

* Studies in Molecular Dynamics. I. General Method

by Alder and Wainwright

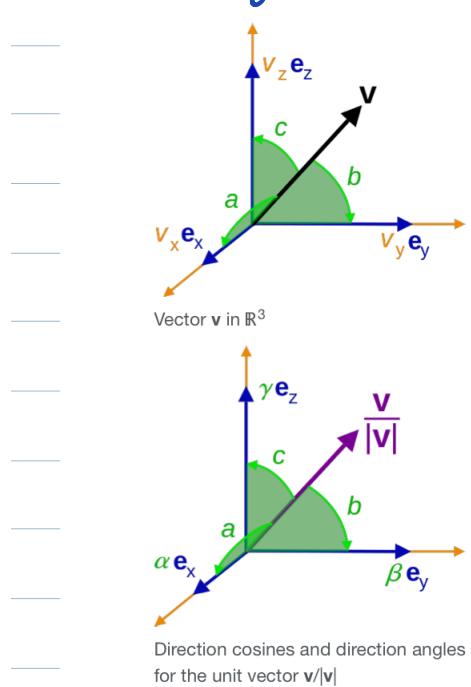
1. Limitations:

Limit	Causes	Solutions
- small number of particles that can be handled	speed of computation	DMD, parallel DMD
- representing macro-system	only simulations of small molecules	periodic boundaries
- statistical fluctuations of properties	representing infinite systems by small systems	averaging large number of calcs. with a small system rather than small number of calcs in a large system.
- crystallization	conflict between lattice type and periodic boundary	translational displacement starting system in various initial configurations ⇒ same final state
- slow convergence to equilibrium configuration.	equilibrium or metastable?	
long molecules	outside P.B. box	averaging potential.

2. Description of the method: MD not DMD

- calculating force apply on 1 molecule by its neighbors
 ➔ trajectories for a short time
 ➔ recalculate force
- interaction hardsphere or square well potentials allow the sequence of events in many-body system to be described by a series of 2 body collisions.
- no velocity changes until entering discontinuous point of a potential
- Initial configurations:
 - + equal initial kinetic energies: $KE = \frac{1}{2}mv^2$

⇒ mass and velocity are balanced to keep constant KE
 + velocity:



If \mathbf{v} is a Euclidean vector in three-dimensional Euclidean space, \mathbb{R}^3 ,

$$\mathbf{v} = v_x \mathbf{e}_x + v_y \mathbf{e}_y + v_z \mathbf{e}_z,$$

where $\mathbf{e}_x, \mathbf{e}_y, \mathbf{e}_z$ are the standard basis in Cartesian notation, then the direction cosines are

$$\begin{aligned}\alpha &= \cos a = \frac{\mathbf{v} \cdot \mathbf{e}_z}{\|\mathbf{v}\|} = \frac{v_z}{\sqrt{v_x^2 + v_y^2 + v_z^2}}, \\ \beta &= \cos b = \frac{\mathbf{v} \cdot \mathbf{e}_y}{\|\mathbf{v}\|} = \frac{v_y}{\sqrt{v_x^2 + v_y^2 + v_z^2}}, \\ \gamma &= \cos c = \frac{\mathbf{v} \cdot \mathbf{e}_x}{\|\mathbf{v}\|} = \frac{v_x}{\sqrt{v_x^2 + v_y^2 + v_z^2}}.\end{aligned}$$

It follows that by squaring each equation and adding the results

$$\cos^2 a + \cos^2 b + \cos^2 c = \alpha^2 + \beta^2 + \gamma^2 = 1.$$

Here a, β and γ are the direction cosines and the Cartesian coordinates of the unit vector $\mathbf{v}/|\mathbf{v}|$, and a, b and c are the direction angles of the vector \mathbf{v} .

The direction angles a, b and c are acute or obtuse angles, i.e., $0 \leq a \leq \pi$, $0 \leq b \leq \pi$ and $0 \leq c \leq \pi$, and they denote the angles formed between \mathbf{v} and the unit basis vectors, $\mathbf{e}_x, \mathbf{e}_y$ and \mathbf{e}_z .

