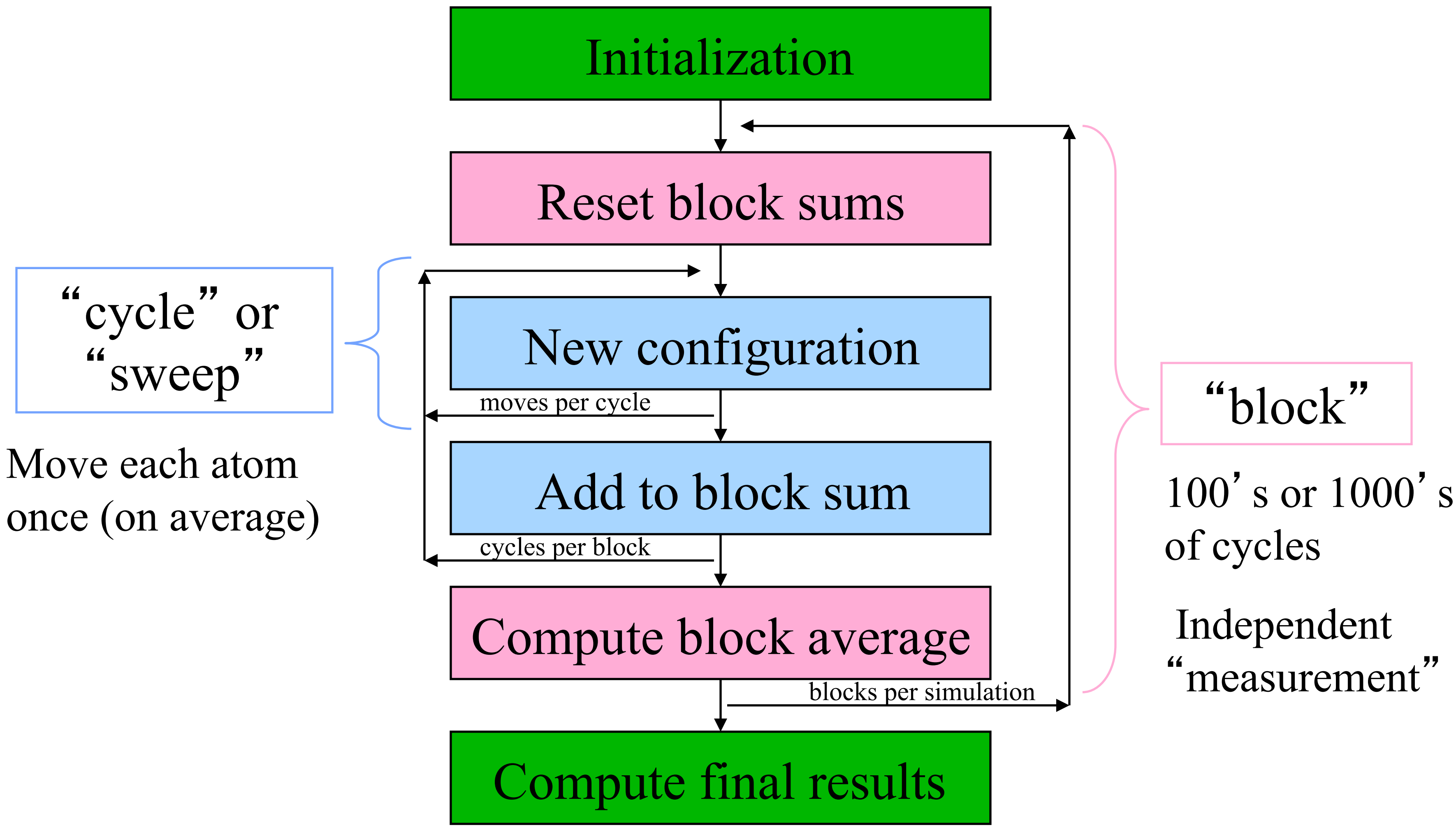
Implementing Cubic Periodic Boundaries 3. Nearest-image codes

- Simply apply (-1/2,1/2) central-image code to raw difference!
  - `dr.x = r1.x - r2.x; //unit box length`
  - `if(dr.x > 0.5) dr.x -= 1.0;`
  - `if(dr.x < -0.5) dr.x += 1.0;`
  - `dr.x *= dimensions.x;`

