

Computational Physics

Molecular Dynamics Simulations

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1 Introduction

The idea of Molecular Dynamics (MD) is that of numerically integrating the classical equations of motion to generate a trajectory of a system with N particles in time. The N particles are characterized by $6N$ coordinates, namely positions and momenta in a three dimensional volume space. Let a particle i be subject to a force \vec{f}_i at time t . Molecular Dynamics solves Newton's equations **for the positions of the particles**

$$\frac{d^2\vec{r}_i}{dt^2} = \frac{\vec{f}_i(\vec{r}_1, \vec{r}_2, \dots, \vec{v}_1, \vec{v}_2, \dots)}{m_i} \quad (1)$$

where the force depends on the particles positions and eventually velocities. **In all examples we will consider mainly forces which are independent on velocities¹ and thus obtained as gradient of a coordinates-dependent potential energy.**

Molecular dynamics is intensively used to investigate the physical properties of liquids and gases, biomolecules (as proteins or DNA), nanomaterials and crystals, membranes and soft matter systems. MD simulations neglect quantum effects. This is a good approximation when studying the motion of large biomolecules (proteins, DNA) as major conformational changes, folding, or binding. Quantum effects can be neglected in liquids, soft matter systems and nanomaterials if the temperature is high enough so that the contribution of zero-point energy or tunneling are small.

Quantum mechanics must be considered when dealing with: (a) Chemical reactions as bond making/breaking requires electronic structure information, (b) Low temperatures, when quantum zero-point motion becomes important (e.g., in superfluid helium), (c) Light particles: Especially hydrogen, where tunneling and quantization of vibrations matter. (d) Excited states or electron transport: Requires quantum dynamics or time-dependent DFT. (e) Magnetic or optical properties: Need quantum treatment of spins or photons. Several algorithms have been developed to deal with quantum effects, but those will not be discussed in this course.

A typical Molecular Dynamics program follows this scheme:

1. At time $t = 0$ initialize the system by choosing positions and velocities of the particles. Choose also a value for Δt , the time step used in the numerical integration of the equations of motion.
2. Compute the forces on all particles.
3. Integrate the Newton's equations of motion using an appropriate integration scheme. Update positions and velocities of particles at time $t + \Delta t$.
4. Go back to step 2.

¹We therefore will not consider charged particles in magnetic fields which are subject to the Lorentz force $\vec{f} = q\vec{v} \times \vec{B}$. We will, however, consider non-conservative frictional forces $\vec{f} = -\gamma\vec{v}$, see Sec. 8.

Molecular Dynamics is essentially a *deterministic* method, differently from Monte Carlo simulations which have a *stochastic* nature. Given an initial condition a molecular dynamics program will always generate the same trajectory in phase space. There are however versions of a MD algorithm with **stochastic elements**. Examples are discussed in Sections 7.3 and 8.

In MD simulations physical quantities are calculated from time averages along the trajectories. Let A be a quantity depending on positions and velocities $A(t) = A(\vec{r}_1(t) \dots \vec{r}_N(t), \vec{v}_1(t), \dots \vec{v}_N(t))$. Its average value is defined as

$$\langle A \rangle = \frac{1}{N} \sum_{n=0}^{N-1} A(t_0 + n\Delta t) \quad (2)$$

where t_0 is an initial time. Typically, a physical quantity is characterized by some relaxation time τ_A , which is the time one has to wait until A reaches an average equilibrium value. If one is interested in equilibrium quantities it is then safer to take averages starting from a given time $t_0 > \tau_A$.

There are several integration schemes based on some discretization of the differential equation (1), as we will show in the next Section.

2 Integration schemes

The simplest integration scheme and also the mostly used is the so-called Verlet's algorithm. Let us consider the development of the positions up to the fourth order for $\vec{r}_i(t + \Delta t)$ and $\vec{r}_i(t - \Delta t)$:

$$\vec{r}_i(t + \Delta t) = \vec{r}_i(t) + \vec{v}_i(t)\Delta t + \frac{\vec{a}_i(t)}{2}\Delta t^2 + \frac{\vec{g}_i(t)}{6}\Delta t^3 + O(\Delta t^4) \quad (3)$$

$$\vec{r}_i(t - \Delta t) = \vec{r}_i(t) - \vec{v}_i(t)\Delta t + \frac{\vec{a}_i(t)}{2}\Delta t^2 - \frac{\vec{g}_i(t)}{6}\Delta t^3 + O(\Delta t^4) \quad (4)$$

where $\vec{v}_i = d\vec{r}_i/dt$ (velocity), $\vec{a}_i = d^2\vec{r}_i/dt^2$ (acceleration) and $\vec{g}_i = d^3\vec{r}_i/dt^3$.

By summing up the two equations one arrives at the

Verlet algorithm

$$\vec{r}_i(t + \Delta t) = 2\vec{r}_i(t) - \vec{r}_i(t - \Delta t) + \vec{a}_i(t)\Delta t^2 + O(\Delta t^4) \quad (5)$$

The positions are calculated accurately up to the fourth order in Δt . The velocities are not explicitly calculated, but they can be derived from the knowledge of the trajectory as

$$\vec{v}_i(t) = \frac{\vec{r}_i(t + \Delta t) - \vec{r}_i(t - \Delta t)}{2\Delta t} + O(\Delta t^2) \quad (6)$$

which is accurate only to the order Δt^2 . Hence, quantities depending on the velocities, as the total kinetic energies are not very accurately determined.

The position of the particles at time step $t + \Delta t$ depends on positions at times t and $t - \Delta t$, which gives the problem of initialization: we cannot directly apply Eq. (5) using initial conditions in which the $t = 0$ positions and velocities are given. The problem is solved in the following way. Given the initial positions and velocities $\vec{r}_i(0)$ and $\vec{v}_i(0)$ one approximates

$$\vec{r}_i(\Delta t) \approx \vec{r}_i(0) + \vec{v}_i(0)\Delta t + \frac{\vec{a}_i(0)}{2}\Delta t^2 \quad (7)$$

From it one can calculate the forces, hence $\vec{a}_i(\Delta t)$, and then apply iteratively Eq. (5).

An alternative and much better integration scheme, where positions and velocities are simultaneously updated, is the so-called

Velocity Verlet algorithm

$$\vec{r}_i(t + \Delta t) = \vec{r}_i(t) + \vec{v}_i(t)\Delta t + \frac{\vec{a}_i(t)}{2}\Delta t^2 + O(\Delta t^4) \quad (8)$$

$$\vec{v}_i(t + \Delta t) = \vec{v}_i(t) + \frac{\vec{a}_i(t + \Delta t) + \vec{a}_i(t)}{2}\Delta t \quad (9)$$

Although it may not be clear from Eqs.(8) and (9) it can be shown that in the velocity Verlet algorithm the positions are calculated accurately up to the fourth order in time. In order to show this let us replace $t \rightarrow t - \Delta t$ in Equation (8). We find:

$$\vec{r}_i(t - \Delta t) = \vec{r}_i(t) - \vec{v}_i(t - \Delta t)\Delta t - \frac{\vec{a}_i(t - \Delta t)}{2}\Delta t^2 \quad (10)$$

Summing the previous equation to Eq. (8) one gets

$$\begin{aligned} \vec{r}_i(t + \Delta t) &= 2\vec{r}_i(t) - \vec{r}_i(t - \Delta t) + (\vec{v}_i(t) - \vec{v}_i(t - \Delta t))\Delta t + \frac{\vec{a}_i(t) - \vec{a}_i(t - \Delta t)}{2}\Delta t^2 \\ &= 2\vec{r}_i(t) - \vec{r}_i(t - \Delta t) + \vec{a}_i(t)\Delta t^2 \end{aligned} \quad (11)$$

where we have used Eq. (9) at time $t - \Delta t$ to simplify the expression. Equation (11) is identical to the position update in the standard Verlet algorithm (Eq. (5)), hence of fourth order in Δt .

An important feature of the Verlet and velocity Verlet algorithms is that they are fully time reversal²: Eq. (5) remains invariant by interchanging $\Delta t \rightarrow -\Delta t$. What

²There exist other Molecular Dynamics integration schemes which are not time reversal, or better they are time reversal only up to some given order in Δt .

is impractical of the velocity Verlet algorithm as given in Eqs. (8) and (9) is that it requires storage of accelerations at two different time steps. An implementation avoiding this is the following

Implementation of the Velocity Verlet algorithm

- 1) Given $\vec{r}_i(t)$, $\vec{v}_i(t)$ and $\vec{a}_i(t)$ update the positions to

$$\vec{r}_i(t + \Delta t) = \vec{r}_i(t) + \vec{v}_i(t)\Delta t + \frac{\vec{a}_i(t)}{2}\Delta t^2 \quad (12)$$

- 2) Calculate the velocities at an intermediate time step

$$\vec{v}_i(t + \Delta t/2) = \vec{v}_i(t) + \frac{1}{2}\vec{a}_i(t)\Delta t \quad (13)$$

- 3) From the positions at time $t + \Delta t$ calculate the forces and hence accelerations. If forces are derived from a (velocity independent potential) $V()$ one has

$$\vec{a}_i(t + \Delta t) = -\frac{1}{m}\nabla_i V(\vec{r}_1(t + \Delta t) \dots \vec{r}_N(t + \Delta t)) \quad (14)$$

- 4) Update the velocities to

$$\vec{v}_i(t + \Delta t) = \vec{v}_i(t + \Delta t/2) + \frac{1}{2}\vec{a}_i(t + \Delta t)\Delta t \quad (15)$$

Note that the algorithm is identical to that of Eqs. (8) and (9). The difference is that Eq. (9) is implemented in two steps. The new implementation requires less memory: there is no need to store data at two different time steps. For a system of N particles in three dimensions one needs $9N$ memory locations: $3N$ for positions, $3N$ for velocities and $3N$ for accelerations.

The timestep in a MD simulation should be chosen so that the simulations is long enough to be relevant to the time scales of the natural processes being studied. But Δt should be small enough to avoid discretization errors, for instance should be smaller than the fastest vibrational frequency of the system.

2.1 On the symplectic nature of the Velocity Verlet algorithm

A property of the velocity Verlet algorithm is that it is a *symplectic integrator*. Such algorithms have the property that their trajectories conserve exactly a “pseudo-energy” which differs from the true energy by a small amount (vanishing as $\Delta t \rightarrow 0$). This avoids long time drifts of the trajectories from the true ones, due to the accumulation of

numerical errors during the time evolution. The problem 13.2 illustrates the importance of a symplectic algorithm. Symplectic Integrators preserve phase-space volume and allow for stable simulations with large numbers of time steps.