+ positions:

- face centered cubic lattice (fcc)

- unit length box

- Number of molecules:

$$N = 4n^3 \leftarrow \text{unit length}$$

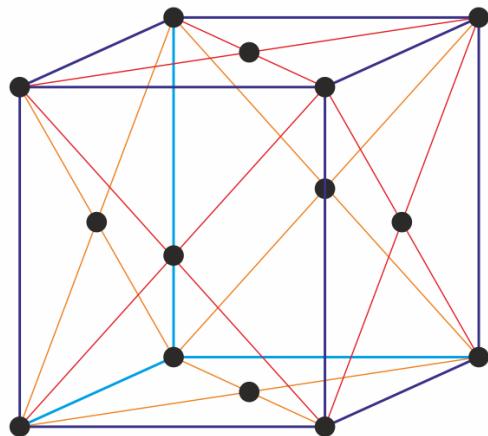
\nearrow 4 lattice sites of box

- specific volume: v \leftarrow assume compact???

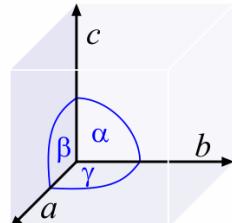
- close-packed specific volume: v_0

$$v = \frac{1}{\rho} \Rightarrow v_0 < v ???$$

$$\left. \begin{aligned} \frac{v}{v_0} &= \frac{\sqrt{2}}{N\sigma_i^3} \\ \end{aligned} \right\}$$



CRYSTAL LATTICE
face-centered cubic



$$a = b = c$$

$$\alpha = \beta = \gamma = 90^\circ$$

- separation of the molecules i, j:

$$r_i = r_{i0} + u_i t$$

$$r_j = r_{j0} + u_j t$$

$$\Rightarrow r_i - r_j = (r_{i_0} - r_{j_0}) + (u_i - u_j)t$$

$$\Rightarrow (r_i - r_j)^2 = [(r_{i_0} - r_{j_0}) + (u_i - u_j)t]^2$$

$$= (r_{i_0} - r_{j_0})^2 + 2t(r_{i_0} - r_{j_0})(u_i - u_j) + t^2(u_i - u_j)^2$$

\Rightarrow Collision time:

$$t = \frac{-b_{ij} \pm \sqrt{b_{ij}^2 - u_{ij}^2 c_{ij}}}{u_{ij}^2}$$

$$\text{where: } r_{ij} = r_{i_0} - r_{j_0} ; b_{ij} = r_{i_0} \cdot u_{ij}$$

$$u_{ij} = u_i - u_j ; c_{ij} = r_{i_0}^2 - \sigma^2$$

$$\sigma = r_i - r_j$$

In my own words:

$$(u_i - u_j)^2 t^2 + 2(r_{i_0} - r_{j_0})(u_i - u_j)t + (r_{i_0} - r_{j_0})^2 - (r_i - r_j)^2 = 0$$

$$\Delta = 4(r_{i_0} - r_{j_0})^2(u_i - u_j)^2 - 4(u_i - u_j)^2[(r_{i_0} - r_{j_0})^2 - (r_i - r_j)^2]$$

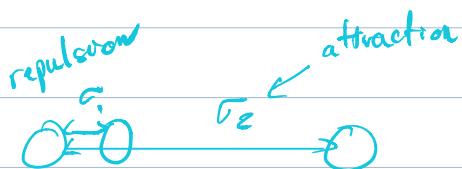
$$\Rightarrow t = \frac{-2(r_{i_0} - r_{j_0})(u_i - u_j) \pm \sqrt{4(r_{i_0} - r_{j_0})^2(u_i - u_j)^2 - 4(u_i - u_j)^2[(r_{i_0} - r_{j_0})^2 - (r_i - r_j)^2]}}{2(u_i - u_j)^2}$$