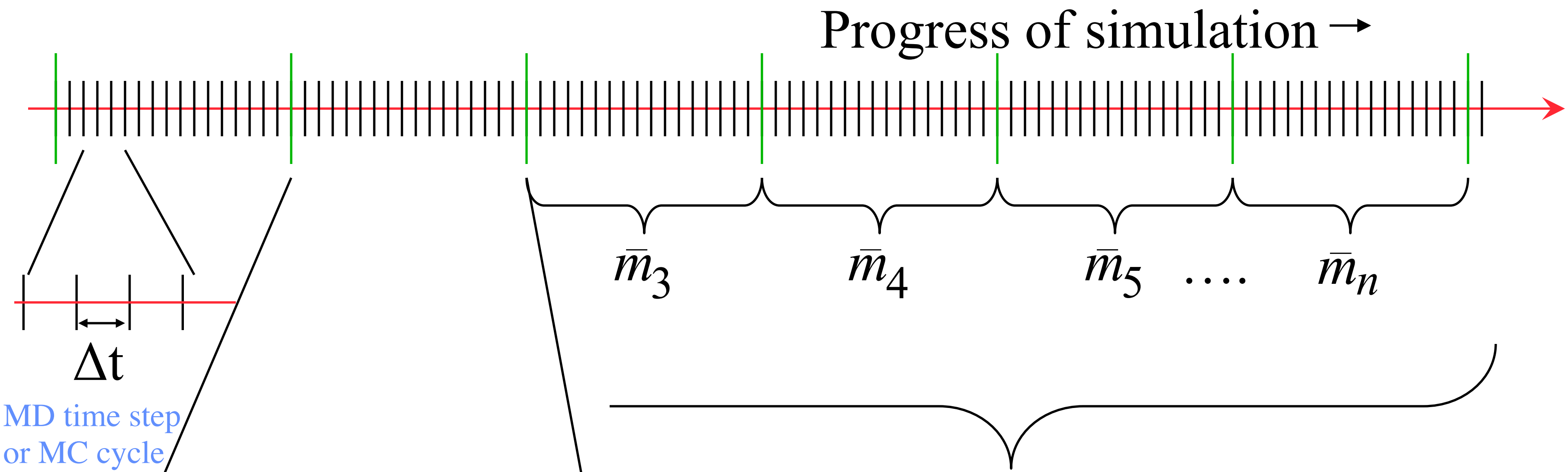


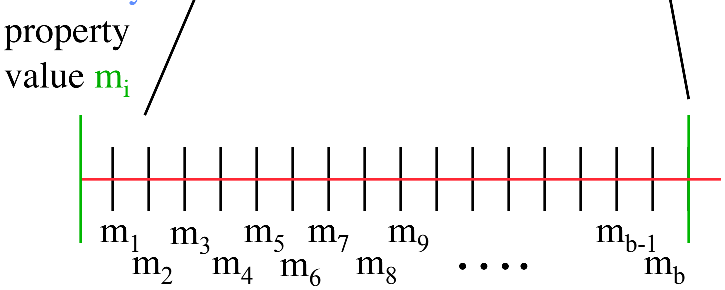
- Or…
  - `dr.x = r1.x - r2.x; //true box length`
  - `dr.x -= dimensions.x * Math.round(dr.x/dimensions.x);`
- Take care not to lose correct sign, if doing force calculation
- Nearest image for non-cubic boundary not always given simply in terms of a central-image algorithm

Structure of a Molecular Simulation 1.



Structure of a Molecular Simulation 2.





Simulation block

block average

$$\bar{m} = \frac{1}{b}\sum_{i=1}^{b} m_i$$

Complete simulation

- simulation average

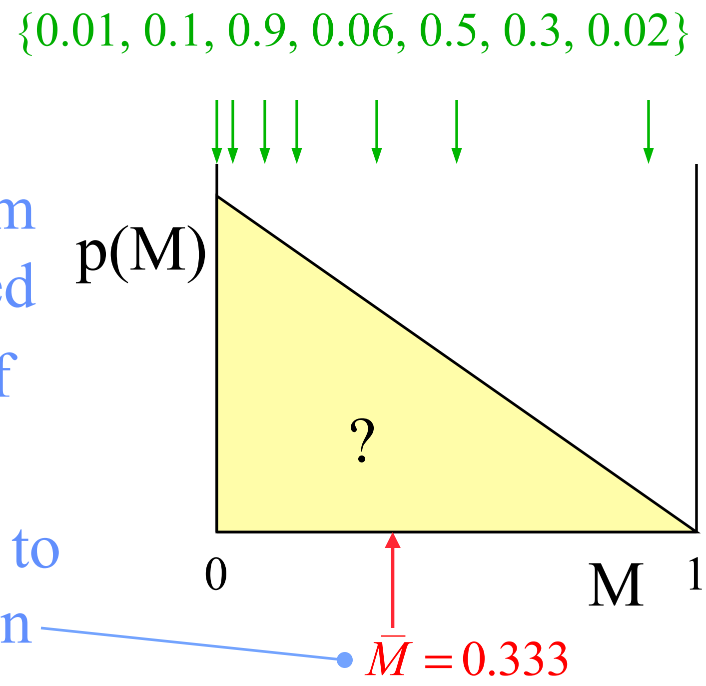
$$\langle m \rangle = \frac{1}{n}\sum_{k=1}^{n} \bar{m}_k$$

