Notas de Dinámica Molecular.

In this method the equations of motion of a system of N interacting particles are solved numerically. Depending on the imposed constrainst, $3N$ or less equations will have to be solved, one for each degree of freedom. Suppose there are $3N$ of such degrees, taken here to be the positions $\mathbf{r}_i$, $i = 1, ..., N$. The central quantity is the potential energy,

$$U = U(\{\mathbf{r}_i\}) = U(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N).$$

The equations of motion are:

$$\begin{cases} \dfrac{d\mathbf{r}_i}{dt} = \mathbf{v}_i \\ \\ m\dfrac{d\mathbf{v}_i}{dt} = -\nabla_i U(\{\mathbf{r}_j\}) \end{cases}$$

where $\mathbf{v}_i$ is the velocity of the i–th particle, and m is the mass of the particles. Since the dynamics is energy–conserving, the evolution of the system proceeds as if the state point moved on the hypersurface defined by $H(\{\mathbf{r}_i, \mathbf{v}_i\})$ =const. in the $3N$–dimensional phase space.

3.b Methods of integration

The numerical solution of the equations of motion is performed with an algorithm based on finite differences. Time is discretised using a time interval h. Knowledge of the positions and velocities of all particles at time t allows calculation of the forces at time t, $\mathbf{F}_i$, on all particles, and the problem is how to obtain the positions and velocities at a later time $t + h$. The simplest algorithm is the *Verlet algorithm*, which we now derive.

- **Verlet algorithm**. We write the following Taylor expansions:

$$\mathbf{r}_i(t+h) = \mathbf{r}_i(t) + h\mathbf{v}_i(t) + \frac{h^2}{2m}\mathbf{F}_i(t) + \frac{h^3}{6}\ddot{\mathbf{v}}_i(t) + ...$$

$$\mathbf{r}_i(t-h) = \mathbf{r}_i(t) - h\mathbf{v}_i(t) + \frac{h^2}{2m}\mathbf{F}_i(t) - \frac{h^3}{6}\ddot{\mathbf{v}}_i(t) + ...$$

  Adding, neglecting terms of order $O(h^4)$, and reshuffling,

$$\mathbf{r}_i(t+h) = 2\mathbf{r}_i(t) - \mathbf{r}_i(t-h) + \frac{h^2}{m}\mathbf{F}_i(t)$$

  This recurrence formula allows to calculate the new position if one knows the positions $\mathbf{r}_i(t)$ and $\mathbf{r}_i(t-h)$. It is an $O(h^3)$ algorithm [i.e. the new positions contain errors of $O(h^4)$].

  This version of the algorithm is the *Newtonian* version. The velocities are not required to calculate the new positions, but of course they are needed in case we

wanted to calculate the kinetic energy, related to an important quantity such as the temperature. Velocities can be approximated with the expansion

$$\mathbf{r}_i(t+h) = \mathbf{r}_i(t-h) + 2h\mathbf{v}_i(t) + O(h^3)$$

and from here

$$\mathbf{v}_i(t) = \frac{\mathbf{r}_i(t+h) - \mathbf{r}_i(t-h)}{2h}$$

which contains errors of $O(h^3)$. The kinetic energy, at time t, can be estimated from

$$E_c(t) = \sum_{i=1}^{N} \frac{1}{2} m \left|\mathbf{v}_i(t)\right|^2$$

and the temperature, using the equipartition theorem, is

$$\left\langle \frac{1}{2} m v_\alpha^2 \right\rangle = \frac{kT}{2} \quad \rightarrow \quad T = \left\langle \sum_{i=1}^{N} \frac{m\left|\mathbf{v}_i(t)\right|^2}{kN_f} \right\rangle$$

where α denotes an arbitrary degree of freedom, and N_f is the number of degrees of freedom of the system ($N_f = 3N$ if no contraints are imposed; in simulations it is quite common to fix the position of the centre of mass, so we would have $N_f = 3N - 3$).

leap-frog **version**. This version is numerically more stable than Verlet's. One first defines:

$$\mathbf{v}_i\left(t - \frac{h}{2}\right) = \frac{\mathbf{r}_i(t) - \mathbf{r}_i(t-h)}{h}, \quad \mathbf{v}_i\left(t + \frac{h}{2}\right) = \frac{\mathbf{r}_i(t+h) - \mathbf{r}_i(t)}{h}.$$