* Evaluating sequence of calculations:

$$b_{ij} = (r_{i_0} - r_{j_0}) \cdot (u_i - u_j) \begin{cases} < 0 : \text{center approaching} \quad ?? \\ > 0 : \text{center recede} \end{cases}$$

$$c_{ij} = (r_{i_0} - r_{j_0})^2 - (r_i - r_j)^2 \begin{cases} < 0 : \text{within attractive range} \\ > 0 : \text{outside attractive range} \end{cases}$$

$$b_{ij}^2 - u_{ij}^2 c_{ij}$$



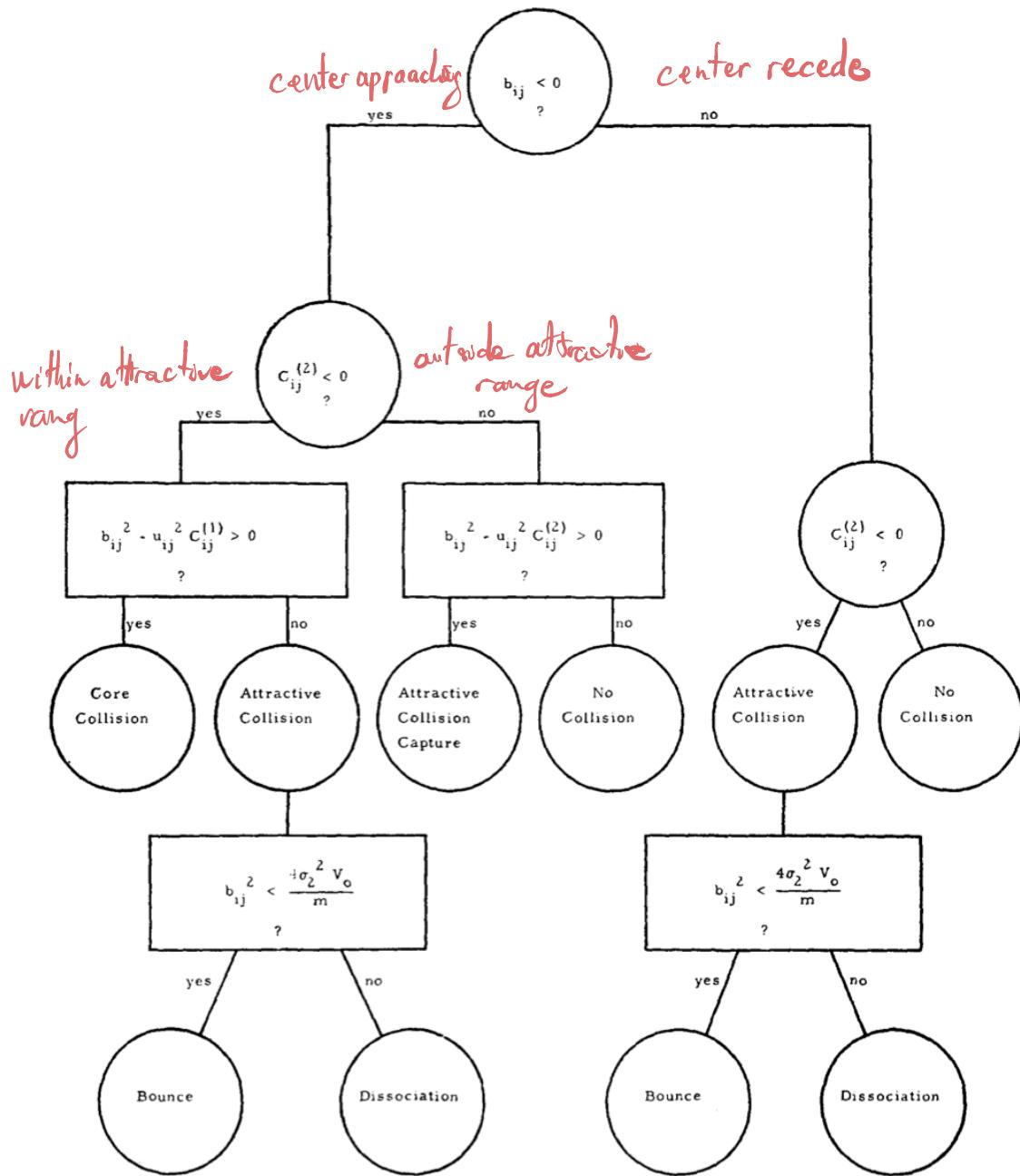
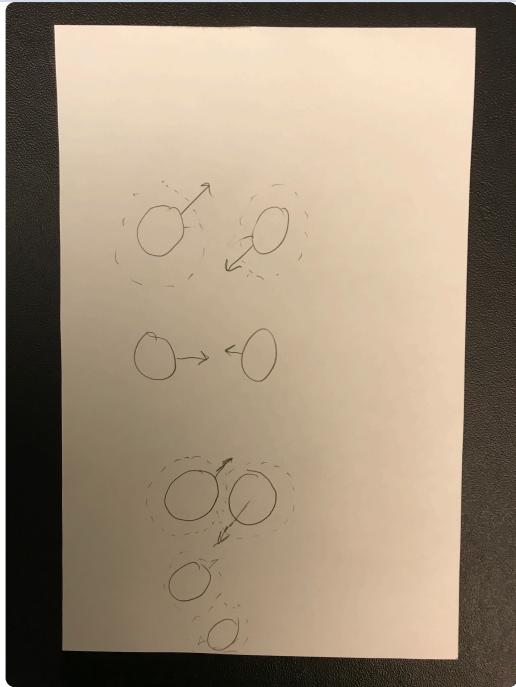
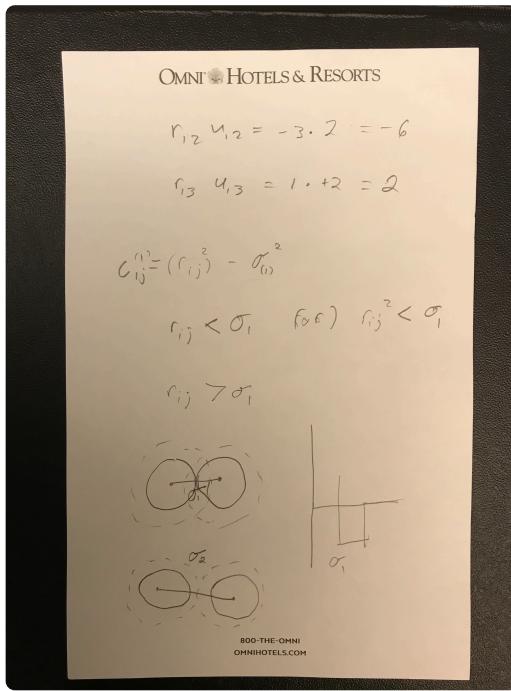
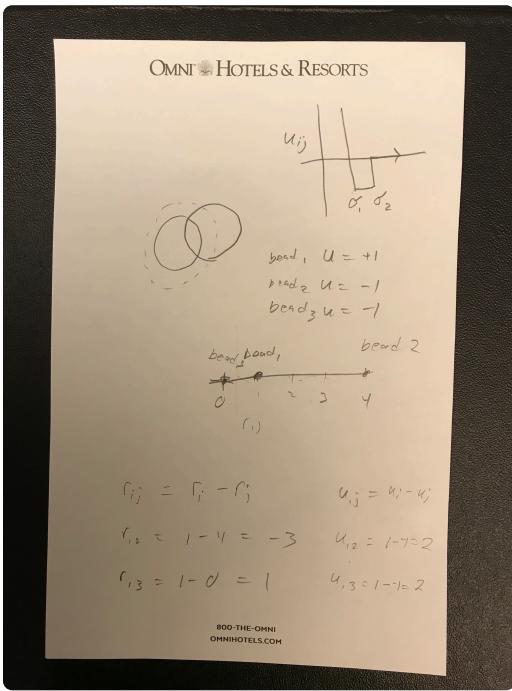


FIG. 1. Schematic diagram of the logical sequence of the calculations.

why $\frac{1}{2}$?