- simulation error bar

$$\sigma_{\langle m \rangle} = \frac{\sigma_{\bar{m}}}{\sqrt{n-1}} \quad ; \quad \sigma_{\bar{m}} = \left[\frac{1}{n}\sum_{k=1}^{n} \bar{m}_k^2 - \langle m \rangle^2\right]^{1/2}$$

Confidence Limits on Simulation Averages 1.

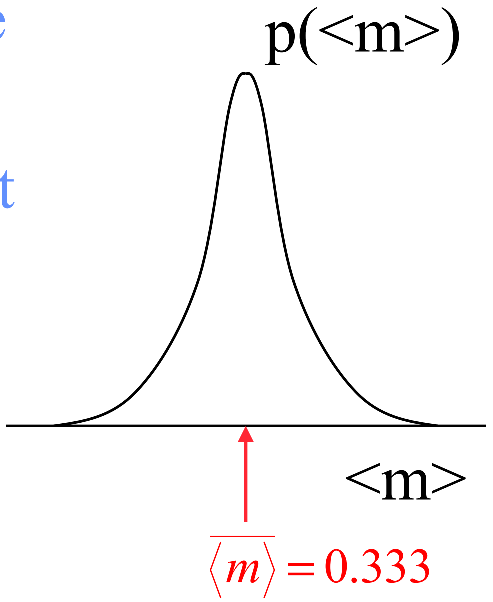
- Given a set of measurements $\{m_i\}$, for some property M
- There exists a distribution of values from which these measurements were sampled
- We do not know, *a priori*, any details of this distribution
- We wish to use our measurements $\{m_i\}$ to estimate the mean of the true distribution
- Not surprisingly, the best estimate of the mean of the true distribution is given by the mean of the sample $\bar{M} \approx \frac{1}{n}\sum m_i \equiv$ <m> = (0.01+0.1+0.9+0.06+0.5+0.3+0.02)/7 = 0.27
- We need to quantify our confidence in the value of this estimate for the mean
- We must do this using only the sample data



$$\bar{M} \approx 0.27 \pm ?$$

Confidence Limits on Simulation Averages 2.

- Imagine repeating this experiment many (infinity) times, each time taking a sample of size *n*.
- If we say "68% of all the sample means <m> lie within [some value] of the true mean."…
- …then [some value] serves as a confidence limit
- According to the Central Limit Theorem, the distribution of observations of the sample mean <m> will follow a gaussian, with
  - *mean* $\overline{\langle m \rangle} = \bar{M}$
  - *variance* $\sigma^2_{\langle m \rangle} = \frac{1}{n}\sigma^2_M$
- Our confidence limit is then $\sigma_{\langle m \rangle}$
- We can only estimate this using the sample variance



$$\sigma_{\langle m \rangle} = \frac{1}{\sqrt{n}}\sigma_M \approx \frac{1}{\sqrt{n}}\left[\frac{1}{n}\sum m_i^2 - \left(\frac{1}{n}\sum m_i\right)^2\right]^{1/2} = 0.12$$

$\frac{1}{\sqrt{7}}\sigma_M = 0.09$ (true value)