To understand the properties of a symplectic algorithm we use the Hamilton's formalism of classical mechanics. This uses positions (typically indicated as \vec{q}_i instead of \vec{r}_i as in the previous section) and momenta $\vec{p}_i \equiv m\vec{v}_i$. The Hamiltonian of the system is defined as the sum of kinetic and potential energies (thus the total mechanical energy of the system) as

$$H = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} + V(\vec{q}_1, \dots, \vec{q}_N) \quad (16)$$

It is easy to show that the Newton's equations of motion can be written in the following form

$$\begin{cases} \frac{d\vec{q}_i}{dt} = \frac{\partial H}{\partial \vec{p}_i} \\ \frac{d\vec{p}_i}{dt} = -\frac{\partial H}{\partial \vec{q}_i} \end{cases} \quad (17)$$

where $\partial/\partial \vec{p}$ denotes the gradient with respect to \vec{p} .

To simplify the discussion we focus from now on to a system consisting of a single particle in one dimension, thus the state of the system is described by a two dimensional vector (q, p) . Given two arbitrary continuous and differentiable functions $f(q, p)$ and $g(q, p)$ we define the Poisson bracket

$$\{f, g\} \equiv \frac{\partial f}{\partial q} \frac{\partial g}{\partial p} - \frac{\partial f}{\partial p} \frac{\partial g}{\partial q} \quad (18)$$

From which these relations easily follow

$$\{q, f(q, p)\} = \frac{\partial f}{\partial p} \quad \{p, f(q, p)\} = -\frac{\partial f}{\partial q} \quad (19)$$

Let us introduce the two dimensional vector $z \equiv (q, p)$ and define the linear operator $D_H f \equiv \{f, H\}$. The Hamilton equations (17) take the form

$$\dot{z} = \{z, H(q, p)\} = D_H z \quad (20)$$

As the Hamiltonian H is the sum of kinetic and potential energies it is convenient to split the contributions of the two terms as

$$D_H f = \{f, T + V\} = \{f, T\} + \{f, V\} = D_T f + D_V f \quad (21)$$

We can formally integrate the equation of motion (20) as follows

$$z(t) = e^{tD_H} z(0) = \left(\sum_{n=0}^{\infty} \frac{t^n}{n!} D_H^n \right) z(0) \quad (22)$$

given the initial condition $z(0)$. This however does not solve the problem as the calculation of the exponential of an operator cannot be performed in general. We can

however introduce some approximations. We first note that our interest is in an algorithm which generates the evolution of the system for a small time step $t \rightarrow t + \Delta t$ for which we can write

$$z(t + \Delta t) = e^{\Delta t(D_T + D_V)} z(t) \quad (23)$$

Next it can be easily shown that for any operators A and B one has

$$e^{\Delta t(A + B)} = e^{\Delta t A} e^{\Delta t B} + \mathcal{O}(\Delta t^2) \quad (24)$$

We recall that $\exp(A + B) = \exp(A) \exp(B)$ only if the operators commute $AB = BA$, which is not the case for D_T and D_V . Using the above factorization we can write

$$\begin{aligned} p(t + \Delta t) &= e^{\Delta t D_V} e^{\Delta t D_T} p(t) = e^{\Delta t D_V} p(t) = (1 + \Delta t D_V) p(t) \\ &= p(t) + \Delta t \{p, V(q)\} = p(t) - \Delta t \frac{\partial V}{\partial q} = p(t) + \Delta t f(q(t)) \end{aligned} \quad (25)$$

with $f = -\partial V/\partial q$ is the force acting on the particle. To find the final expression we used the following relations $D_T p = \{p, p^2/2m\} = 0$ and $D_V^2 p = \{\{p, V\}, V\} = -\{\partial V/\partial q, V\} = 0$. Through these one can calculate easily the exponentials as any higher powers $D_T^k p = D_V^m p = 0$ for $k \geq 1$ and $m \geq 2$. For the position a similar calculation gives

$$\begin{aligned} q(t + \Delta t) &= e^{\Delta t D_V} e^{\Delta t D_T} q(t) = e^{\Delta t D_V} (1 + \Delta t D_T) q(t) = e^{\Delta t D_V} \left[q(t) + \frac{\Delta t}{m} p(t) \right] \\ &= q(t) + \frac{\Delta t}{m} p(t) - \frac{\Delta t^2}{m} \frac{\partial V}{\partial q} = q(t) + \frac{\Delta t}{m} p(t + \Delta t) \end{aligned} \quad (26)$$

where we have used Eq. (25) in the final form. Writing $p = mv$ and $f = ma$ we can rewrite (25) and (26) in the following form

$$q(t + \Delta t) = q(t) + v(t + \Delta t) \Delta t \quad (27)$$

$$v(t + \Delta t) = v(t) + a(t) \Delta t \quad (28)$$

We have derived here a symplectic algorithm accurate to second order in Δt . We can increase the accuracy using a better approximation, namely the relation

$$e^{\Delta t(A + B)} = e^{\Delta t A/2} e^{\Delta t B} e^{\Delta t A/2} + \mathcal{O}(\Delta t^3) \quad (29)$$

Working this out in a similar manner as done above with $A = D_V$ and $B = D_T$ it can be shown that one generates the Velocity Verlet algorithm (8), (9), see problem 13.3.

To understand the importance of a symplectic algorithm let us first discuss some general properties of Hamiltonian mechanics. Let us consider one dimensional system consisting of a single particle and a square in phase space of size $dq dp$ at time $t = 0$. Under the Hamiltonian dynamics each point in phase space evolves in time and the shape will no longer be that of a square at later times. A generic property is that although the shape will change, the volume will remain constant in time, see Fig. ???. Viewing every point at time $t = 0$ in phase space as the motion of fluid, the Liouville

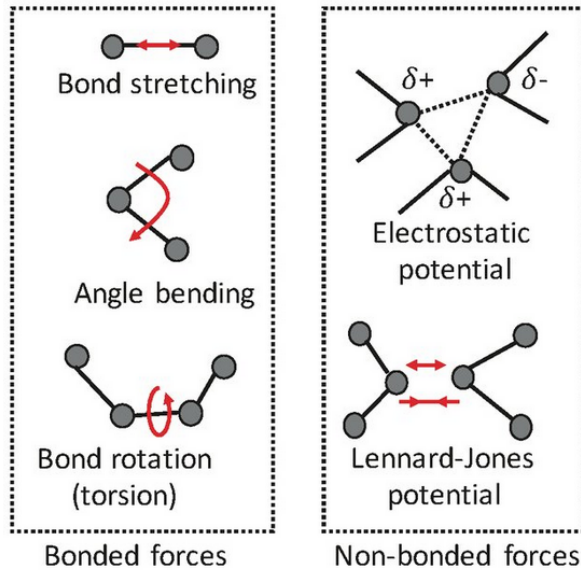


Figure 1: Two classes of interactions are typically considered in MD simulations involving bonded and non-bonded interactions. The former type describes structures and deformations of covalent bonds, the latter all other type of interactions not-involving covalent bonding (from Waidyasooriya et al. "An FPGA accelerator for molecular dynamics simulation using OpenCL." *Int. Journ. of Networked and Distributed Computing* 5.1 (2017): 52-61.).

theorem states that "fluid" of points doesn't compress or expand – it flows incompressibly through phase space. The same property is fulfilled by symplectic integrators. One can show that the transformations $\exp(\Delta t D_T)$ and $\exp(\Delta t D_V)$ conserve the volume in phase space. This volume preserving property is important for the numerical stability of the algorithm. This means that trajectories generated via the discretization never drift away from the true trajectory.

3 Force fields

In Molecular Dynamics (MD), the term force field refers to the potential energy of a system to describe interactions between atoms or molecules. It provides the forces that drive particle motion according to Newton's laws. Force fields are central to the accuracy and applicability of MD simulations. Given the potential energy function $V(\vec{r}_1, \vec{r}_2 \dots)$ with \vec{r}_i the position of the particle $i = 1, 2 \dots N$ one obtains the forces acting on the particle i as

$$\vec{f}_i = -\nabla_{\vec{r}_i} V(\vec{r}_1, \vec{r}_2 \dots) \quad (30)$$

A typical classical force field decomposes the potential energy into bonded and non-bonded terms:

$$V = V_{\text{bonded}} + V_{\text{non-bonded}} \quad (31)$$

3.1 Bonded Interactions

Bonded interactions in Molecular Dynamics (MD) simulations are used to model interactions between atoms that are connected through chemical bonds—i.e., atoms that are part of the same molecule or molecular substructure. These interactions help maintain the molecular geometry during the simulation and are essential for correctly capturing intra-molecular dynamics.

- **Bond stretching:** This interaction describes the vibrational motion of two atoms connected by a covalent bond. It prevents bonds from elongating or compressing unrealistically and it is typically described by a harmonic potential

$$V_{\text{bonds}} = \frac{1}{2}k_b(r - r_0)^2 \quad (32)$$

Other forms are possible. For instance the FENE potential (Finite Extensible Nonlinear Elastic) is a nonlinear spring potential commonly used for polymer chains

$$V_{\text{FENE}} = -\frac{1}{2}KR_0^2 \log \left[1 - \left(\frac{r}{R_0} \right)^2 \right] \quad (33)$$

It models bonds that behave like springs at small extensions, but cannot stretch beyond a threshold value R_0 .

- **Angle bending:** Consecutive chemical bonds form a given angle. Vibrations of bond angles between three bonded atoms are also usually described by quadratic potentials

$$V_{\text{angles}} = \frac{1}{2}k_\theta(\theta - \theta_0)^2 \quad (34)$$

Consider for instance a water molecule in which the oxygen atom is bonded to two hydrogen atoms. The angle formed between the two O-H bonds is known as the H-O-H bond angle and it is on average of 104° . In MD in the so-called TIP3P model of water one uses the parameters $\theta_0 = 104.52^\circ$ and $k_\theta \approx 100 \text{ kcal/mol} \cdot \text{rad}^2$.

- **Dihedral torsions:** Four consecutive atoms are connected by three bond vectors \vec{a} , \vec{b} and \vec{c} . These form two planes, one spanned by \vec{a} and \vec{b} and the other by \vec{b} and \vec{c} . The dihedral angle ϕ is the angle between these two intersecting planes which is defined as $\cos \phi = \hat{u} \cdot \hat{v}$ with the unit vectors are $\hat{u} \equiv \vec{a} \times \vec{b} / |\vec{a} \times \vec{b}|$ and $\hat{v} \equiv \vec{b} \times \vec{c} / |\vec{b} \times \vec{c}|$. The potential energy for a dihedral angle ϕ usually takes the form

$$V_{\text{dihedrals}} = \sum_n \frac{V_n}{2} [1 + \cos(n\phi - \gamma_n)] \quad (35)$$

where the sum is over a few terms (usually $1 \leq n \leq 3$). Here V_n is the barrier height and γ_n the phase offset. A three terms potential with $V_1 = 0.5$, $V_2 = 1$, $V_3 = 0.2$, $\gamma_1 = \gamma_3 = 0$ and $\gamma_2 = 180^\circ$ is shown in Fig. 2.

