I. EXAMPLE: MOLECULAR DYNAMICS SIMULATION OF SIMPLE FLUIDS

Markus Holzmann LPMMC, Maison de Magistère, Grenoble, and LPTMC, Jussieu, Paris markus@lptl.jussieu.fr http://www.lptl.jussieu.fr/users/markus/cours.html (Dated: March 2, 2010)

A. Lennard-Jones fluid

Pair potential. The effective pair potential between two molecules in a fluid can often by described by the phenomenological Lennard-Jones 12-6 potential

$$v^{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$$
(1)

where r is the distance between them. The potential has a long ranged attractive tail $-1/r^6$, a negative well of depth ϵ , and a steeply rising repulsive wall at distances $r \lesssim \sigma$. For example, liquid argon can be well described using $\sigma \approx 0.34nm$, and $\epsilon/k_B \approx 120K$.

Neglecting three-body (and higher) interaction potentials, we are interested in describing the properties of the idealized system of N molecules inside a box of volume V described by the Hamiltonian

$$H = \sum_{i=1}^{N} \frac{\mathbf{p}_{i}^{2}}{2m} + \sum_{i < j} v^{LJ}(r_{ij})$$
(2)

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. In general, we will be interested in properties in the thermodynamic limit, $N \to \infty$, $V \to \infty$, at constant density, $\rho = N/V$.

Reduced Units. Before trying to solve numerically Newton's equation for the time evolution of the particles, it is useful to think about the units we want to choose. From the Lennard-Jones potential, it is natural to choose σ as unit of length, and ϵ as unit of energy, such that

$$\frac{v^{LJ}(r)}{\epsilon} = v^*(r^*) \tag{3}$$

$$v^*(r^*) = 4\left[\left(\frac{1}{r^*}\right)^{12} - \left(\frac{1}{r^*}\right)^6\right]$$
 (4)

$$r^* = \frac{r}{\sigma} \tag{5}$$

and we can introduce the natural unit of time, $\sqrt{m\sigma^2/\epsilon}$, by inspection of the kinetic energy

$$\frac{1}{\epsilon} \frac{1}{2} m \left(\frac{dr}{dt}\right)^2 = \frac{1}{2} \left(\frac{dr^*}{dt^*}\right)^2 \tag{6}$$

$$t^* = \sqrt{\frac{\epsilon}{m\sigma^2}}t \tag{7}$$

Further, temperature is naturally expressed in units of $k_B\epsilon$, or $T^* = T/(k_B\epsilon)$. Using reduced units, we expect that all quantities of interest are of order 1, and very large or very small numbers should not occur (e.g. $10^{\pm 10}$). Further, results in reduced units, can be easily converted to all fluids with Lennard-Jones potentials, and are not limited to a particlular system like argon (of course different systems at the same reduced temperature will have different real temperatures...). In the following we will always use reduced coordinates, but using the original notation $\mathbf{r} \to \mathbf{r}^*$, etc.

Finite size considerations, periodic boundary conditions. Next, since we can only simulate a finite number of particles, we have to specify the boundary conditions. If the particles are inside a container, we must include the collissions between particles and walls, and the particle-wall interaction introduces surface effects. Here, we are interested in the bulk behavior, so we want to eliminate (or minimize) surface effects. Using periodic boundary conditions is one standard method to simulate bulk behavior. Therefore, we consider a box of length L in each dimension, d. Any particle, i inside the box around the origin, $0 \le r_{i\alpha} < L$ (with $\alpha = 1, \ldots d$ describes the spatial dimension) will interact not only with all other particles inside the box, \mathbf{r}_j , $j \ne i$, but also with all periodic images of all partcles to different boxes. When v(r) is the original pair-interaction, using periodic boundary conditions, the total interaction energy, V_{PBC} , writes

$$V_{PBC} = \frac{1}{2} \sum_{i \neq j} \sum_{\mathbf{i}} v(|\mathbf{r}_i - \mathbf{r}_j - \mathbf{i}L|) + \frac{1}{2} \sum_{i} \sum_{\mathbf{i} \neq (0,0,0)} v(|\mathbf{i}L|)$$
(8)

where $\mathbf{i} = (i_1, i_2, i_3)$ is a vector with integer components i_{α} . Note that the second sum on the rhs of Eq. (8) is due to the interaction of the particle with its own images in the other box. We can write the total potential energy as

$$V_{PBC} = \frac{N}{2} v_s + \sum_{i < j} v_{PBC}(\mathbf{r}_{ij}) \tag{9}$$

$$v_{PBC}(\mathbf{r}) \equiv \sum_{\mathbf{i}} v(|\mathbf{r} + \mathbf{i}L|) \tag{10}$$

