fundación D.I.P.C. DONOSTIA INTERNATIONAL PHYSICS CENTER

The action of the Liouville operator

$$iLf := \{f, \mathcal{H}\} = \sum_i \left\{ \frac{\partial f}{\partial q_i}\frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial f}{\partial p_i}\frac{\partial \mathcal{H}}{\partial q_i} \right\}$$

$$= \sum_i \left[\frac{p_i}{m_i}\frac{\partial}{\partial q_i} + F_i \frac{\partial}{\partial p_i} \right] f$$

$$= i(L_q + L_p) f$$

Let us look at: $e^{i\frac{\Delta t}{2}L_p} f(q_1, \dots, q_N, p_1, \dots, p_N)$

$$\equiv f\left(q_1, \dots, q_N, p_1 + \frac{F(q_1)}{2}\frac{\Delta t}{2}, p_2 + \frac{F(q_2)}{2}\Delta t, \dots, p_N + F(q_1, \dots, q_N)\frac{\Delta t}{2}\right)$$

$$\equiv f(q_1, \dots, q_N, p_1', \dots, p_N')$$

$$e^{i\Delta t L_q} f = f\left(q_1 + \frac{p_1'}{m_1}\Delta t, q_2 + \frac{p_2'}{m_2}\Delta t, \dots, q_N + \frac{p_N'}{m_N}\Delta t, p_1', \dots, p_N'\right)$$

$$= f(q_1', \dots, q_N', p_1', \dots, p_N')$$

$$e^{i\frac{\Delta t}{2}L_p} f(q_1', \dots, q_N', p_1', \dots, p_N') = f\left(q_1', \dots, q_N', p_1' + F(q_1', \dots, q_N')\frac{\Delta t}{2}, \dots, p_N' + F(q_1', \dots, q_N')\frac{\Delta t}{2}\right)$$

So after complete application of $e^{i\frac{\Delta t}{2}L_p} e^{i\Delta t L_q} e^{i\frac{\Delta t}{2}L_p}$ we have:

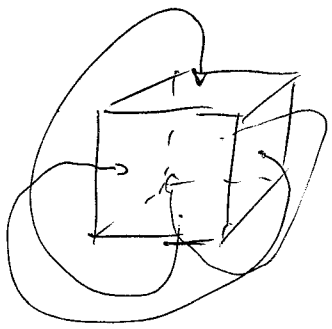
$$\boxed{q_i(\Delta t) = q_i' = q_i(0) + \frac{p_i(0)}{m_i}\Delta t + \frac{1}{2}\frac{F_i(0)}{m_i}\Delta t^2}$$

$$p_i(\Delta t) = p_i' + F_i(q_1(\Delta t), \dots, q_N(\Delta t))\frac{\Delta t}{2}$$

$$\Rightarrow \boxed{p_i(\Delta t) = p_i(0) + \frac{\Delta t}{2}\left[F_i(0) + F_i(\Delta t)\right]}$$

Practical implementation of MD

Let us assume for the beginning that we are interested in bulk properties → we do not want surface effects to play a role, i.e., we want to approximate a translation invariant behavior → use periodic boundary conditions

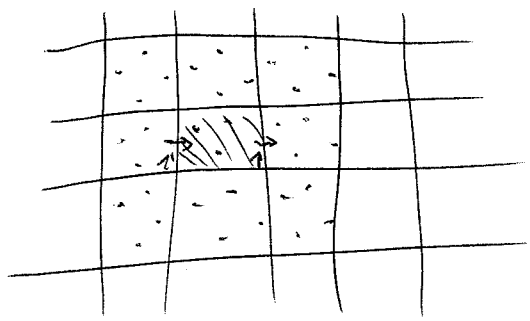


(i) assume box placement:

$$[0,L] \times [0,L] \times [0,L]$$

⇒ a particle leaving box at $x=L$ enters at the same time at $x=0$

2d illustration:



central box is repeated periodically infinitely often in each direction

particle 1 leaves the box

particle 1' enters the box

(ii) Problem: assume pairwise interactions

$$\vec{F}_i = \sum_{\text{image}} \left(\sum_{j \neq i} \vec{F}_{ij} \right) + \sum_{j \neq i} \vec{F}_{ij}$$

⇒ infinitely many terms ☹

Pair correlation function

Let us define the one and two-particle densities.