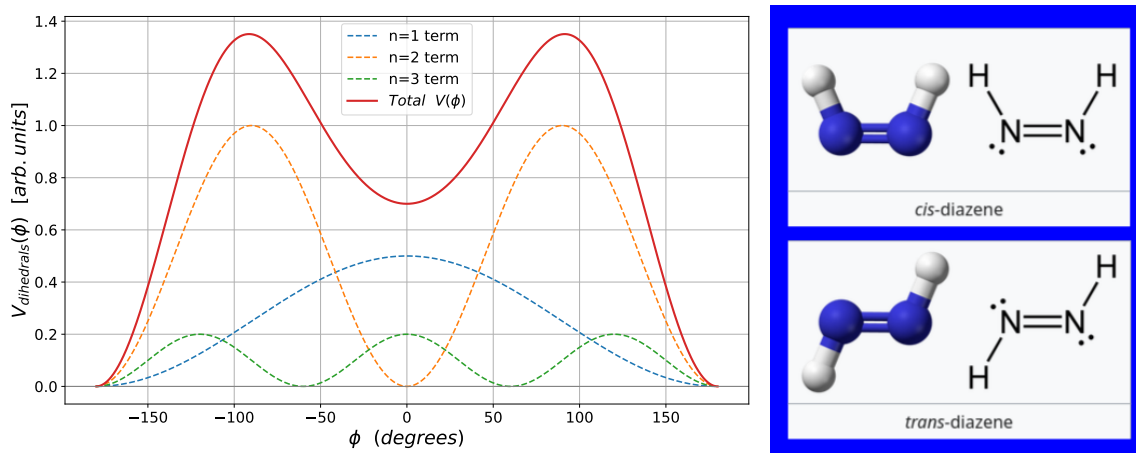


Figure 2: Left: Example of dihedral potential (35) with $V_1 = 0.5$, $V_2 = 1$, $V_3 = 0.2$, (arbitrary units) $\gamma_1 = \gamma_3 = 0$ and $\gamma_2 = 180^\circ$. The dotted lines are the three terms $n = 1, 2, 3$. The red solid line is the total potential obtained as the sum of the three. The potential has an absolute minimum at $\phi = 180^\circ$ and a local minimum at $\phi = 0$. Right: Examples of cis-trans isomerism for the diazene molecule (N_2H_2). In the cis-state the dihedral angle is $\phi = 0$ and in the trans-state is $\phi = 180^\circ$ (from Wikipedia).

Bonded interactions are effective potentials that encode quantum mechanical behavior into classical MD simulations. These classical potential allow fast simulation by avoiding time consuming quantum calculations.

3.2 Non-Bonded Interactions

In Molecular Dynamics (MD), non-bonded interactions describe the physical forces between atoms not directly connected by chemical bonds. These interactions originate from electromagnetic forces at the atomic and molecular level, and they are crucial for capturing intermolecular behavior, macromolecular structure, and condensed-phase properties (e.g., folding, aggregation, solvation).

- **Lennard-Jones potential:** This is typically of the form

$$V_{LJ} = \sum_{i < j} 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]$$

The potential has a short range repulsive term $\sim 1/r^{12}$ and a long range attractive term $\sim 1/r^6$. The origin of attractive $\sim 1/r^6$ force is quantum-mechanical and due to fluctuating dipoles (van der Waals interactions). The choice of a power $\sim 1/r^{12}$ at short distances has no theoretical justification. Its origin is related to the Pauli principle: when the electronic clouds surrounding the atoms start to overlap, the energy of the system increases abruptly. The exponent $\sim 1/r^{12}$ was chosen exclusively because of ease of computation (it is the square of the attractive

Name	Type ^(*)	Common Use	Characteristics
AMBER	AA	Proteins, DNA	Empirical, additive
CHARMM	AA	Biomolecules	Detailed dihedral terms
OPLS	AA	Organic molecules, drugs	Optimized non-bonded parameters
GROMOS	AA	Biopolymers	Coarse-grained variants exist
ReaxFF	AA	Chemical reactions	Bond breaking/forming
Martini	CG	Biological systems	Reduced resolution models
SIRAH	CG	Proteins, nucleic acids, lipids	Explicit electrostatics handling

Table 1: Popular force fields and their typical applications.

(*): AA=All-Atom, CG=Coarse-Grained.

term). The Lennard-Jones potential approximates very well interaction in rare gases as Ar or Kr whose interactions are dominated by van der Waals forces and electrons are in closed shells³. The Lennard-Jones potential has also played a central role in the development of molecular dynamics methods and has been widely used to investigate fundamental issues as phase transitions, the effect of surfaces, small clusters etc. Usually infinitely ranged potentials are truncated to a finite radius R_c so that one approximates the LJ potential with:

$$\hat{V}_{LJ}(r) = \begin{cases} V_{LJ}(r) - V_{LJ}(R_c) & \text{if } r \leq R_c \\ 0 & \text{if } r > R_c \end{cases} \quad (36)$$

The term $V_{LJ}(R_c)$ is a small constant shift to avoid jumps in the potential which would lead to infinite forces.

- **Electrostatics (Coulomb):** If electrostatic charges are present, one should consider the appropriate Coulomb potentials

$$V_{elec.}(r) = \frac{Q_1 Q_2}{4\pi\epsilon_0 r} \quad (37)$$

where Q_1, Q_2 are the charges and ϵ_0 the permittivity in free space. Note that the Coulomb potential has a much slower decay ($\sim 1/r$) at large distances compared to the Lennard-Jones case ($\sim 1/r^6$). Truncations as that given in Eq. (36) are not applicable to the Coulomb potential case. However, methods like the Ewald summation scheme (for more details see [1]) have been devised to deal with the long range forces arising from Coulomb potentials.

³Note that in lighter noble gases as He and Ne quantum mechanical effects are usually dominant close to their liquid-gas transition point. The molecular dynamics methods we discussed here apply exclusively to classical systems. To know whether quantum mechanical effects are of importance in a system one can compare the de Broglie wavelength $\Lambda = h/\sqrt{2\pi m k_B T}$ (h is the Planck's constant) to the typical interatomic distance a . Quantum effects dominate if $\Lambda \gg a$, i.e. for light atoms and molecules and at low temperatures.

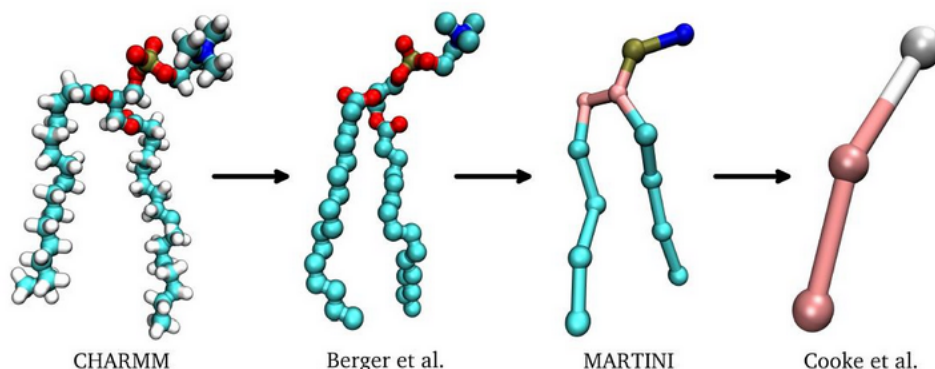


Figure 3: Different representations of a lipid molecule from all-atom (left) to increasing levels of coarse-graining (right).

3.3 All-atom and coarse-grained models

Force field parameters are typically derived from quantum chemical calculations, experimental data (e.g., bond lengths, angles ...) and from fitting to reproduce thermodynamic or structural properties. Table 1 shows some examples of force fields currently used and their properties. One distinguishes between all-atom (AA) and coarse-grained (CG) approaches.

In all-atom MD simulations, every atom in the system – including hydrogens – is explicitly modeled. This high-resolution representation captures detailed interatomic interactions such as van der Waals forces, hydrogen bonds, and electrostatics with high fidelity. Force fields like AMBER, CHARMM, or OPLS define the parameters governing these interactions, which are often derived from quantum mechanical calculations and experimental data. The all-atom approach is very accurate: it can capture fine molecular details, making it suitable for tasks like investigating protein folding, ligand binding, conformational transitions, or enzymatic mechanisms. However, this accuracy comes at a cost: AA simulations are computationally intensive and typically limited to systems containing up to a few hundred thousand atoms and timescales ranging from nanoseconds to microseconds.

In contrast, coarse-grained MD simulations reduce the level of detail by grouping several atoms—typically 3 to 5 heavy atoms and associated hydrogens—into single interaction centers or "beads." This drastically reduces the number of particles in the system and smooths out high-frequency motions, allowing for larger time steps and longer trajectories. Force fields such as MARTINI are widely used for CG simulations, with parameters often tuned to reproduce either the results of higher-resolution simulations or experimental observables, such as partition coefficients or radial distribution functions. CG simulations are well suited for studying large-scale or long-time processes, such as membrane fusion, protein aggregation, and the assembly of viral capsids. With lower computational demands, they can simulate systems on the order of millions of particles for milliseconds or longer.

4 Initialization

A MD simulation begins with giving a set of initial positions and velocities to the particles $(\vec{r}_1(0), \vec{r}_2(0), \dots, \vec{r}_N(0), \vec{v}_1(0), \vec{v}_2(0), \dots)$. The positions can be initialized by putting for instance the particles in some lattice points. The velocities can be selected from some distribution. For instance every velocity component could be taken uniformly from the interval $[-0.5v_0, 0.5v_0]$, where v_0 is some velocity scale, **or from the Maxwell velocity distribution from equilibrium statistical mechanics**

$$p(v_x) \propto e^{-mv_x^2/2k_B T} \quad (38)$$

One imposes the condition that the total momentum vanishes. So if the initial selection yields

$$\vec{P}_{\text{TOT}} = \sum_{i=1}^N m_i \vec{v}_i(0) \neq 0 \quad (39)$$

we can subtract from all momenta a component

$$\vec{v}_i(0) \rightarrow \vec{v}_i(0) - \frac{\vec{P}_{\text{TOT}}}{m_i N} \quad (40)$$

One important test that one needs to perform to check the stability of MD simulation is the conservation of the total energy. The energy is a sum of kinetic K and potential V energies ($E = K + V$). Both K and V fluctuate during the simulation, but their sum should be constant⁴. **Because the initial conformation of the system is rarely representative of a true equilibrium state, it is necessary to allow the simulation to evolve for a period of time before collecting data. This equilibration phase enables the system to relax from its initial configuration and to adjust its structural and dynamical variables toward their target values. During equilibration the overall potential and kinetic energies stabilize. Only once the system has reached a stable thermodynamic state, with fluctuations characteristic of equilibrium, can the production phase begin. In this phase, trajectories are recorded for subsequent analysis, and reliable estimates of physical properties can be extracted without contamination from transient, non-equilibrium artifacts.**

5 Measured quantities

5.1 Temperature

For a system in equilibrium at some given temperature T , the theorem of equipartition states that the average kinetic energy per particle is related to T as

$$\frac{m}{2} \langle v^2 \rangle = \frac{3}{2} k_B T \quad (41)$$

⁴Actually only approximately constant, because of discretization errors accumulating during the run, due to a finite Δt

One can then compute the temperature in a MD simulation from the total kinetic energy of the system using the relation⁵

$$T_K = \frac{1}{3Nk_B} \sum_i m_i \vec{v}_i^2 \quad (42)$$

Note that as the kinetic energy fluctuates in time, the previous relation defines a so-called “instantaneous temperature” which is also a time fluctuating quantity. Usually if one simulates a sufficiently large number of particles T_K (after some equilibration time) converges to a roughly constant values as fluctuations for large N are small⁶.