Positions are then updated with

$$\mathbf{r}_i(t+h) = \mathbf{r}_i(t) + h\mathbf{v}_i\left(t + \frac{h}{2}\right)$$

Using the Verlet algorithm,

$$\mathbf{r}_i(t+h) - \mathbf{r}_i(t) = \mathbf{r}_i(t) - \mathbf{r}_i(t-h) + \frac{h^2}{m}\mathbf{F}_i(t)$$

so that

$$\mathbf{v}_i\left(t + \frac{h}{2}\right) = \mathbf{v}_i\left(t - \frac{h}{2}\right) + \frac{h}{m}\mathbf{F}_i(t).$$

From here the *Hamiltonian* version of the Verlet algorithm follows:

$$\begin{cases} \mathbf{r}_i(t+h) = \mathbf{r}_i(t) + h\mathbf{v}_i\left(t + \frac{h}{2}\right), \\ \mathbf{v}_i\left(t + \frac{h}{2}\right) = \mathbf{v}_i\left(t - \frac{h}{2}\right) + \frac{h}{m}\mathbf{F}_i(t). \end{cases}$$

Note that the positions and velocities are out–of–phase by a time interval $h/2$. Velocities at t can be calculated from the expression

$$\mathbf{v}_i(t) = \frac{\mathbf{v}_i\left(t+\frac{h}{2}\right) + \mathbf{v}_i\left(t-\frac{h}{2}\right)}{2}. \tag{11}$$

- **Another version**. The problem with the latter version is that $\mathbf{r}_i(t)$ and $\mathbf{v}_i(t)$ are not obtained at the same order in h at the same time t. A possible modification that avoids this is

$$\begin{cases} \mathbf{r}_i(t+h) = \mathbf{r}_i(t) + h\mathbf{v}_i\left(t+\frac{h}{2}\right), \\ \\ \mathbf{v}_i(t+h) = \mathbf{v}_i(t) + \frac{h}{2m}\left[\mathbf{F}_i(t+h) + \mathbf{F}_i(t)\right]. \end{cases} \tag{12}$$

This numerical scheme is completely equivalent to Verlet's. To check it out, note that

$$\mathbf{r}_i(t+2h) = \mathbf{r}_i(t+h) + \mathbf{v}_i(t+h)h + \frac{h^2}{2m}\mathbf{F}_i(t+h),$$

$$\mathbf{r}_i(t) = \mathbf{r}_i(t+h) - \mathbf{v}_i(t+h)h - \frac{h^2}{2m}\mathbf{F}_i(t).$$

Adding,

$$\mathbf{r}_i(t+2h) + \mathbf{r}_i(t) = 2\mathbf{r}_i(t+h) + h\left[\mathbf{v}_i(t+h) - \mathbf{v}_i(t)\right] + \frac{h^2}{2m}\left[\mathbf{F}_i(t+h) - \mathbf{F}_i(t)\right].$$

Using the second of Eqns. (12), we obtain

$$\mathbf{r}_i(t+h) = 2\mathbf{r}_i(t) - \mathbf{r}_i(t-h) + \frac{h^2}{m}\mathbf{F}_i(t),$$

which is precisely Verlet's algorithm.

3.c Stability of trajectories

Systems with many degrees of freedom are prone to being unstable in the following sense. Take two possible trajectories in phase phase that start from very close initial conditions. Let us calculate the distance $\delta(t)$ between these two trajectories as if phase space were Euclidean. Expressing the distance in terms of an exponential function (Fig. 23) as $\delta(t) \sim e^{\lambda t}$, we say that the system is

- STABLE if $\lambda < 0$ or δ decreases more slowly than exponentially
- UNSTABLE if $\lambda > 0$; now the system is said to be *chaotic*

The coefficient λ is known as *Lyapunov exponent*. The criterion for the separation between trajectories based on an exponential comes naturally from a linear analysis of the effect a perturbation of amplitude δ would have on a given trajectory; the linear equation