$$\rho_1(\vec{r}) = \left\langle \sum_{i=1}^{N} \delta(\vec{r} - \vec{r}_i) \right\rangle \equiv \text{prob to find particle at } \vec{r}$$

$$\rho_2(\vec{r}, \vec{r}') = \left\langle \sum_{i=1}^{N} \sum_{j \neq i} \delta(\vec{r} - \vec{r}_i)\, \delta(\vec{r}' - \vec{r}_j) \right\rangle \equiv \text{prob to find particle at } \vec{r} \text{ and other particle at } \vec{r}'$$

Let us now assume that we are simulating a gas or a liquid.

i) translation invariance

$$\rho_1(\vec{r}) = \rho_1(\vec{r} + \vec{t}) = \rho_1(\vec{r}) = \text{const} \equiv \rho_0$$

$$\rho_2(\vec{r}, \vec{r}') = \rho_2(\vec{r} + \vec{t}, \vec{r}' + \vec{t}) \Rightarrow \rho_2(\vec{r}, \vec{r}') = \rho_2(\vec{r} - \vec{r}')$$

ii) isotropy: $\rho_2(\vec{r} - \vec{r}') \equiv \rho_2(|\vec{r} - \vec{r}'|)$

For large $|\vec{r} - \vec{r}'|$ the probability of finding a particle at $\vec{r}'$ will not depend on the presence of a particle at $\vec{r}$:

$$\rho_2(|\vec{r} - \vec{r}'|) =: \rho_0^2\, g(|\vec{r} - \vec{r}'|)$$

$g(r)$: pair correlation function

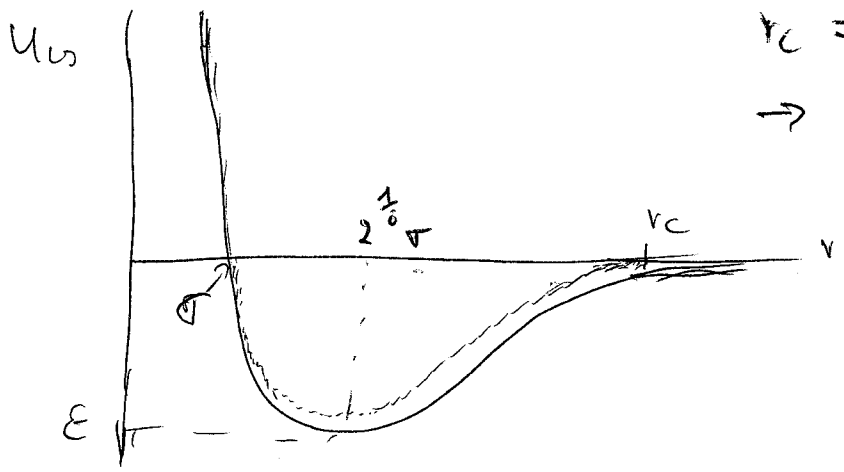
$g(r) \to 1$ for $r \to \infty$

Solutions cut the interaction at some finite range

For example using the Lennard-Jones potential

$$U_{LJ}(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

$$\Rightarrow U_{LJ}^{\text{truncated}}(r_{ij}) = \begin{cases} 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right) + U_{LJ}(r_c) & ; r_{ij} \le r_c \\ 0 & ; r_{ij} \ge r_c \end{cases}$$