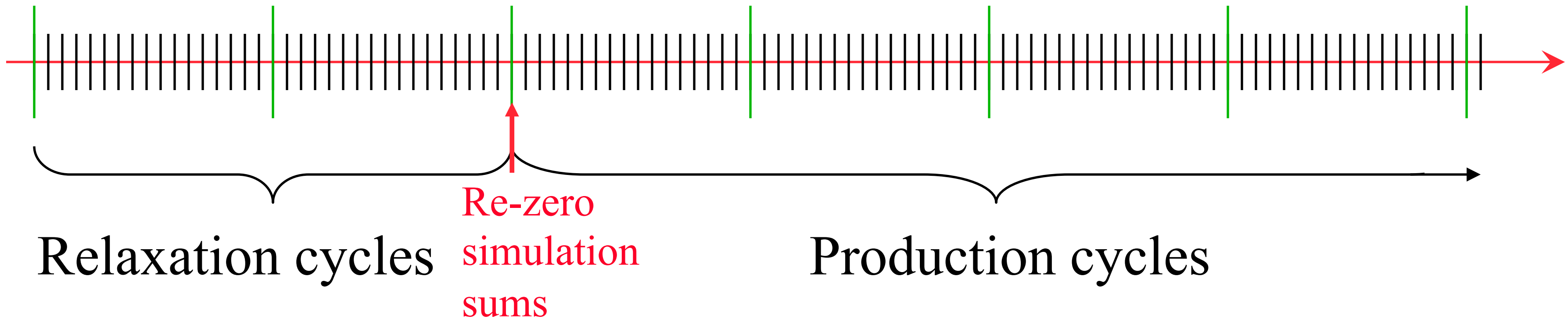
Confidence Limits on Simulation Averages 3.

- Expression for confidence limit (error bar) assumes independent samples
  - *successive configurations in a simulation are (usually) not independent*
  - *block averages are independent for "sufficiently large" blocks*
- Often 2σ is used for error bar (95% confidence interval)
  - *when reporting error bars it is good practice to state definition*
- Confidence limits quantify only statistical errors. Sometimes other sources of error are more significant
  - *systematic errors*
    - poor sampling (non-ergodic)
    - finite-size effects
    - insufficient equilibration
  - *programming errors*
  - *conceptual errors*
  - *limitations of the molecular model*

Simulation Initialization

- Need to establish initial values for atom positions and momenta before simulation can begin
- Two options
  - *use values from end of another simulation*
  - *generate configuration from scratch*
- Often an equilibration period is warranted
  - *lets system "forget" artificial initial configuration*
  - *length of period depends on relaxation time of system*

5000 cycles typical



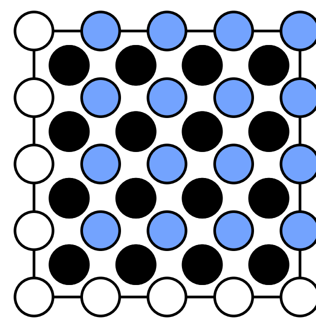
Generating an Initial Configuration

- Placement on a lattice is a common choice
  - *gives rise to "magic" numbers frequently seen in simulations*

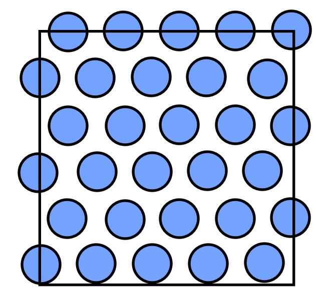
    2D; $N = 2n^2$ (8, 18, 32, 50, 72, 98, 128, …)

    3D, face-center cubic (fcc);

    $N = 4n^3$ (32, 128, 256, 500, 864, 1372, 2048,…)



- Other options involve "simulation"
  - *place at random, then move to remove overlaps*
  - *randomize at low density, then compress*
  - *other techniques invented as needed*
- Orientations done similarly
  - *lattice or random, if possible*



Initial Velocities

- Random direction
  - *randomize each component independently*
  - *randomize direction by choosing point on spherical surface*
- Magnitude consistent with desired temperature. Choices:
  - *Maxwell-Boltzmann:* $prob(v_x) \propto \exp\left(-\frac{1}{2}mv_x^2/kT\right)$
  - *Uniform over (-1/2,+1/2), then scale so that* $\frac{1}{N}\sum v_{i,x}^2 = kT/m$
  - *Constant at* $v_x = \pm\sqrt{kT/m}$
  - *Same for y, z components*
- Be sure to shift so center-of-mass momentum is zero

$$P_x \equiv \frac{1}{N}\sum p_{i,x}$$

$$p_{i,x} \to p_{i,x} - P_x$$

- Unnecessary for Monte Carlo simulations (of course)

Summary of Simulation Elements

- Specification of state
- Units and dimensions, scaling
- Initialization
- Generation of configurations
- Property measurement
- Confidence limits
- Cycles and blocks
- Periodic boundaries
- Organizing and cycling through atom lists