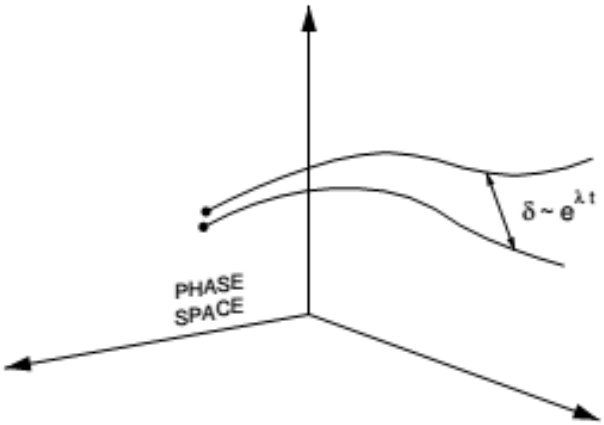

Figure 23: Exponential increase of the separation between two trajectories that started very close in phase space.

would be $\dot{\delta} \sim \delta$, which gives an exponential as a solution.

The Lyapunov instability occurs when $\lambda > 0$; there are two reasons why it is important:

- gives a limiting upper time beyond which an accurate and trustable numerical solution can be found
- in order to reach a high precision when computing a trajectory after a time t, we would need to know the initial condition with an unreasonably accuracy, since the number of digits grows linearly with time: if ϵ is the number of digits,

$$e^{\lambda t} \sim 10^{-\epsilon} \quad \rightarrow \quad \epsilon \sim \frac{\lambda t}{\log 10}$$

It turns out that systems with many degrees of freedom, such as those encountered in condensed–matter physics, are intrinsically unstable, and hence intrinsically chaotic. Which are the practical consequences of all this? Obviously use of high–precision numerical algorithms to integrate the equations of motion with high accuracy is not only costly from the computational point of view but also useless in practical terms.

The basic properties that a numerical integration scheme must meet in order to be useful in condensed–matter physics are:

1. It should be time–reversible

   Reversibility is a basic property of the microscopic equations of motion:

$$\begin{cases} \dfrac{d\mathbf{r}_i}{dt} = \mathbf{v}_i \\ \\ m\dfrac{d\mathbf{v}_i}{dt} = -\nabla_i U \end{cases}$$

If we make the transformation

$$t \rightarrow -t$$
$$\mathbf{v}_i \rightarrow -\mathbf{v}_i$$

(i.e. the arrow of time is reversed and, at the same time, the sign of the velocities is reversed, the equations remain unchanged. In Newtonian language,

$$m\frac{d^2\mathbf{r}_i}{dt^2} = -\nabla_i U$$

reversibility with respect to the transformation $t \rightarrow -t$ is also obvious. It is easy to see that the Verlet algorithm respects the property of invariance with respect to the operation $h \rightarrow -h$:

$$\mathbf{r}_i(t+h) = 2\mathbf{r}_i(t) - \mathbf{r}_i(t-h) + \frac{h^2}{m}\mathbf{F}_i(t)$$

$$\longrightarrow \quad \mathbf{r}_i(t-h) = 2\mathbf{r}_i(t) - \mathbf{r}_i(t+h) + \frac{h^2}{m}\mathbf{F}_i(t)$$

If terms are rearranged in the second equation we obtain the first. The built-in irreversibility of some integration algorithms induces an 'intrinsic energy dissipation' and non–energy–conserving dynamics. This problem may give rise to unwanted and sometimes even spurious results in the simulations. But there is still the problem of the irreversibility introduced by the round–off errors in the computer due to use of floating–point arithmetics, which necessarily involves a finite number of decimal digits. These effects are usually negligible.

It should be symplectic

This means the following. Let $f(q,p,t)$ be the probability distribution of the system so that

$$f(q,p,t)dqdp$$

is the number of points (configurations) in phase space contained in a differential volume $dqdp$ centred at (q,p) at time t. Each point propagates in time according to the dynamical equations (e.g. Hamilton's equations). The *Liouville' theorem* says that the probability distribution function $f(q,p,t)$ evolves in time like an incompressible fluid, which in mathematical terms means that $\dot{f} = 0$, where the dot implies total time derivative. Fig. 24 represents pictorially this flow. This property can be shown to be contained in the dynamical equations, and of course has to be respected by the numerical integration scheme used.