5.2 Diffusion coefficient

The diffusion coefficient can be computed from the mean squared displacement of the particles as

$$D = \lim_{t \rightarrow \infty} \frac{\langle [\vec{r}(t) - \vec{r}(0)]^2 \rangle}{6t} \quad (43)$$

Alternatively one can use the Green-Kubo relations which relates it to the integral of the velocity autocorrelation function:

$$D = \frac{1}{3} \lim_{t \rightarrow \infty} \int_0^t \langle \vec{v}(\tau) \cdot \vec{v}(0) \rangle d\tau \quad (44)$$

5.3 Pressure

Usually pressure is calculated from the virial theorem

$$PV = Nk_B T + \frac{1}{3} \sum_{i=1}^N \langle \vec{r}_i \cdot \vec{F}_i \rangle \quad (45)$$

To prove this relation one starts from computing the time average of

$$W = \sum_{i=1}^N \vec{r}_i \cdot \vec{F}_i^{TOT} \quad (46)$$

where \vec{F}_i^{TOT} is the total force acting on the i -th particle. Using the Newton's equation ($\vec{F}_i^{TOT} = m_i \ddot{\vec{r}}_i$) and an integration by parts one finds

$$\langle W \rangle = \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t \sum_{i=1}^N \vec{r}_i \cdot \vec{F}_i^{TOT} d\tau = \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t \sum_{i=1}^N \vec{r}_i \cdot m_i \ddot{\vec{r}}_i = - \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t \sum_{i=1}^N m_i \left| \dot{\vec{r}}_i \right|^2 d\tau \quad (47)$$

⁵We use the subscript K to stress that this temperature is defined from the Kinetic energy K of the system

⁶Fluctuations of T_K in equilibrium are discussed in Section 7

So that the average of W is equal to twice the total kinetic energy of the system, hence using the equipartition theorem

$$\langle W \rangle = -3Nk_B T \quad (48)$$

Note that the total force has two components:

$$\vec{F}_i^{TOT} = \vec{F}_i + \vec{F}_i^{EXT} \quad (49)$$

the first component, \vec{F}_i , is due to the interaction with all other particles in the system, the second component, \vec{F}_i^{EXT} , arises from interactions with the walls of the container.

We prove next that

$$\left\langle \sum_{i=1}^N \vec{r}_i \cdot \vec{F}_i^{EXT} \right\rangle = -3PV \quad (50)$$

where P is the pressure and V the volume of the container.

To show this consider a container of the form of a rectangular parallelepiped with sides of lengths L_x , L_y and L_z . Setting the origin of the axes in the edge as indicated in Fig. 4 one finds that the average in Eq. (50) gets three contribution from the three dashed sides of the container. The force is perpendicular to the sides. For the side perpendicular to the x -axis the average force is PL_yL_z (recall the pressure equals the force per unit area), whereas the position of the particles hitting the side is $\vec{r}_i = (L_x, y_i, z_i)$. The side perpendicular to the x -axis contributes to the average of Eq. (50) with a term $-PL_yL_zL_x = -PV$. The factor 3 in Eq. (50) comes from the contributions from the two other sides perpendicular to the y - and z -axes.

Combining Eqs. (46), (48), (49) and (50) we obtain the virial theorem of Eq. (45).

If the interparticle forces arise from a pair potential $V(r)$ where r is the distance between the pairs, then the virial theorem can be written as follows:

$$PV = Nk_B T - \frac{1}{3} \sum_{i < j} \left\langle r_{ij} \frac{dV(r_{ij})}{dr_{ij}} \right\rangle \quad (51)$$

where the sum is extended to all pairs of particles. The proof is left to the reader.

6 Constraints

In simulations of molecular systems one has multiple timescales in the problem: short timescales are due, for instance, to vibrations of bond lengths around their equilibrium values, long timescales involve the dynamics of the whole molecule. It is customary to take the bonds as being constrained to have fixed length. In this way one ignores short timescales and focuses on slower dynamics phenomena. Ignoring short timescales means also that one can take longer time steps Δt , which leads to a longer time sampling of the physical quantities and thus more efficient simulations. In classical mechanics, constraints are introduced through the Lagrangian or Hamiltonian formalisms. The

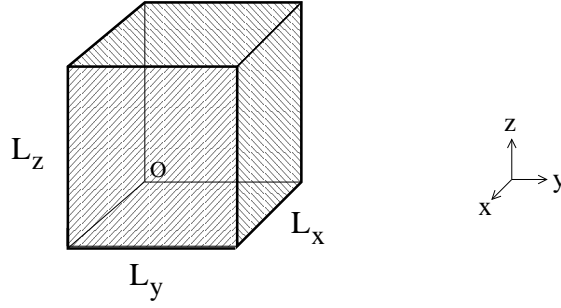


Figure 4: The contribution of the average of the left hand side of Eq. (50) equals to $-PV$ for each of the three dashed sides in the figure.

constraint imposes an additional force to the system⁷. A constraint of fixed bond length b between atoms 1 and 2 may be written as follows

$$\sigma(\vec{r}_1, \vec{r}_2) = (\vec{r}_1 - \vec{r}_2)^2 - b^2 = 0 \quad (52)$$

and the associated force to the i -th particle is $\vec{G}_i = -\lambda \nabla_i \sigma$, where λ is a so-called Lagrange multiplier. Its value can be fixed using Lagrangian formalism of classical mechanics. Here we show how λ can be fixed in the context of the integration scheme of an MD simulation. For simplicity we restrict ourselves to a particle constrained to remain at a fixed distance d from the origin, with constraint:

$$\sigma(\vec{r}) = \vec{r}^2 - d^2 \quad (53)$$

For simplicity, we restrict ourselves to the Verlet algorithm, although it is possible to extend the discussion of constraint to the velocity Verlet or other integration schemes. We assume that the positions at time steps $t - \Delta t$ and t satisfy the constraint thus $\sigma(\vec{r}(t - \Delta t)) = \sigma(\vec{r}(t)) = 0$. The Verlet algorithm gives:

$$\vec{r}(t + \Delta t) = 2\vec{r}(t) - \vec{r}(t - \Delta t) - \lambda \vec{\nabla} \sigma(t) \Delta t^2 = \vec{r}_u(t + \Delta t) - \frac{\lambda}{m} \vec{r}(t) \Delta t^2 \quad (54)$$

where we have introduced the unconstrained evolution $\vec{r}_u(t + \Delta t) \equiv 2\vec{r}(t) - \vec{r}(t - \Delta t)$. The Lagrange multiplier λ is fixed from the requirement that the position at time $t + \Delta t$ satisfy the constraints:

$$\sigma(\vec{r}(t + \Delta t)) = \vec{r}_u^2(t + \Delta t) - 2\frac{\lambda \Delta t^2}{m} \vec{r}(t) \cdot \vec{r}_u(t + \Delta t) + \frac{\lambda^2 \Delta t^4}{m^2} \vec{r}^2(t) - d^2 = 0 \quad (55)$$

which we obtained by squaring the right hand side of Eq. (54). As the constraint is satisfied at times t then $\vec{r}^2(t) = d^2$. We then obtain from (55) the following second order equation for λ :

$$\lambda^2 \frac{d^2 \Delta t^4}{m^2} - 2\lambda \frac{\Delta t^2}{m} \vec{r}(t) \cdot \vec{r}_u(t + \Delta t) + \vec{r}_u^2(t + \Delta t) - d^2 = 0 \quad (56)$$

⁷A known example is the centripetal force.

We plug then the value of λ which is solution of this equation into Eq. (54), so that the constraint is exactly satisfied. This is however a rather simple case of a single particle with one constraint. In the most general case we will have N particles and l constraints the Verlet algorithm will take the form:

$$\vec{r}_i(t + \Delta t) = \vec{r}_{u,i}(t + \Delta t) - \frac{\Delta t^2}{m} \sum_{k=1}^l \lambda_k \vec{\nabla}_i \sigma_k(t) \quad (57)$$

where $\vec{r}_{u,i}$ is the unconstrained position, where σ_k ($k = 1, 2, \dots, l$) denote the constraints⁸ and λ_k are the Lagrange multiplier which remain to be fixed. Following the same reasoning as done above for a single constraint we would obtain a set of coupled quadratic equations in the λ 's. Differently from the single constraint case there is no analytical solution. In the general case, several different methods have been devised to fix the values of the Lagrange multipliers in an approximate way. The discussion of these methods goes beyond the purposes of this course.

7 Simulations at constant temperature

The MD simulations discussed so far are performed in the so-called microcanonical ensemble: the number of particles (N), volume (V) and energy (E) are fixed. For this reason it is customary to indicate the microcanonical as the NVE ensemble. This setup is quite different from experimental conditions in which the temperature is fixed.

When the temperature is fixed the total energy is not conserved anymore, and in equilibrium it is distributed according to

$$p(E) = \frac{e^{-E/k_B T}}{Z} \quad (58)$$

where k_B is the Boltzmann's constant and Z is the partition function

$$Z = \int d\Gamma e^{-E/k_B T} \quad (59)$$

where the integral is extended to all position and momenta of the system ($d\Gamma = dr_1 dr_2 \dots dr_N dp_1 \dots dp_N$, with N the number of particles in the system). Considering that E is a sum of kinetic and potential energies

$$E = K + V = \sum_{i=1}^N \frac{p_i^2}{2m} + V(r_1, r_2 \dots r_N) \quad (60)$$

If we integrate out over all positions of the particles in Eq. (58) we find that the probability distribution of the velocity of a single particle is

$$p(\vec{v}) \propto \exp\left(-\frac{m\vec{v}^2}{2k_B T}\right) \quad (61)$$

⁸We write $\sigma_k(t)$ as a shorthand notation for $\sigma_k(\vec{r}_1(t), \dots, \vec{r}_N(t))$. $\vec{\nabla}_i$ is the gradient of σ_k with respect to the position of the i -th particles. For constraints on bond lengths σ involves only pairs of particles.

where we used $p = mv$. In Section 5.1 we have introduced the instantaneous temperature T_K from the average total kinetic energy. A simple calculation shows that the relative variance of T_K in the canonical ensemble is given by [1]

$$\frac{\sigma_{T_K}^2}{\langle T_K \rangle^2} \equiv \frac{\langle T_K^2 \rangle - \langle T_K \rangle^2}{\langle T_K \rangle^2} = \frac{2}{3N} \quad (62)$$

where the averages are taken according to the canonical ensemble. The instantaneous temperature defined through Eq. (42) in the canonical NVT ensemble fluctuates.