- Velocity change:

+ core collision:

$$\Delta v_i = -\Delta v_j = \frac{-r_{ij} b_{ij}}{\sigma_2^2}$$

+ attractive collision:

. well capture:

$$\Delta v_i = -\Delta v_j = \frac{-r_{ij}}{2\sigma_2^2} \left[\left(\frac{4\sigma_2^2 V_0}{m} + b_{ij}^2 \right)^{1/2} + b_{ij} \right]$$

. well dissociation:

$$\Delta v_i = -\Delta v_j = -\frac{r_{ij}}{2\sigma_2^2} \left[- \left(\frac{-4\sigma_2^2 V_0}{m} + b_{ij}^2 \right)^{1/2} + b_{ij} \right]$$

. well bounce:

$$\Delta v_i = -\Delta v_j = -\frac{r_{ij} b_{ij}}{\sigma_2^2}$$

* Results from conservation of momentum and energy of the classical two-body problem for square-well molecules.

- Conservation of momentum:

$$m_i u_{i0} + m_j u_{j0} = m_i u_i + m_j u_j$$

- Conservation of energy: ???

* Computer Simulation of liquids:

- microscopic state : positions and momenta

- classical mechanics :

+ trajectory (position) : $r_i(t)$

$$+ \text{Newton's law: } m_i \frac{d^2 r_i}{dt^2} = F_i = - \frac{\partial U}{\partial r_i}$$

$$+ \text{Energy: } H = \sum_i \frac{p_i^2}{2m_i} + U(r_1 \dots r_n)$$

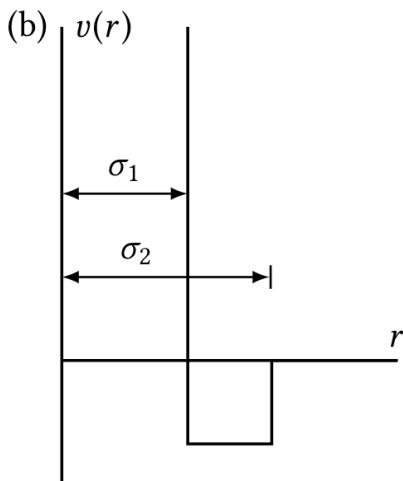
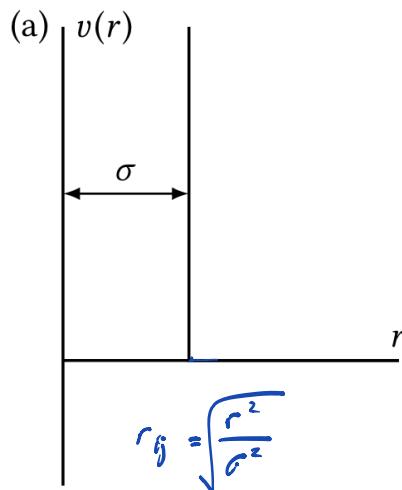
$$H(p, q) = K(p) + V(q)$$

where : p is momentum

- * Hamiltonian (H) an operator corresponding to sum of K and V (or U) \rightarrow equilibrium distribution function
- * V (or U) = potential energy = intermolecular interactions

$\Rightarrow f_i$ and τ_i acting on molecules.

$\Rightarrow H$ and V are inputs



$$1 - r_{ij} > tol \Rightarrow r_{ij} < 1 - tol$$

$$v^{HS}(r) = \begin{cases} \infty & r < \sigma \\ 0 & \sigma \leq r \end{cases}$$

$$v^{DW}(r) = \begin{cases} \infty & r < \sigma_1 \\ -\epsilon & \sigma_1 \leq r < \sigma_2 \\ 0 & \sigma_2 \leq r \end{cases}$$

* Calculating the potential: example in Leonard-Jones
→ write its

* FORTRAN code is evaluated:

- why FORTRAN?

- + compact notation for arrays and array operations
- + simple to be read as pseudo-code

* Is DMD practice code periodic boundary?