A *symplectic* numerical scheme respects Liouville's theorem, i.e. *it conservs phase space volume*. If the numerical algorithm is written in matrix form, this means that the Jacobian transformation that takes the system from time t to time $t+h$ has to be equal to unity:

$$\begin{pmatrix} r(t+h) \\ v(t+h) \end{pmatrix} = M \begin{pmatrix} r(t) \\ v(t) \end{pmatrix}, \qquad \mathrm{Jac}(M) = 1$$

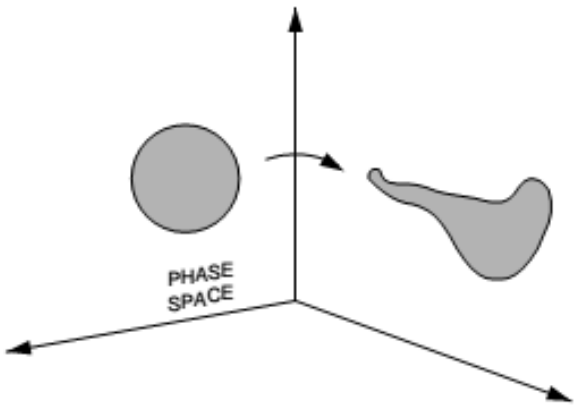

Figure 24: Liouville theorem: volume of phase space is a constant in time and therefore behaves as an incompressible fluid.

where M is the dynamical matrix associated with the particular numerical algorithm. For instance, the Verlet algorithm, written in Hamiltonian form,

$$\begin{cases} \mathbf{r}_i(t+h) = \mathbf{r}_i(t) + h\mathbf{v}_i\left(t+\frac{h}{2}\right) \\ \\ \mathbf{v}_i\left(t+\frac{h}{2}\right) = \mathbf{v}_i\left(t-\frac{h}{2}\right) + \frac{h}{m}\mathbf{F}_i(t) \end{cases}$$

can be written, with the help of the vectors

$$(x_1, y_1, z_1, x_2, y_2, z_2, ..., x_N, y_N, z_N, v_1^x, v_1^y, v_1^z, v_2^x, v_2^y, v_2^z, ..., v_N^x, v_N^y, v_N^z)$$

in terms of the matrix

$$M = \left(\begin{array}{c|c} 1 & h.1 \\ \hline 0 & 1 \end{array}\right),$$

the determinant of which is obviously equal to unity.

3.d. The Lennard–Jones potential: practical implementation

The Lennard–Jones potential, $\phi_{LJ}(r)$, is a pair potential that depends on the distance r between two particles. Its functional form is

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

and it contains two parameters: ϵ, an energy parameter which is equal to the depth of the potential well (see Fig. 25), and a length parameter, σ, which is the root of the potential and can be taken roughly as the diameter of the particles. The potential has a repulsive part at short distances, which accounts for the repulsion felt by two spherically-symmetric

atoms at close distance due to the overlap of electronic clouds and to the Pauli exclusion principle. At long distances the potential is attractive, due to van der Waals interaction. At intermediate distances, there is a potential well.

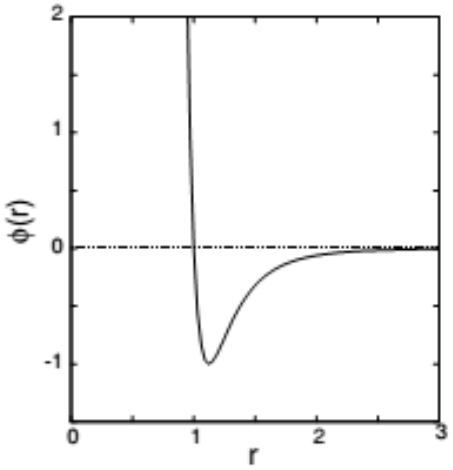

Figure 25: The Lennard–Jones pair potential.

We will illustrate the Molecular Dynamics technique using this model potential. The interest in the Lennard–Jones potential is due to the fact that a system of particles interacting via this pair potential presents a 'realistic' phase diagram, containing liquid–vapour and fluid–solid transitions. The first is a due to the presence of attractions in the potential. Note that the hard–sphere model does not contain this feature.