In the next sections we discuss about different ways of “fixing” the temperature in a MD simulation. These methods are referred to as *thermostats*. Only one of the methods presented (the Nosé-Hoover thermostat discussed in Sec. 7.4) reproduces the fluctuations of the canonical ensemble.

7.1 Velocity rescaling

The simplest thermostat consists in a rescaling of all the velocities after each integration step. If we obtain from an integration scheme as the velocity Verlet $\vec{v}_i(t)$ and $\vec{r}_i(t)$ we rescale all velocities by a factor λ as follows:

$$\vec{v}_i'(t) = \lambda \vec{v}_i(t) \quad (63)$$

while the positions are unaffected. We proceed with the integration of the equations of motion at $t + \Delta t$ using these new velocities. The factor λ is obtained from

$$\lambda = \sqrt{\frac{T_0}{T_K(t)}} \quad (64)$$

where $T_K(t)$ is the instantaneous temperature defined by Eq. (42) and T_0 is the desired temperature. The velocity rescaling fixes $T_K(t)$ to a constant value T_0 at each integration step, therefore it does not reproduce the fluctuations expected from the canonical ensemble (Eq. (62)).

7.2 Berendsen thermostat

The Berendsen thermostat is also based on some velocity rescaling. However the rescaling is “softer”, compared to that of Eq. (64). The rescaling factor is given by:

$$\lambda^2 = 1 + \frac{\Delta t}{\tau} \frac{T_0 - T_K(t)}{T_K(t)} \quad (65)$$

where τ is a characteristic time to be fixed at the beginning of the simulation. Note that the smallest allowed value $\tau = \Delta t$ yields the velocity rescaling method of Section 7.1. If $\tau \rightarrow \infty$ then no rescaling is done as $\lambda = 1$. For finite and not too small τ the rescaling is $\lambda = 1 + \mathcal{O}(\Delta t)$. If $T_K(t) > T_0$ then $\lambda < 1$, whereas if $T_K(t) < T_0$ then $\lambda > 1$ so that the velocities are increased or decreased according to the value of the instantaneous temperature. The system reaches the desired temperature T_0 only after a characteristic time of the order τ . As the method of Section 7.1, the Berendsen thermostat does not reproduce the canonical distribution of energies.

7.3 Andersen thermostat

In the Andersen thermostat some particles undergo random “collisions” with external degrees of freedom. When they do so their velocity is changed and taken from the Gaussian distribution of Eq. (61). If the collisions are sufficiently frequent this procedure induces a canonical distribution of the velocities. In practice the thermostat is implemented as follows. First a collision frequency ν is chosen. All velocities and positions are updated according to the desired scheme (for instance the velocity Verlet). One then runs through all the N particles of the system and select for each of them a random number uniformly distributed in $[0, 1[$. Let $0 \leq r_i < 1$ the random number corresponding to the i -th particle. If $r_i < \nu\Delta t$ the velocity of the i -th particle is replaced from a value selected from the distribution of Eq. (61). Because of the random update to the velocities, the Andersen thermostat is an example of a MD algorithm in which the deterministic evolution is combined with a stochastic update.

7.4 Nosé-Hoover thermostat

In this scheme the system is brought in contact with a “thermal bath”. The system plus bath form a closed universe, so their total energy is conserved. The system however exchanges energy with the bath. The net result of this exchange is that the energy of the system is distributed according to the canonical distribution.

Differently from the Andersen thermostat the Nosé-Hoover thermostat is deterministic. Time evolution is described by the following equations of motion:

$$\ddot{\vec{r}}_i = \frac{\vec{F}_i}{m_i} - \gamma \dot{\vec{r}}_i \quad (66)$$

$$\dot{\gamma} = \frac{1}{Q} \left(\sum_i \frac{p_i^2}{m_i} - 3Nk_B T_0 \right) \quad (67)$$

Equation (66) is the Newton equation with an additional friction term with a time-dependent “friction” coefficient equal to γ , whose time evolution is described by Eq. (67). The friction coefficient γ can be either positive or negative in the course of time, for this reason it cannot be considered as a real friction coefficient. If γ is positive energy is taken from the system, whereas if γ is negative energy is given to the system. The quantity between parenthesis becomes twice the kinetic energy of the system minus $3Nk_B T_0$. The form of Equation (67) is such that γ tends to a value such that the quantity between parenthesis vanishes so that the kinetic energy is forced to be close to $\frac{3}{2}Nk_B T_0$. Fluctuations around this value are however possible. It can be rigorously shown that the Nosé-Hoover thermostat reproduces the canonical fluctuation exactly [1]. The Equations (66) and (67) follow from an extended Hamiltonian in which system and bath degrees of freedom are coupled.

8 Langevin dynamics

The Langevin equation is a stochastic differential equation which describes a system coupled to fast degrees of freedom, where the latter are not explicitly taken into account, but implicitly by means of a random force. The typical example is a molecule immersed in a solvent (like water), where the molecule has much larger mass compared the solvent molecules and therefore moves much faster. The solvent molecules are in constant motion due to thermal agitation, they collide with the large particle and exchange energy with it. If we are not interested in the motion of the solvent molecules (fast degrees of freedom), but only in the large particle (slow degrees of freedom), we may assume that the solvent molecules exert some random forces on the latter. Collisions occur at a characteristic time $\tau_{coll.}$. The Langevin equation description applies at times $t \gg \tau_{coll.}$, when a very large number of collisions have occurred.

In the one dimensional case the Langevin equation takes the form:

$$m\dot{v} = F - m\gamma v + f_R \quad (68)$$

where m is the particle mass, v its velocity, F is a deterministic force applied to the particle, γ the friction coefficient and f_R a random force. In absence of friction and random forces ($\gamma = 0$ and $f_R = 0$) Eq. (68) reduces to the Newton's equation of motion. The random force is assumed to have the following properties:

$$\langle f_R(t) \rangle = 0 \quad (69)$$

$$\langle f_R(t)f_R(t') \rangle = 2A\delta(t - t') \quad (70)$$

where $\langle \rangle$ denotes the average value and A is a constant to be determined. The δ -function indicates that the random forces at different times are uncorrelated, which should happen if $t \gg \tau_{coll.}$. The parameter A is related to the characteristic amplitude of the random force.

Consider now the case $F = 0$. The equation (68) can be integrated exactly. Given v_0 the initial velocity we find:

$$v(t) = v_0 e^{-\gamma t} + \frac{1}{m} e^{-\gamma t} \int_0^t e^{\gamma s} f_R(s) ds \quad (71)$$

Which implies that the average velocity vanishes asymptotically as

$$\langle v(t) \rangle = v_0 e^{-\gamma t} \quad (72)$$

where $\tau = 1/\gamma$ is a characteristic relaxation time. One can compute the fluctuation around the average:

$$\left\langle (v(t) - v_0 e^{-\gamma t})^2 \right\rangle = \frac{A}{m^2 \gamma} (1 - e^{-2\gamma t}) \quad (73)$$

At times $t \gg 1/\gamma$ the system relaxes to equilibrium and the equipartition theorem⁹ holds:

$$m \langle v(t)^2 \rangle = k_B T \quad (74)$$

⁹The equipartition theorem states that the average kinetic energy per particle in a three dimensional system in equilibrium is $\varepsilon_{kin} = 3k_B T/2$. In one dimension (the case considered here) $\varepsilon_{kin} = k_B T/2$.

which implies:

$$A = m\gamma k_B T \quad (75)$$

We can integrate equation (71) further to get the position

$$x(t) = x_0 + \int_0^t v(s) ds \quad (76)$$

to obtain the mean square displacement

$$\langle (x(t) - x_0)^2 \rangle = \int_0^t ds ds' \langle v(s)v(s') \rangle \quad (77)$$

For the velocity-velocity correlator we find from (71):

$$\langle v(s)v(s') \rangle = \left(v_0^2 - \frac{A}{m^2\gamma} \right) e^{-\gamma(s+s')} + \frac{A}{m^2\gamma} e^{-\gamma|s-s'|} \quad (78)$$

which substituted into Eq. (77) gives

$$\langle (x(t) - x_0)^2 \rangle = \left(v_0^2 - \frac{A}{m^2\gamma} \right) \left(\frac{1 - e^{-\gamma t}}{\gamma} \right)^2 + \frac{2A}{m^2\gamma} \left(t - \frac{1 - e^{-\gamma t}}{\gamma} \right) \quad (79)$$

This expression has two interesting limiting behaviors. At short times $t \ll 1/\gamma$ one finds:

$$\langle (x(t) - x_0)^2 \rangle \approx v_0^2 t^2 \quad (80)$$

which is the ballistic motion, i.e. the particle moves with a constant speed v_0 . At much longer times $t \gg 1/\gamma$ one has

$$\langle (x(t) - x_0)^2 \rangle \approx \frac{2A}{m^2\gamma^2} t \quad (81)$$

which describes a diffusive behavior, with the mean squared displacement increasing linearly with time. The prefactor is $2D$ with D the diffusion constant which then takes the form:

$$D = \frac{k_B T}{m\gamma} \quad (82)$$

which is known as the Einstein relation. Having summarized the basic properties of the Langevin equation we present next an algorithm which is used for its numerical integration.

8.1 Numerical integration of the Langevin equation

We show now how the Langevin equation can be discretized to implement it in molecular dynamics simulations. From the analysis of the previous section we have fixed the amplitude A and we can write the equation in the following form

$$m\ddot{r}(t) = F(r(t)) - m\gamma\dot{r}(t) + \sqrt{2m\gamma k_B T}\eta(t) \quad (83)$$

with $\langle \eta(t)\eta(t') \rangle = \delta(t' - t)$. Although $\eta(t)$ is not differentiable, we can define integrals of these processes, and therefore, it is useful to introduce a process $w(t)$, known as a *Wiener process*, such that $\eta(t) = dw/dt$. We can derive some properties of $w(t)$ if we assume a small time interval Δt .