$r_c = 2 \cdot 2^{1/6}\sigma$

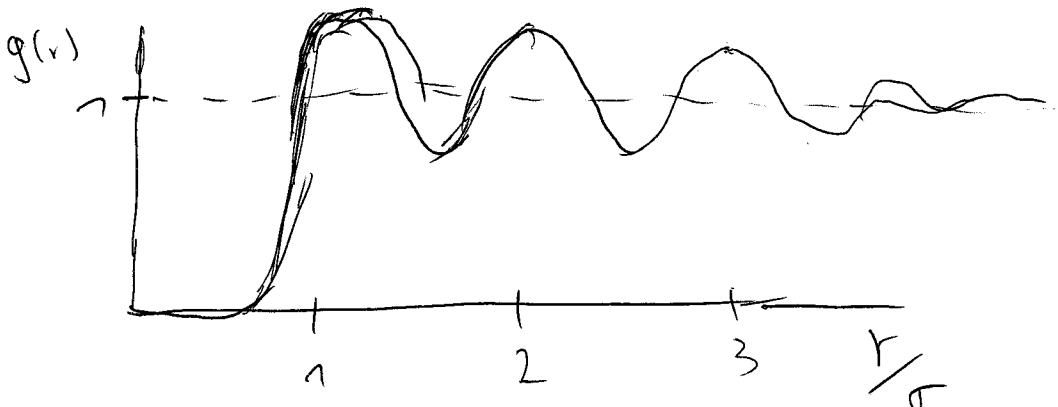
$\rightarrow$ force is discontinuous

$\Rightarrow$ need only to calculate contributions to the force of particles which are at a most r_c removed from central particle

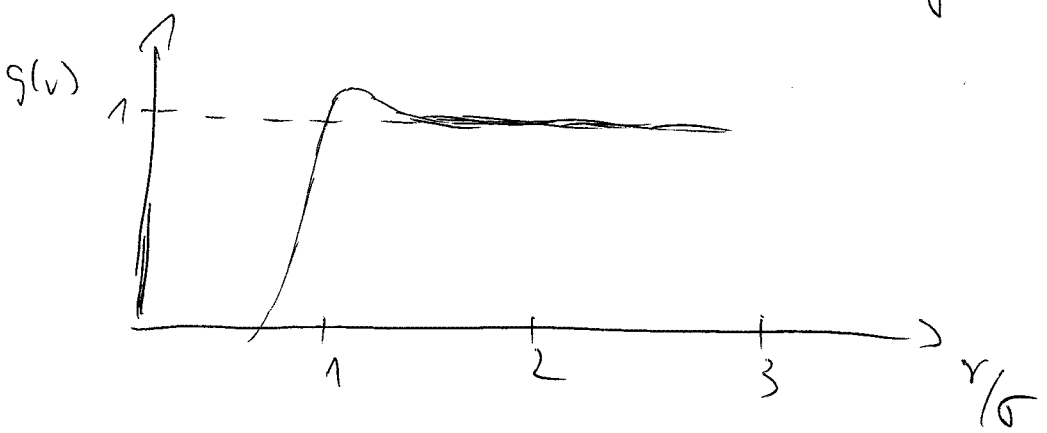
Is What error does this introduce?

To get an idea about this let us look at something called the pair correlation function.

$g(r) \to 0$ for $r \to 0$



dense liquid



gas

The internal energy of an N-particle system is

$$\langle E \rangle = \left\langle \sum_{i,j} u(r_{ij}) \right\rangle$$

$$= \left\langle \sum_{i,j} u(r_{ij}) \right\rangle_{r_{ij} < r_c} + \left\langle \sum_{i,j} u(r_{ij}) \right\rangle_{r_{ij} > r_c}$$

$$= \langle E_{sim} \rangle + \left\langle \sum_{i,j} \int d\vec{r} \int d\vec{r}\,' \, u(|\vec{r} - \vec{r}\,'|) \, \delta(\vec{r} - \vec{r}_i) \, \delta(\vec{r}\,' - \vec{r}_j) \right\rangle_{r_{ij} > r_c}$$

$$= \langle E_{sim} \rangle + \int d\vec{r} \underbrace{\int d\vec{r}\,'}_{|\vec{r} - \vec{r}\,'| > r_c} u(|\vec{r} - \vec{r}\,'|) \, \rho^2 \, g(|\vec{r} - \vec{r}\,'|)$$

$$= \langle E_{sim} \rangle + \rho N 2\pi \int_{r_c}^{\infty} dr \, r^2 \, u(r) \, g(r)$$

$$= \langle E_{sim} \rangle + E_{LR}$$

$$E_{LR} \simeq 2\pi\rho N \int_{r_c}^{\infty} dr\, r^2 U(r) \quad ; \quad g(1) \simeq 1$$

For the Lennard-Jones potential

$$\bar{E}_{LR} = \frac{8\pi\rho^* N}{3 r_c^{*3}} \left(\frac{1}{3 r_c^{*6}} - 1 \right) \simeq - \frac{8\pi\rho^* N}{3 (r_c^*)^3}$$