The central problem of Molecular Dynamics is the calculation of forces. In our case the forces can be calculated analytically by differentiation of the potential. Let N be the number of particles in the system. The potential energy of the system is:

$$U(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) = \frac{1}{2}\sum_{i=1}^{N} \sum_{\substack{j=1 \\ j \neq i}}^{N} \phi_{LJ}\left(|\mathbf{r}_j - \mathbf{r}_i|\right) = \sum_{i=1}^{N}\sum_{j<i}^{N} \phi_{LJ}\left(|\mathbf{r}_j - \mathbf{r}_i|\right)$$

The first version includes a $1/2$ prefactor in order not to count the same pair of particles twice. The force on particle i is:

$$\mathbf{F}_i = -\nabla_{\mathbf{r}_i} U = -\sum_{j \neq i} \nabla_{\mathbf{r}_i} \phi_{LJ}\left(|\mathbf{r}_j - \mathbf{r}_i|\right) \equiv \sum_{j \neq i} \mathbf{F}_{ij}$$

Note that $\mathbf{F}_{ij} = -\nabla_{\mathbf{r}_i} \phi_{LJ}\left(|\mathbf{r}_j - \mathbf{r}_i|\right)$ is the contribution of particle j to the force on particle i, and that, by Newton's third law, $\mathbf{F}_{ij} = -\mathbf{F}_{ji}$; this property helps save valuable computer time. Now:

$$\nabla_{\mathbf{r}_i} \phi_{LJ}\left(|\mathbf{r}_j - \mathbf{r}_i|\right) = \phi'_{LJ}\left(|\mathbf{r}_j - \mathbf{r}_i|\right) \nabla_{\mathbf{r}_i} |\mathbf{r}_j - \mathbf{r}_i| = \phi'_{LJ}\left(|\mathbf{r}_j - \mathbf{r}_i|\right) \frac{\mathbf{r}_j - \mathbf{r}_i}{|\mathbf{r}_j - \mathbf{r}_i|}$$

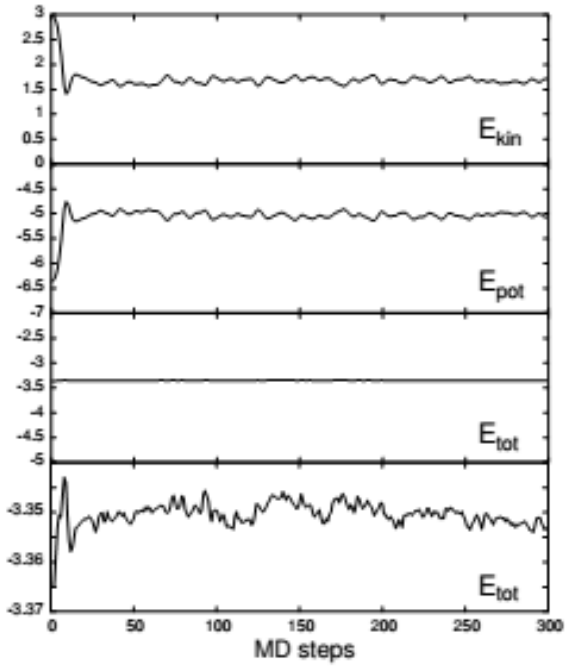

Figure 26: Time evolution of (from top to bottom): kinetic, potential, total energy (all shown with the same vertical scale) and total energy (at a much lower scale) from a MD simulation of a Lennard–Jones liquid at reduced density $\rho\sigma^3 = 0.8$ and reduced (initial) temperature $kT/\epsilon = 2$.

Since

$$\phi'_{LJ}(r) = -\frac{48\epsilon}{\sigma^2}\left[\left(\frac{\sigma}{r}\right)^{13} - \frac{1}{2}\left(\frac{\sigma}{r}\right)^{7}\right]$$

we finally have

$$\mathbf{F}_i = \frac{48\epsilon}{\sigma^2}\sum_{j\neq i}\left[\left(\frac{\sigma}{r_{ij}}\right)^{14} - \frac{1}{2}\left(\frac{\sigma}{r_{ij}}\right)^{8}\right](\mathbf{r}_j - \mathbf{r}_i)\,.$$

Once the forces are known, the dynamics can be calculated by means of the numerical integration algorithm.