One of the main properties of the Wiener process is the following:

$$\langle w(s)w(s') \rangle = \int_0^s \int_0^{s'} \langle \eta(t)\eta(t') \rangle dt dt' = \int_0^s \int_0^{s'} \delta(t' - t) dt dt' = \min(s, s') \quad (84)$$

(to prove the last step one can consider separately the two cases $s > s'$ and $s' > s$.) Using the previous relation we can show that

$$\langle (w(t + \Delta t) - w(t))^2 \rangle = \langle w^2(t + \Delta t) + w^2(t) - 2w(t + \Delta t)w(t) \rangle = \Delta t \quad (85)$$

We can generate the random variable $w(t + \Delta t) - w(t)$ using at any time step a gaussian distributed random number ξ with zero mean and unit variance (i.e. $\langle \xi \rangle = 0$ and $\langle \xi^2 \rangle = 1$) as follows:

$$w(t + \Delta t) - w(t) = \sqrt{\Delta t} \xi \quad (86)$$

From this relation we can easily derive a first order integrator of the Langevin equation (83) in the overdamped limit (i.e. the high friction limit in which the inertial term $m\ddot{r}$ is neglected). The first order discretization of the derivatives gives:

$$m\gamma (r(t + \Delta t) - r(t)) = F(r(t))\Delta t + \sqrt{2mk_B T} [w(t + \Delta t) - w(t)] \quad (87)$$

and using (86) we get the

First order integrator of the overdamped Langevin equation

$$r(t + \Delta t) = r(t) + \frac{F(r(t))}{m\gamma} \Delta t + \sqrt{\frac{2k_B T}{m\gamma}} \xi \sqrt{\Delta t} \quad (88)$$

In practice at any time step one needs to generate a random number ξ with zero mean and unit variance¹⁰. The peculiar feature of this integrator is the presence of a square root of the time step Δt . This factor is due to the property (86), which has a clear physical origin. The Wiener process is the integral of the random noise $w(\tau) = \int_0^\tau \eta(t)dt$. We can view $\eta(t)$ as the steps of a random walk and $w(\tau)$ is then the sum of all increments i.e. the total distance covered by the walker after a time τ . Due to the diffusive nature of random walks this distance scales as $\sqrt{\tau}$.

Having discussed the main features of the integrator in the simple overdamped case we are ready to present a more detailed integrator which takes the inertial term into

¹⁰In Matlab you can use the command `randn(N,1)` to generate a vector with N random numbers selected from a gaussian distribution with zero mean and unit variance.

account and it is accurate to order Δt^2 . The algorithm has been derived by Vanden-Eijnden and Ciccotti [4]. We express the Langevin equation in the following differential form:

$$dr(t) = v(t)dt \quad (89)$$

$$dv(t) = f(r(t))dt - \gamma v(t)dt + \sigma dw(t) \quad (90)$$

where $\sigma = \sqrt{2k_B T \gamma / m}$ and $f(r) = F(r)/m$ and $w(t)$ is the Wiener process. This expression can be easily expanded to a system of n particles in three dimensions. Here, for simplicity, we focus on a single particle in one dimension.

We start by integrating Eqs. (89) and (90) from t to $t + \Delta t$:

$$r(t + \Delta t) = r(t) + \int_t^{t+\Delta t} v(s)ds \quad (91)$$

$$v(t + \Delta t) = v(t) + \int_t^{t+\Delta t} f(r(s))ds - \gamma \int_t^{t+\Delta t} v(s)ds + \sigma[w(t + \Delta t) - w(t)] \quad (92)$$

Note that these contains integrals in v and f which produce terms of the order Δt and higher in the discretization. We start from the integral in the velocity for which Eq. (92) can be used to lowest order:

$$v(s) \approx v(t) + (s - t)f(r(t)) - (s - t)\gamma v(t) + \sigma[w(s) - w(t)] \quad (93)$$

where $t \leq s \leq t + \Delta t$. Integrating the previous result from t to $t + \Delta t$ we get:

$$\int_t^{t+\Delta t} v(s) ds = \Delta t v(t) + C(t) \quad (94)$$

where we have defined

$$C(t) \equiv \frac{\Delta t^2}{2}[f(r(t)) - \gamma v(t)] + \sigma \int_t^{t+\Delta t} [w(s) - w(t)]ds \quad (95)$$

This expression can be used as approximant of the integrals of the velocity on the Eqs. (91) and (92).

To approximate the time integral of the force appearing in equation (92) we proceed in a similar manner. Using the relation

$$\frac{df}{dt} = \frac{\partial f}{\partial r} \dot{r} = \frac{\partial f}{\partial r} v \quad (96)$$

we obtain:

$$f(r(s)) = f(r(t)) + \int_t^s v(y)f'(r(y))dy \approx f(r(t)) + (s - t)v(t)f'(r(t)) \quad (97)$$

Again we integrate this equation from t to $t + \Delta t$ and get

$$\int_t^{t+\Delta t} f(r(s)) ds = \Delta t f(r(t)) + \frac{\Delta t^2}{2}v(t)f'(r(t)) = \Delta t \frac{f(r(t + \Delta t)) + f(r(t))}{2} \quad (98)$$

where the last step is performed to eliminate the inconvenient derivative of the force using the following relation:

$$f(r(t + \Delta t)) = f(r(t)) + f'(r(t))(r(t + \Delta t) - r(t)) = f(r(t)) + f'(r(t))v(t)\Delta t \quad (99)$$

For the computation of the term $w(t + \Delta t) - w(t)$ in Eq. (92) we use again (86). In order to end the calculation we still need to compute $C(t)$ in Eq. (95), which contains integral of the difference between two Wiener functions. We note that using (84) one can easily prove that:

$$\left\langle (w(t + \Delta t) - w(t)) \int_t^{t+\Delta t} ds' (w(s') - w(t)) \right\rangle = \frac{\Delta t^2}{2} \quad (100)$$

$$\left\langle \int_t^{t+\Delta t} ds (w(s) - w(t)) \int_t^{t+\Delta t} ds' (w(s') - w(t)) \right\rangle = \frac{\Delta t^3}{3} \quad (101)$$

which can be viewed as higher order counterparts of Eq. (85). Using the same strategy as for the first order integrator we see that Eq. (101) can be fulfilled if:

$$\int_t^{t+\Delta t} ds (w(s) - w(t)) = \Delta t^{3/2} \eta \quad (102)$$

with η a random number with the properties $\langle \eta \rangle = 0$ and $\langle \eta^2 \rangle = 1/3$. Plugging in (102) and (86) in Eq. (100) we find $\langle \xi \eta \rangle = \frac{1}{2}$, hence the two random numbers are correlated. To solve this issue in practice we can decompose η into two uncorrelated random numbers as follows:

$$\eta = a\xi + b\theta \quad (103)$$

with $\langle \xi \theta \rangle = 0$ and $\langle \theta^2 \rangle = 1$. The coefficients a and b can be determined by imposing $\langle \xi \eta \rangle = \frac{1}{2}$ and $\langle \eta^2 \rangle = 1/3$, from which we get $a = 1/3$ and $b = 1/(2\sqrt{3})$. This implies:

$$\int_t^{t+\Delta t} ds (w(s) - w(t)) = \Delta t^{3/2} \left(\frac{\xi}{\sqrt{3}} + \frac{\theta}{2\sqrt{3}} \right) \quad (104)$$

Now plugging in (94), (98), (86) and (104) in (91) and (92) we get the:

Second order integrator of the Langevin equation

$$\begin{aligned} r(t + \Delta t) &= r(t) + \Delta t v(t) + C(t) \\ v(t + \Delta t) &= v(t) + \frac{\Delta t}{2} [f(r(t + \Delta t)) + f(r(t))] - \Delta t \gamma v(t) \\ &\quad + \sigma \sqrt{\Delta t} \xi(t) - \gamma C(t) \\ C(t) &= \frac{\Delta t^2}{2} [f(r(t)) - \gamma v(t)] + \sigma \Delta t^{3/2} \left(\frac{1}{2} \xi(t) + \frac{1}{2\sqrt{3}} \theta(t) \right) \end{aligned} \quad (105)$$

Note: The integrator reduces to the Velocity Verlet integrator if $\gamma = 0$ and $\sigma = 0$.

We are going to use this algorithm in problem 13.6 to investigate the dynamics of a particle crossing a potential barrier (see Fig. 5). The next section discusses the theory of the stochastic dynamics of barrier crossing.

9 Barrier-Crossing Problems

The transition of a system from one state into another can be generally viewed as a barrier-crossing process. In this approach, it is very common to reduce the complexity of the system, usually having many degrees of freedom, into a single parameter x called *reaction coordinate*. An appropriate choice of x should allow for a clear distinction between the two states, i.e. one should be able to know the state of the system, just by looking at the value of x .

In this section, we will calculate the rate at which a system will be crossing the energetic barrier, i.e. it will make the transition between two states. For this purpose, we will first present a phenomenological derivation of the Smoluchowski equation, which we will use to calculate the rate.

9.1 Smoluchowski Equation

Suppose we have a large ensemble of identical and non-interacting systems, placed within a solvent, which are described by a probability density function $p(x, t)$. By definition, if we choose randomly a system from that ensemble at time t , then $p(x, t)dx$ will express the probability of it having its reaction coordinate in the interval $[x, x + dx]$.¹¹ In absence of external forces, p will evolve in time according to the diffusion equation

$$\frac{\partial p}{\partial t} = D \frac{\partial^2 p}{\partial x^2}$$

where D is the so-called *diffusion coefficient*. Moreover, p must satisfy the continuity equation at all times

$$\frac{\partial p}{\partial t} + \frac{\partial j}{\partial x} = 0 \quad (106)$$

where $j = j(x, t)$ is the probability current, i.e. the rate at which the probability “flows” through x at time t .¹² By comparing those two expressions, we identify

$$j_{\text{diffusion}} = -D \frac{\partial p}{\partial x} \quad (107)$$

as the diffusion current, i.e. the current that tends to balance any inhomogeneities in p .

If we now introduce a potential energy¹³ $V(x)$, a general force $F = -dV/dx$ will act on every system, depending on its reaction coordinate x . This will give rise to an additional probability current of the form

$$j_{\text{drift}} = p v_{\text{drift}} \quad (108)$$

¹¹In order to make the notation simple, we will use $p(x, t) = p$ from now on, keeping in mind that it will, in general, be a function of both x and t .

¹²Although this may seem rather abstract, it has a more intuitive interpretation. More specifically, if one is studying a very large number N of identical and non-interacting systems, $Nj(x, t)$ will represent how many systems per unit time pass through x , i.e. they go from $x - dx$ to $x + dx$.

¹³Note here that, owing to the reduction of the degrees of freedom into a single reaction coordinate, $V(x)$ will not simply be the mechanical energy of the system, but it will represent a generalised energy, which may also contain entropic contributions etc.

where v_{drift} is the “velocity” of the probability density flow, due to the force.

As already mentioned, we are assuming that every system is placed within a solvent, which has a friction coefficient γ . In the previous section, we discussed the effect of such a solvent, for the case of a single particle. In particular, we saw that it leads to two additional terms in the equation of motion

$$m \frac{dv}{dt} = F - m\gamma v + f_R$$

where $-m\gamma v$ represents the friction force that the particle feels as it moves with velocity v through the solvent and $f_R = f_R(t)$ is the random force that mimics the collisions with the solvent particles.