Problem: disrupt correction for

i) Coulomb, gravitational $U(r) \sim \frac{1}{r}$

ii) dipolar interactions $U(r) \sim \frac{1}{r^3}$

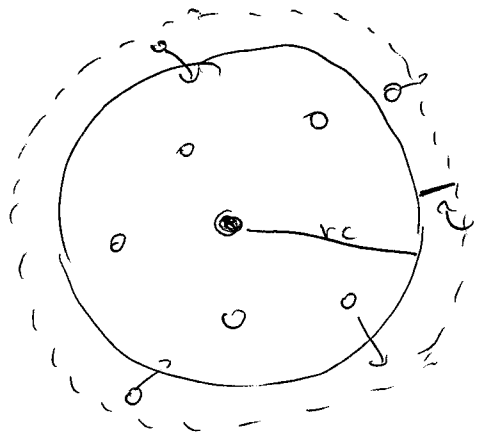
→ In these cases one has to sum up all contributions from all periodic images

→ EWALD sum technique

For typical Van der Waals forces (dipole induced dipole, Lennard Jones) one can cut the potential.

Let us now consider that we are working with a potential where we only need to consider interactions with particles in a neighbour shell of radius r_c.

→ neighbour list



particles move in and out of interaction range

→ without skin: need to update list of interacting neighbours in every integration step ⇒ time consuming (see below)

→ with skin: neighbour list remains valid as long as the maximum displacement of any particle is smaller than width of the skin s. (need to monitor δ)

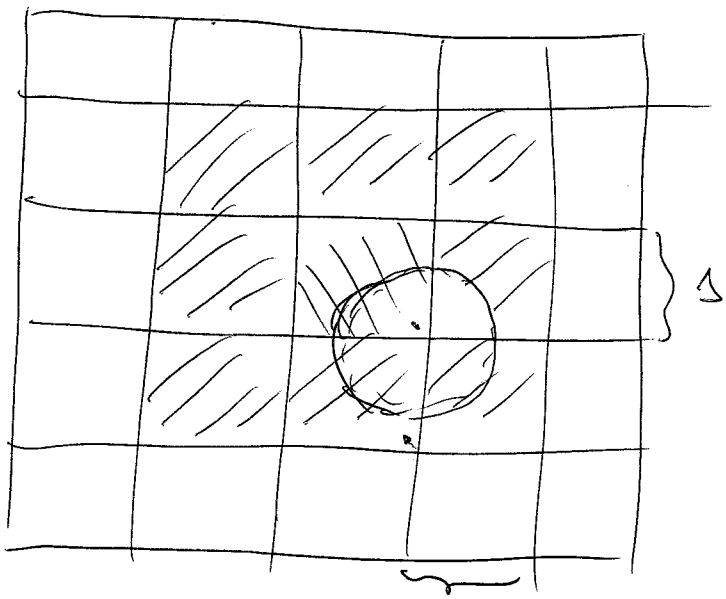
→ optimal choice of s depends on mobility of the particles: - too small : update too often
- too long : determination of new neighbour list too expensive

→ typically neighbour list remains valid a few ($\lesssim 5$) integration steps.

→ typical choice for [7]: $s \equiv 0.3\sigma$

How to update the neighbour list

Subbox method



for every particle:
know to which subbox it belongs

for every box:
know which particles are in it.

$s > r_c + \varsigma$: have to check 26 neighbour boxes in 3 dimensions.

Other choices possible ⇒ performance study: the smaller the sub-boxes the better a sphere is approximated.

neighbour list update of particle i":

- find out subbox
- go through neighbouring boxes
- find out which particle $j > i$ in these has distance $r_{ij} < r_c + s$
- update lists of particles i and j (third Newton)

Task:

- Set up simulation using velocity Verlet of 256 particles in a cubic box
- choose box size L such that reduced volume fraction

$$\phi = N \frac{4\pi}{3} \sigma^3 / V = 8 \frac{4\pi}{3} \sigma^3 = 0.6$$

- first do without neighbour list then with and compare simulation time for 50000 integration steps
- use $\Delta t = 0.002$ as time step
  $\rightarrow t_{max}(50000) = 100$
- measure pair correlation function
- measure velocity distributions $p(|v|)$ and $p(v_x)$ [average over x, y, z]

Topics for seminars

I - The Ewald summation technique and its modern variants for the treatment of Coulomb interactions

II - Cluster algorithms for the Ising model: the Fortuyn - Kasteleijn transform, the Wolff - algorithm or the Swendsen / Wang algorithm