Quantities can be calculated as time averages (instead as configuration averages, like in the MC method). For example, the pressure can be calculated from the virial theorem which, for pair–wise additive forces, reads:

$$p = \rho kT - \frac{1}{3V}\left\langle \sum_i \sum_{j>i} \mathbf{r}_{ij}\cdot\mathbf{F}_{ij}\right\rangle_t ,$$

where the brackets indicate time average. The dot product is:

$$\sum_i\sum_{j>i}\mathbf{r}_{ij}\cdot\mathbf{F}_{ij} = -\phi'_{LJ}(|\mathbf{r}_j - \mathbf{r}_i|)\frac{\mathbf{r}_{ij}\cdot\mathbf{r}_{ij}}{|\mathbf{r}_j - \mathbf{r}_i|} = \frac{48\epsilon r_{ij}}{\sigma^2}\left[\left(\frac{\sigma}{r_{ij}}\right)^{13} - \left(\frac{\sigma}{r_{ij}}\right)^{7}\right]$$

The temperature is computed, as discussed before, with

$$T = \left\langle \sum_{i=1}^{N} \frac{m\,|\mathbf{v}_i(t)|^2}{kN_f} \right\rangle_t ,$$

and the potential energy is

$$U = \left\langle \sum_{i=1}^{N} \sum_{j<i}^{N} \phi_{\text{LJ}}\left(|\mathbf{r}_j - \mathbf{r}_i|\right) \right\rangle_t .$$

The total energy,

$$E = \left\langle \sum_{i=1}^{N} \frac{1}{2} m\,|\mathbf{v}_i(t)|^2 \right\rangle_t + \left\langle \sum_{i=1}^{N} \sum_{j<i}^{N} \phi_{\text{LJ}}\left(|\mathbf{r}_j(t) - \mathbf{r}_i(t)|\right) \right\rangle_t ,$$

is useful to check that the MD code is free from errors, since it has to be constant during the simulation. If the leap–frog algorithm is used, on has to be careful to use the velocities at time t, i.e. at the same time as the positions, using Eqn. (11).

Let us now discuss the question of units. Natural units of energy and length are ϵ and σ, respectively, and from these a LJ time scale is $\tau = (m\sigma^2/\epsilon)^{1/2}$. Therefore dimensionless positions, velocities and forces are:

$$\mathbf{r}_i^* = \frac{\mathbf{r}_i}{\sigma}, \qquad \mathbf{v}_i^* = \frac{\mathbf{v}_i}{\sigma/\tau} = \mathbf{v}_i \left(\frac{m}{\epsilon}\right)^{1/2}, \qquad \mathbf{F}_i^* = \frac{\mathbf{F}_i}{\epsilon/\sigma} = \frac{\mathbf{F}_i \sigma}{\epsilon}.$$

The equation that updates positions in the leap–frog algorithm becomes:

$$\mathbf{r}_i^*(t+h)\sigma = \mathbf{r}_i^*(t)\sigma + h\left(\frac{\epsilon}{m}\right)^{1/2} \mathbf{v}_i^*\left(t + \frac{h}{2}\right) \quad \rightarrow \quad \mathbf{r}_i^*(t+h) = \mathbf{r}_i^*(t) + h^* \mathbf{v}_i^*\left(t + \frac{h}{2}\right),$$

where $h^* = h/\tau$. The equation for velocities is:

$$\mathbf{v}_i^*\left(t + \frac{h}{2}\right)\left(\frac{\epsilon}{m}\right)^{1/2} = \mathbf{v}_i^*\left(t - \frac{h}{2}\right)\left(\frac{\epsilon}{m}\right)^{1/2} + \frac{h^*}{m}\left(\frac{m\sigma^2}{\epsilon}\right)^{1/2}\left(\frac{\epsilon}{\sigma}\right)\mathbf{F}_i^*(t)$$

so that

$$\mathbf{v}_i^*\left(t + \frac{h}{2}\right) = \mathbf{v}_i^*\left(t - \frac{h}{2}\right) + h^* \mathbf{F}_i^*(t).$$