In analogy with that, the drift velocity v_{drift} of the probability density will obey a similar equation

$$\mu \frac{dv_{\text{drift}}}{dt} = F - \gamma v_{\text{drift}}$$

where μ is a generic mass,¹⁴ which we have incorporated in γ . We also used the fact that the force f_R , having random orientation, has no contribution to the net drift velocity of the probability density.¹⁵ If we now take the friction coefficient to be very large, which is the so-called *overdamped limit*, it can be shown that the acceleration term becomes negligible, so that the velocity is simply proportional to the force

$$v_{\text{drift}} = \frac{F}{\gamma}$$

With this approximation, we can now rewrite the expression (108) for the drift current in the following manner

$$j_{\text{drift}} = -\frac{1}{\gamma} \frac{dV}{dx} p \quad (109)$$

Using the expressions (107) and (109) we have found, we can now write the net probability current $j = j_{\text{diffusion}} + j_{\text{drift}}$ as follows

$$j = -D \frac{\partial p}{\partial x} - \frac{1}{\gamma} \frac{dV}{dx} p \quad (110)$$

An important property can be derived from this result. More specifically, if we take the case of an equilibrium distribution, for which we know that $p = \exp(-V/k_B T)/Z$, the current (110) vanishes (see continuity equation (106)) and we obtain the *Einstein relation*

$$D = \frac{k_B T}{\gamma} = \frac{1}{\gamma \beta} \quad (111)$$

¹⁴Apart from the total mass of the system, μ will also depend on the nature of the reduction we make, when describing the whole system with a single reaction coordinate x .

¹⁵Note, however, that it is this force which gives rise to the diffusion current of equation (107). The fact that the solvent is responsible for both $j_{\text{diffusion}}$ and j_{drift} will become more apparent when we derive the Einstein relation (111), which shows that the diffusion constant is connected to the friction coefficient.

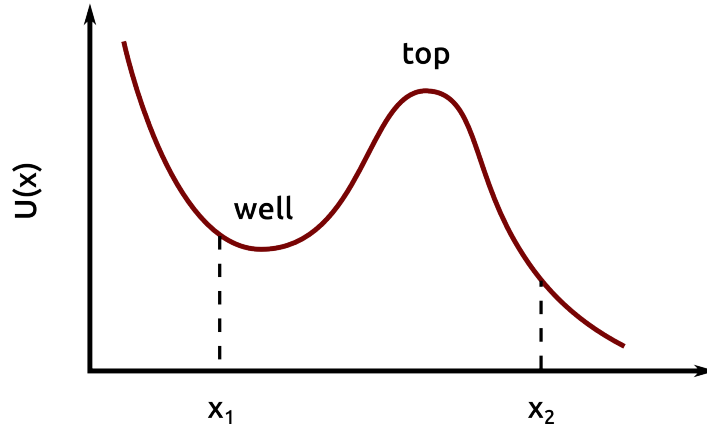


Figure 5: Energy landscape of a typical barrier-crossing problem. We assume that the system is initially inside a potential well (W) and, in order to reach a lower-energy state and thus minimise its energy, it first needs to cross an energy barrier (T). With x_1 and x_2 we denote two reference points, which we will use in order to calculate the barrier-crossing rate.

where we have introduced the inverse temperature $\beta \equiv 1/k_B T$. We can now plug this in equation (110) and rewrite it in the following compact way

$$j = -D \left(\frac{\partial p}{\partial x} + \beta \frac{dV}{dx} p \right) = -D e^{-\beta V} \frac{\partial}{\partial x} (p e^{\beta V}) \quad (112)$$

Finally, we can use this expression, in order to rewrite the continuity equation (106) and obtain the so-called

Smoluchowski equation

$$\frac{\partial p(x, t)}{\partial t} = -\frac{\partial}{\partial x} \left[-D e^{-\beta V(x)} \frac{\partial}{\partial x} (p(x, t) e^{\beta V(x)}) \right] \quad (113)$$

which gives the time evolution of the probability density.

9.2 Kramers' Theory

We will now present a simplified version of Kramers' theory, valid in the overdamped limit. Suppose that the energy $V(x)$ of the system, as a function of the reaction coordinate, has the general form of Figure 5. We consider a large ensemble of identical and non-interacting systems, which are all initially placed at the energetic well on the left. We would like to calculate the average rate at which a crossing of the barrier takes place.

Since we are only interested in the transitions that take place in one direction, i.e. from left to right, we can take periodic boundary conditions. More specifically, we will

“collect” any system that reaches the right part of the barrier (e.g. beyond x_2) and will “place” it again inside the well. This way, we can sustain a steady flow of probability from left to right, which is translated to a constant current, both in time and space. Thus, we can start from the expression (112) for the current

$$j = -De^{-\beta V} \frac{\partial}{\partial x} (pe^{\beta V})$$

and integrate it, with respect to x , bearing in mind that j is a constant

$$\frac{j}{D} \int_{x_1}^{x_2} e^{\beta V(x)} dx = p(x_1)e^{\beta V(x_1)} - p(x_2)e^{\beta V(x_2)}$$

where x_1 is somewhere within the energetic well and x_2 is at the right of the barrier, as shown in Figure 5.

In order to proceed, we will need to make some approximations. More specifically, we will assume that *the height of the barrier is large enough*, so that the probability of finding a system in the vicinity of x_1 , i.e. within the well, is much higher than finding it around x_2 . Thus, we can neglect the second term in the right-hand side of the previous expression,¹⁶ so that we will have

$$\frac{j}{D} \int_{x_1}^{x_2} e^{\beta V(x)} dx \simeq p(x_1)e^{\beta V(x_1)} \quad (114)$$

Moreover, we can approximate the integral in the left-hand side as follows

$$\int_{x_1}^{x_2} e^{\beta V(x)} dx \simeq \int_{\text{top}} e^{\beta V(x)} dx$$

since $e^{\beta V(x)}$ is much larger at the top of the barrier, compared to its sides. Note also that, owing to the large height of the barrier, every system will have enough time to equilibrate¹⁷ within the well, before it crosses the barrier. In other words, we can approximate

$$p(x_1) \simeq \frac{1}{Z_{\text{well}}} e^{-\beta V(x_1)}, \quad \text{where } Z_{\text{well}} = \int_{\text{well}} e^{-\beta V(x)} dx$$

Plugging the above results in equation (114), we obtain

$$\frac{j}{D} \simeq \left[\int_{\text{well}} e^{-\beta V(x)} dx \int_{\text{top}} e^{\beta V(x)} dx \right]^{-1} \quad (115)$$

We now need to calculate the integrals appearing in equation (115). For this purpose, let us first expand the potential energy $V(x)$ around the bottom of the well x_w

$$V(x) \simeq V_w + \frac{\omega_w^2}{2} (x - x_w)^2$$

¹⁶This is also supported by the fact that $e^{\beta V(x_1)} \gg e^{\beta V(x_2)}$.

¹⁷A system that is placed within the deep energetic well has no means to “know” that there are more states available beyond the barrier, without crossing it. If the barrier is high enough, this will require long times, which will enable the system to reach a *local equilibrium*.

where we have introduced $V_w \equiv V(x_w)$ the energy at the bottom of the well and $\omega_w^2 \equiv V''(x_w)$ its curvature. Using this, we can rewrite the first integral in (115) as follows

$$\int_{\text{well}} e^{-\beta V(x)} dx \simeq e^{-\beta V_w} \int_{\text{well}} \exp \left[-\beta \frac{\omega_w^2}{2} (x - x_w)^2 \right] dx$$

Moreover, since the integrand decays exponentially around x_w , we can expand the limits of the integration to $-\infty$ and $+\infty$ without large errors. This way, carrying out the integration¹⁸ yields the following result

$$\int_{\text{well}} e^{-\beta V(x)} dx \simeq \sqrt{\frac{2\pi}{\beta \omega_w^2}} e^{-\beta V_w}$$

Following a similar procedure for the second integral of equation (115), we find

$$\int_{\text{top}} e^{\beta V(x)} dx \simeq \sqrt{\frac{2\pi}{\beta \omega_t^2}} e^{\beta V_t}$$

where we defined $V_t \equiv V(x_t)$ the energy at the top x_t of the barrier and $\omega_t^2 = -V''(x_t)$ its curvature. Finally, we can plug these results in equation (115) and use the Einstein relation (111), $D = 1/\gamma\beta$, so as to obtain the final result

$$\boxed{j \simeq \frac{\omega_w \omega_t}{2\pi\gamma} e^{-\beta \Delta V}} \quad (116)$$

where $\Delta V \equiv V_t - V_w$ is the height of the energetic barrier.

10 Introduction to LAMMPS

Molecular dynamics simulations can also be performed using special packages. Within these packages one typically finds preimplemented interactions and integrators. Instead of having to explicitly write the code for the system of interest, you can, in a simple way, specify the system and the integrator. The package then takes care of combining the correct, lower-level parts of the code and performs the simulation. In this section the focus will be lie on the freely available Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS).¹⁹ Extensive information and a manual can be found on <http://lammps.sandia.gov>.

LAMMPS typically uses four kind of files:

¹⁸For this purpose, one needs to make a change of variable and use the expression for the Gaussian integral

$$\int_{-\infty}^{+\infty} e^{-x^2} dx = \sqrt{\pi}$$

¹⁹S. Plimpton, **Fast Parallel Algorithms for Short-Range Molecular Dynamics**, J Comp Phys, 117, 1-19 (1995)

- The *input file*. The input file specifies the details of the system and the integrator. E.g. what kind of interactions are there, what are the numeric constants used in these interactions, what kind of integration should be used, ...
- The *configuration file*. The configuration file contains the details of the initial configuration.

Note that it is not always necessary to have this file present. Using the input file it is possible to generate initial configurations, thus eliminating the need of a configuration file. (See e.g. problem 13.8.)

- The *log file*. The log file keeps track of some useful quantities like energy and temperature and also contains the warnings and errors thrown during execution.
- The *output file*. This file contains snapshots of the system on times specified by the user during the simulations.

There are different types of output files and one can have more than one output file per simulation run.

The harmonic oscillator is an excellent example to illustrate the basic working of LAMMPS. In this section the NVE and Langevin integration of two particles connected by a Hookean spring will be presented. The spring constant k is set to 2 and the equilibrium length r_0 of the spring is 0. The initial extension of the spring is 1. The input and configuration file for this system can be found at the end of this section. They should be sufficiently self-explanatory.