$$v_s \equiv \lim_{r \to 0} \left[v_{PBC}(\mathbf{r}) - v(r) \right] \tag{11}$$

Note, that the periodic potential v_{PBC} in general depends on the vector \mathbf{r} , and not only on the distance $r = |\mathbf{r}|$. For any potentials of finite range with $v(r) \equiv 0$ for $r \geq L/2$, the periodic boundary conditions are reduced to the *nearest image potential*, V_{ni} , where only interactions via the bare potential v, between one particle and the nearest image of all the other particles are needed

$$V_{ni} = \frac{1}{2} \sum_{i \neq j} v_{ni}(|\vec{p}(\mathbf{r}_{ij})|)$$
(12)

$$\vec{p}(\mathbf{r}) = \mathbf{r} - \operatorname{nint}(\mathbf{r}/L) L \tag{13}$$

where the "nint" function rounds a real number to its closest integer, such that $\vec{p}(\mathbf{r})$ has all of its coordinates between -L/2 and L/2. Since the Lennard-Jones potential has a long ranged tail, we cannot directly use v^{LJ} together with the nearest image convention. However, we can use a modified potential, $\tilde{v}^{LJ}(r)$, which vanishes for distances larger than a cut-off radius $r_c \leq L/2$, e.g.

$$\tilde{v}^{LJ}(r) = v^{LJ}(r) - v^{LJ}(r_c), \quad r \le r_c$$
(14)

and $\tilde{v}^{LJ}(r) = 0$ for $r > r_c$. Notice that we \tilde{v}^{LJ} is continuous at r_c , in order to avoid a divergent contribution when calculating the forces.

Improvements: tail corrections.

B. Program

Initial Conditions. We start putting the particles on a lattice inside the box, and give them a random velocity between -0.5 and 0.5. We calculate the velocity of the center of mass $\mathbf{V} = \sum_i \mathbf{v}_i$ shift all velocities to remove the center of mass motion, $\mathbf{v}_i \to \mathbf{v}_i - \mathbf{V}/N$. In thermal equilibrium, we know that the individual velocity is gaussian distributed for each spatial component, so that its variance is given by the temperature

$$\langle v_{i\alpha}^2 \rangle = T \tag{15}$$

We can define an instantanous temperture T(t) via

$$T(t) = \frac{1}{dN} \sum_{i} \mathbf{v}_{i}^{2}$$
(16)

and we can always adjust the temperature by rescaling all velocities with $\sqrt{T/T(t)}$. For many algorithms we need the previous positions of the particles

$$\mathbf{x}_i(t - dt) = \mathbf{x}_i(t) - \mathbf{v}_i dt \tag{17}$$

Notice that the initial conditions are important, since the total energy will be (approximately) conserved. If, initially, we put the particles into regions with high potential energy, we cannot reach easily low temperatures.

Calculation of forces. Using the nearest image potential, $\tilde{v}^{LJ}(r)$ depends only on radial distances. In general, for any radial potential v(r), the force is given by

$$f_{\alpha}(r) = -\frac{dv(r)}{dr_{\alpha}} = -\frac{r_{\alpha}}{r}\frac{dv(r)}{dr}$$
(18)

Note that the total force on particle i is given by

$$f_{i\alpha} = -\sum_{j \neq i} \frac{dv(|\vec{p}(\mathbf{r}_{ij})|)}{dr_{i\alpha}}$$
(19)

At the same time when calculating the forces, we can also calculate the total potential energy U(t).

Molecular dynamics step. We can now integrate the equation of motion to obtain the new positions using Verlet's algorithm

$$\mathbf{x}_i(t+dt) = 2\mathbf{x}_i(t) - \mathbf{x}(t-dt) + \mathbf{f}_i(t)dt^2$$
(20)

$$\mathbf{v}_i(t) = \frac{\mathbf{x}_i(t+dt) - \mathbf{x}_i(t-dt)}{2dt}$$
(21)

We also calculate the kinetic energy K(t) and the instantaneous temperature, T(t).

C. Download, Compilations, etc.

- Download "md.tar" and untar it: "tar xvf md.tar"
- inside the directory MD you have the main file md.f and all subroutines
- edit the "Makefile" and put in the Fortran compiler installed on the computer in the 6th line "F77 = f77", e.g. if you use "g77" replace the line by "F77 = g77"
- open a terminal, type "make" inside the directory MD
- if the system has compiled everything, you should have the executive file "md.out"
- type "md.out" for running the codes, some observables, like total energy per particle, kinetic energy, etc are averaged over blocks of size 'istep' and written into the file "md.dat"
- the main file is "md.f" you can change number of particles, temperature, etc there. don't forget to recompile everytime you change something!

^[1] M.P. Allen and D.J. Tildesley, Computer Simulation of Liquids

^[2] D. Frenkel and B. Smit, Understanding Molecular Simulation