The dimensionless temperature is $T^* = kT/\epsilon$:

$$T^* = \frac{k}{\epsilon} \times \frac{1}{kN_f} \left\langle \sum_{i=1}^{N} m \left| \left(\frac{\epsilon}{m}\right)^{1/2} \mathbf{v}_i^*(t) \right|^2 \right\rangle_t = \frac{1}{N_f} \left\langle \sum_{i=1}^{N} |\mathbf{v}_i^*(t)|^2 \right\rangle_t .$$

Note that, since all particles are equivalent,

$$T^* = \frac{1}{3N} \times N \left\langle |\mathbf{v}^*(t)|^2 \right\rangle_t \quad \rightarrow \quad \left\langle |\mathbf{v}^*(t)|^2 \right\rangle = 3T^* \tag{13}$$

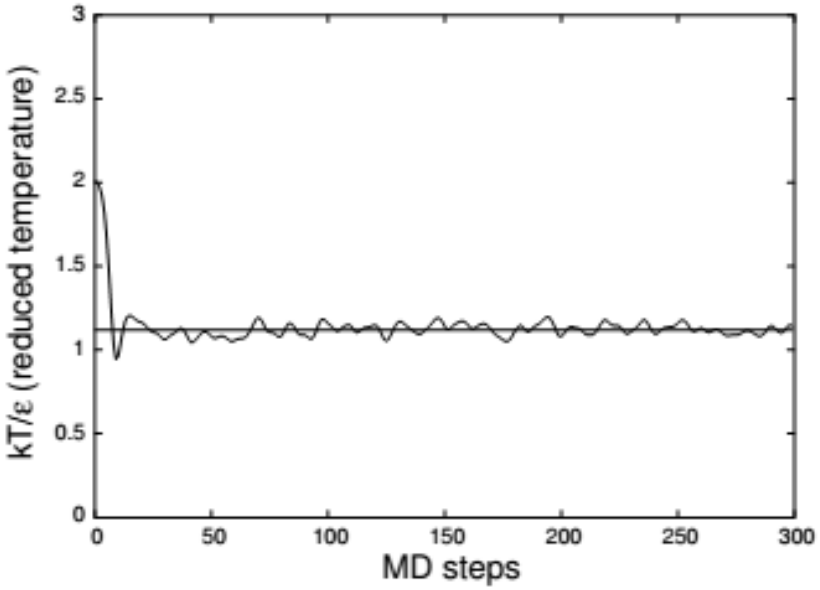

Figure 27: Time evolution of temperature for the same experiment as in Fig. 26.

for a generic particle (here we took $N_f = 3N$). Dimensionless kinetic and potential energies are $E_c^* = E_c/\epsilon$,

$$E_c^* = \frac{1}{\epsilon} \times \frac{1}{2} m \left\langle \sum_{i=1}^{N} \left| \left(\frac{\epsilon}{m}\right)^{1/2} \mathbf{v}_i^*(t) \right|^2 \right\rangle_t = \frac{1}{2} \left\langle \sum_{i=1}^{N} |\mathbf{v}_i^*(t)|^2 \right\rangle_t ,$$

and $U^* = U/\epsilon$. The dimensionless density is $\rho^* = \rho\sigma^3$, and the dimensionless pressure $p^* = p\sigma^3/\epsilon$ is calculated from the virial theorem:

$$\frac{p^*\epsilon}{\sigma^3} = \left(\frac{\rho^*}{\sigma^3}\right) \times k \times \left(\frac{T^*\epsilon}{k}\right) - \frac{1}{3V^*\sigma^3} \left\langle \sum_i \sum_{j>i} \left(\sigma \mathbf{r}_{ij}^*\right) \cdot \left(\frac{\epsilon}{\sigma} \mathbf{F}_{ij}^*\right) \right\rangle_t ,$$

so that

$$p^* = \rho^* T^* - \frac{1}{3V^*} \left\langle \sum_i \sum_{j>i} \mathbf{r}_{ij}^* \cdot \mathbf{F}_{ij}^* \right\rangle_t .$$