YES, IT IS

line 142

Code 1.2 Double loop for Lennard-Jones potential

This code snippet illustrates the calculation of the potential energy for a system of Lennard-Jones atoms, using a double loop over the atomic indices. The declarations at the start are given just to remind us of the types and sizes of variables and arrays (some notes on precision of variables appear in Appendix A).

```

INTEGER :: n, i, j      1 loop of i-j is for 1
REAL , DIMENSION(3,n) :: r      pair
REAL , DIMENSION(3) :: rij
REAL :: epslj, sigma, sigma_sq
REAL :: pot, rij_sq, sr2, sr6, sr12
sigma_sq = sigma ** 2
pot = 0.0 ← stored potential energy
DO i = 1, n-1
    DO j = i+1, n
        rij(:) = r(:,i) - r(:,j) ← each dimension
        rij_sq = SUM ( rij ** 2 ) ← V = 4ε [ (σ/r)^12 - (σ/r)^6 ]
        sr2 = sigma_sq / rij_sq
        sr6 = sr2 ** 3 ← total for all dimension
        sr12 = sr6 ** 2 ← (magnitude):
        pot = pot + sr12 - sr6
    END DO
END DO
pot = 4.0 * epslj * pot

```

* HS:

```

INTEGER :: n, i, j
REAL , DIMENSION (3,n) :: r
REAL , DIMENSION (3) :: rij
REAL :: sigma, pot
pot = 0.0
sigma = (density / REAL(n)) ^ (1/3)

```

```

DO i = 1, n-1
DO j = i+1, n
    r_ij(:) = r(:,i) - r(:,j)
    if r_ij < sigma
        pot = inf
    else
        pot = 0
    end if
END DO

```

- not correct
1. compare r^2 and σ^2 instead of r and σ as r has minus sign.
 2. consider overlap
 3. use finite impulse and kinetic energy conservation, not ∞

* Note on HS DMD code:

- The code doesn't assign an infinite force at collision but calculating a finite impulse that applies on both molecules at collision and change velocity and position of 2 molecules with same magnitude in opposite direction.

$$\vec{p}_1^{\text{new}} = \vec{p}_1^{\text{old}} + \Delta \vec{p}$$

$$\vec{p}_2^{\text{new}} = \vec{p}_2^{\text{old}} - \Delta \vec{p}$$

→ conservation of energy that involves only K

$$\frac{1}{m_1} |\vec{p}_1^{\text{new}}|^2 + \frac{1}{m_2} |\vec{p}_2^{\text{new}}|^2 = \frac{1}{m_1} |\vec{p}_1^{\text{old}}|^2 + \frac{1}{m_2} |\vec{p}_2^{\text{old}}|^2$$

$$\frac{1}{m_1} |\vec{p}_1^{\text{old}} + \Delta \vec{p}|^2 + \frac{1}{m_2} |\vec{p}_2^{\text{old}} - \Delta \vec{p}|^2 = \frac{1}{m_1} |\vec{p}_1^{\text{old}}|^2 + \frac{1}{m_2} |\vec{p}_2^{\text{old}}|^2$$

$$\frac{2}{m_1} \vec{p}_1^{\text{old}} \Delta \vec{p} - \frac{2}{m_2} \vec{p}_2^{\text{old}} \Delta \vec{p} + \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \Delta \vec{p}^2 = 0$$

$$2\vec{v}_1 \Delta \vec{p} - 2\vec{v}_2 \Delta \vec{p} + \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \Delta \vec{p}^2 = 0$$

$$2(\vec{v}_1 - \vec{v}_2) + \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \Delta \vec{p} = 0$$

$$\Rightarrow \Delta \vec{p} = \frac{2(\vec{v}_2 - \vec{v}_1)}{\left(\frac{1}{m_1} + \frac{1}{m_2} \right)}$$

$$= \frac{2m_1 m_2}{m_1 + m_2} (\vec{v}_2 - \vec{v}_1)$$

$$= \frac{2m_1 m_2}{m_1 + m_2} \vec{v}_{z_1}$$

For core collision:

$$\Delta \vec{p} = \frac{2m_1 m_2}{m_1 + m_2} \frac{\vec{v}_{z_2} \vec{r}_{z_2}}{\sigma^2} \vec{r}_{z_2}$$

* Question on line 330: what is e ? why

$$C = e + v_x^2 + v_y^2 + v_z^2 = e + v^2$$

$$e = 0.5c ???$$

$$KE = \frac{1}{2} m v^2$$

\rightarrow assume $m = 1 ???$ unit mass ???

* Choose a set of atom-atom interaction parameters

from Table 1.1 to test HS page 21 (1st edition)

Time:

- time taken for a double loop used to evaluate forces or potential energy is proportional to N^2

* Computer code for periodic boundaries

$$RX(I) = RX(I) - BOXL + ANINT(RX(I)/BOXL)$$

Question on line 13: why coltim(n+1) ?

t = total time

t_{ij} = time travel of each pair

$\rightarrow t_{ij} = \text{coltim}$

\rightarrow move all particles by time t_{ij}

\rightarrow new $t = t + t_{ij}$

$\text{coltim} = \text{coltim} - t_{ij}$

\rightarrow for earliest collision pair: $\text{coltim} = 0$

for the rest \rightarrow shorter predicted
collision time

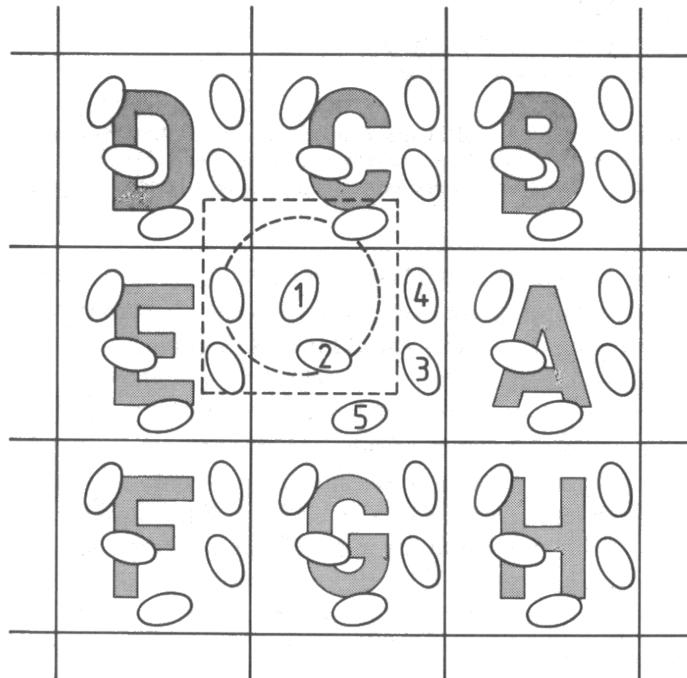
Question on line 66: Enter number of collision required

\rightarrow how do I know how many collision required?

Features Common to MC and MD

- Minimum image convention

Consider molecule 1 in figure. It interacts with the closest periodic images of the other molecules: 2, 3E, 4E, 5C



The minimum image convention in a two-dimensional system. The central box contains five molecules. The 'box' constructed with molecule 1 at its center also contains five molecules. The dashed circle represents a potential cutoff.

Generally used with truncated potentials; note that the simple cut off potential should not be used in MD simulations as the system would no longer conserve energy.

not using cutoff potential

figure taken from M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (1987)

Features Common to MC and MD

- Neighbor lists

- Verlet (1967) suggested keeping a list of the near neighbors for a particular molecule, which is updated periodically.
- Between updates of the list, the program does not check through all the molecules, just those on the list, to calculate distances and minimum images, check distances against cutoff, etc.
- For details check Leach; Frenkel & Smit; Allen & Tildesley

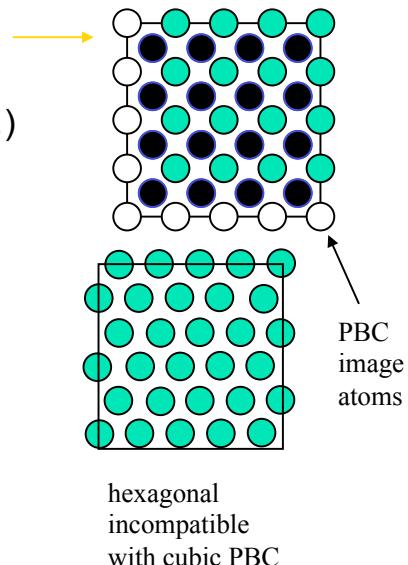
- Solid phases

- If solid phases are present, N and also the cell size and shape must be chosen so that the PBC's can generate a perfect lattice; e.g. for Ar this is a fcc structure, then a cubic box with $N = 4n^3$ is appropriate, where n is an integer. Thus, N could be 108 ($n = 3$), 256 ($n = 4$), 500 ($n = 5$), 864 ($n = 6$), etc. Even if we don't have solid phases present, we may start with molecules on lattice sites and so people commonly use $N=4n^3$.

Features Common to MC and MD

- 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
- MD requires also initial velocities
 - will be discussed later



taken from Dr. D. A. Kofke's lectures on Molecular Simulation, SUNY Buffalo
<http://www.eng.buffalo.edu/~kofke/ce530/index.html>

Features Common to MC and MD

- Equilibration

This simulation period can be monitored in several ways:

- Check instantaneous values of properties: potential energy, pressure, etc.
- If initial configuration was a lattice, track the “melting” of the lattice by monitoring order parameters measuring translational order (e.g., Verlet) and/or rotational order (e.g. Viellard-Baron). For definitions, see Leach, pp. 321-323; Allen & Tildesley, pp. 171-172.
- Monitor mean squared displacements of molecules
- Check radial distribution

Running 1st trial:

$$-\text{reduced density} = \frac{n}{V} \sigma^3 \leftarrow \text{input} \Rightarrow$$

$$n = 108 ; V = ? ; \sigma = 0.228$$

$$\sigma = \sqrt[3]{\frac{\text{density}}{n}} \Rightarrow \underline{\sigma^2} = 0.052$$

$$\text{cal } r_{ij}^2 = r_x^2 + r_y^2 + r_z^2$$

$$r_{ij} = \sqrt{\frac{r_{ij}^2}{\sigma^2}}$$

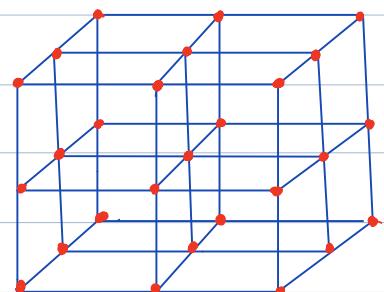
Problem: overlap

$$n = 108 ; nc = \text{number of cells} = 3$$

36.	36	36
-----	----	----

$$\text{cell} = \text{unit cell length} = \frac{\text{unit length}}{nc} = \frac{1}{3} = 0.333$$

$$\text{cell}_z = \text{half box length} = 0.5 \text{ cell}$$



* How to analyse the results:

1. Liquid structure:

- pair distribution function:

$$g(r) = \rho^{-2} \left\langle \sum_i \sum_{j \neq i} \delta(r_i) \delta(r_j - r) \right\rangle$$

$$= \frac{V}{N^2} \left\langle \sum_i \sum_{j \neq i} \delta(r - r_{ij}) \right\rangle$$

→ used in evaluation of $g(r)$ by computer simulation
or # of atoms at distance r from a given atom compared with #
of atoms at the same distance in an ideal gas at same ρ .

* From line 38 → 48:

$$\Delta r = \frac{\text{half box length}}{\text{maxbin}} = \text{width of each bin } (\Delta r)$$

$$\text{maxbin} = 500 ??? - \text{size of hist array}$$

$$\rightarrow \text{each BIN} = (r, r + \Delta r)$$