10.1 NVE Integration

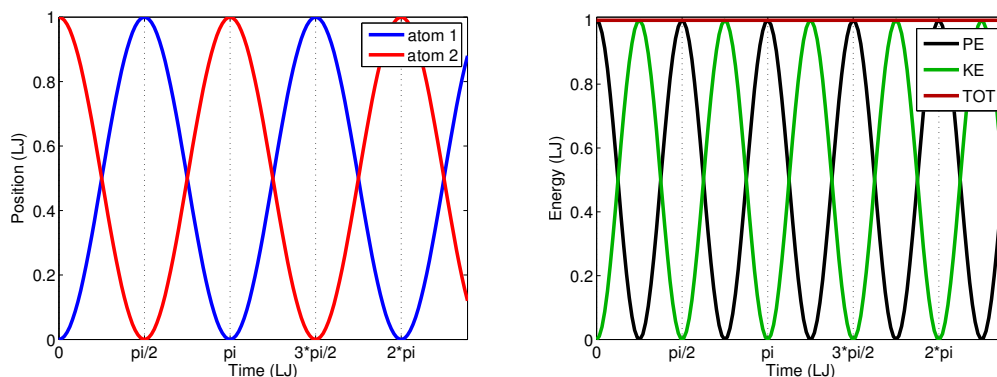


Figure 6: Left: The position of the two particles through time for NVE integration. Right: The energy of the whole system through time for NVE integration.

If we perform NVE integration of this system we know that the two particles start to oscillate. This is illustrated in 6. The period of the motion is 2π , as can be seen on the graph.

When looking at the energy, we see that it is indeed conserved, as expected for NVE integration.

10.2 Langevin Integration

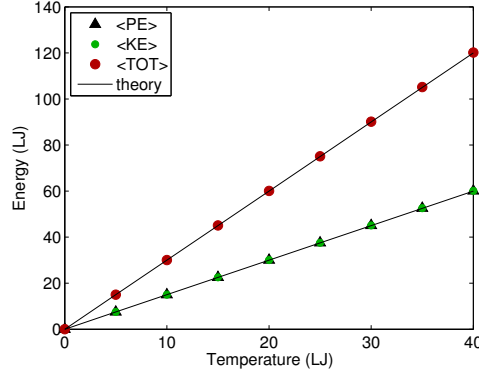


Figure 7: The average energy of the system during Langevin integration.

By turning on the Langevin integrator we are simulating a harmonic oscillator coupled to a heat bath. On 7 we see that the equipartition theorem is nicely satisfied:

$$\langle T \rangle + \langle V \rangle = \frac{3}{2}k_B T + \frac{3}{2}k_B T. \quad (117)$$

To obtain these results an average over many timesteps was taken. The first part of the simulation was discarded, since it was influenced by the initial conditions. I.e. the system was not thermalized yet.

Note: because in the code we impose *zero yes* on our Langevin integrator, we eliminate the degree of freedom the system has to move in space. This thus effectively means that we only look at the degrees of freedom of the system.

10.3 LAMMPS files

Input file

```
#####
#           This input file is used in order to simulate a harmonic           #
#           oscillator in nve and Langevin ensembles.                         #
#####

# This is the correct atom type for the case of an oscillator, having only a
# bond interactions (namely the spring between them).
atom_style      bond

# We have to turn off the sorting in order to avoid an error...
atom_modify     sort 0 0.

# Read in the initial data from the correct file.
read_data       data.harm

# We use a harmonic potential for the bond.
bond_style      harmonic

# The coefficients for the harmonic bond energy are:
# bond type (1 if no other bond types are present), k and r0.
bond_coeff       1 1. 0.

# Set the mass of all (*) atoms equal to 1.
mass * 1.0

# Set the velocity (vx vy vz) of all atoms equal to 0.
velocity all set 0.0 0.0 0.0

# Perform the integration through time.
fix nve_fix all nve

# Apply a Langevin thermostat to all atoms with initial and
# final temperature equal to 4, damping constant 100, a given seed
# and we want the net random force to be zero.
# The '154' in this expression is a seed for the RNG used by the Langevin
# integrator. The 'zero yes' command ensures that the net force in the total
# system is zero.
# UNCOMMENT for Langevin integration
#fix lan_fix all langevin 4 4 100 154 zero yes

# Let LAMMPS calculate the total kinetic energy of the system
# and store it in the compute variable c_Kenergy
compute Kenergy all ke

# Let LAMMPS calculate the total potential energy of the system
# and store it in the compute variable c_Venergy
compute Venergy all pe

# Store the energies (kinetic, potential and total) in three
# variables which can be accessed by the print command. Don't
# set E equal $K+$V, because LAMMPS will complain...
variable K equal c_Kenergy
variable V equal c_Venergy
variable E equal c_Kenergy+c_Venergy

# Store the x-position of the two particles in two variables,
# which can be used by the print command.
variable x1 equal x[1]
variable x2 equal x[2]

# Variable containing the timestep.
variable dt equal 0.005

# Variable containing the current time of the simulation,
# i.e. timestep (internally stored as step) times dt.
variable t equal step*${dt}

# Set the timestep for integration.
timestep        ${dt}

# The 'thermo' command allows you to view some basic information in the
# terminal. Every 50 integration steps this information is printed. The same
# information will also be present in the log file of the simulation.
thermo          50

# The "print" fix prints a certain string to a file at specified intervals.
# This string can contain references to variables, of which the value can
# be obtained using the dollar sign.

# print for NVE
fix energy_print all print 10 "$t $K $V $E" file energy.dat screen no title "#Timestep Kinetic Potential Total"
fix position_print all print 10 "$t ${x1} ${x2}" file position.dat screen no title "#Timestep x1 x2"

# print for Langevin
```

```
#fix energy_print all print 100 "$t $K $V $E" file energy.dat screen no title "#Timestep Kinetic Potential Total"

# The 'run' command starts the time integration over the specified number
# of timesteps.
run      1500    #NVE
#run 1500000 #Langevin
```

Note: if this file is named in.harm, it can be run with LAMMPS using the command “lammmps_daily -in in.harm”.

Note: the configuration file, which you can find below, should be named data.harm for the code to work.

Configuration file

```
#####
#           This data file is used in order to simulate a harmonic           #
#           oscillator in nve and Langevin ensembles.                         #
#####

# Specify the number of atoms. In this example two atoms make up the two ends
# of the oscillator.
2 atoms
# Specify the number of atom types. Our atoms will be identical, so there is
# only one atom type.
1 atom types
# Specify the number of bonds. There is only one bond in the system: the spring
# between the two atoms.
1 bonds
# Specify the number of bond types. There is only one bond, so we define only
# one bond type.
1 bond types

# ----- #

# Set the boundaries of the box. The commands xlo and xhi are preceeded with the
# lower bound for x and the upper bound for x respectively. An analogous thing
# goes for ylo, yhi, zlo and zhi.
-10 10 xlo xhi
-10 10 ylo yhi
-10 10 zlo zhi

# ----- #

# Specify some information about the particles. In the in.harm file we will have
# to specify the kind of atoms we want to use. In this example the type 'bond'
# is used. The documentation [http://lammps.sandia.gov/doc/read\_data.html]
# then tells us that we have to specify the following:
# atom-ID molecule-ID atom-type x y z
# Here x, y and z are the initial positions of the atom.
#
# For the bonds we have to specify:
# ID type atom1 atom2
# Here atom1 and atom2 are the bonds between which the bond is formed.
#
# IMPORTANT: there can be no comments between sections after this!!

Atoms

1 1 1 0. 0. 0.
2 1 1 1. 0. 0.

Bonds

1 1 1 2
```

11 Acknowledgements

We are very grateful to Hans Vandebroek from U. Hasselt who took care of explicitly deriving the calculations of the Langevin integrator of Section 8.1 and for typing part of that Section. Part of the text of the latest edition (2025) was written with the help of ChatGPT.

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13 Assignments

13.1 Halley's comet

We simulate here the trajectory of Halley's comet around the Sun by using the velocity Verlet algorithm

$$x(t + \Delta t) = x(t) + v(t)\Delta t + \frac{a(t)}{2}\Delta t^2 \quad (118)$$

$$v(t + \Delta t) = v(t) + [a(t) + a(t + \Delta t)] \frac{\Delta t}{2} \quad (119)$$

Consider the Sun as a fixed point with mass $M = 2 \cdot 10^{30}$ kg. The gravitational acceleration is given by

$$a = \frac{GM}{r^2} \quad (120)$$

with $G = 6.67428 \cdot 10^{-11} \frac{m^3}{kg \cdot s^2}$. Suppose that the comet starts at its aphelion²⁰ at $5.28 \cdot 10^{12}$ meter distance from the Sun, with a purely tangential speed of $9.13 \cdot 10^2$ m/s.

- Generalize the velocity Verlet algorithm to two dimensions.
- Use this algorithm to simulate the comet's trajectory (use the implementation of Eqs. (12)-(15)). Decide upon a reasonable value of Δt by using the fact that a single orbit takes many years.
- Plot the x and y component of the trajectory in time. Plot the entire trajectory in the x-y plane.
- Verify that the total (kinetic+potential) energy is conserved.
- What is the distance of the perihelion to the Sun? What is the speed there? How long does a single orbit take?

13.2 Symplectic vs.non-symplectic integrators

We compare here the performance of two MD integration schemes for a one dimensional harmonic oscillator **with Hamiltonian**

$$H = \frac{p^2}{2m} + \frac{kq^2}{2}. \quad (121)$$

The Hamilton's equations of motion are:

$$\begin{cases} \dot{p} = -\frac{\partial H}{\partial q} = -kq \\ \dot{q} = \frac{\partial H}{\partial p} = p/m \end{cases} \quad (122)$$

²⁰The farthest point in its orbit. The speed is minimal here, and perpendicular to the axis Sun-comet.

We set for convenience **for the rest of this problem** $k = m = 1$.

The first integrator (Euler integrator) we consider is non-symplectic and it is obtained from the first order expansion in Δt of the equations of motion

$$\begin{cases} p(t + \Delta t) = p(t) - q(t)\Delta t \\ q(t + \Delta t) = q(t) + p(t)\Delta t \end{cases} \quad (123)$$

The second integrator is also first order, but symplectic:

$$\begin{cases} p(t + \Delta t) = p(t) - q(t)\Delta t \\ q(t + \Delta t) = q(t) + p(t + \Delta t)\Delta t \end{cases} \quad (124)$$

Note that there is only a slight difference between the two.

- a) Express Eqs. (123) and (124) in matrix form ²¹

$$\begin{pmatrix} q \\ p \end{pmatrix}_{t+\Delta t} = M \begin{pmatrix} q \\ p \end{pmatrix}_t \quad (125)$$

and show that for Eq. (123) $\det(M) > 1$ while for Eq. (124) $\det(M) = 1$.

Symplectic integrators do not strictly conserve the Hamiltonian H , but they conserve a so-called *shadow*-Hamiltonian H' , which differs from H by terms of order Δt^m . For this reason they do not suffer from long time drift as non-symplectic integrators. Symplectic integrators are also volume preserving. The velocity Verlet scheme is a symplectic integrator (and it is of order $m = 2$). Eq. (124) defines the so-called Euler symplectic integrator of order $m = 1$.

- b) Show analytically that the symplectic integrator defined by Eq. (124) has the following constant of motion (shadow hamiltonian)

$$H' = H - \frac{pq}{2}\Delta t \quad (126)$$

- c) Take $\Delta t = 10^{-3}$ and $\Delta t = 10^{-2}$ with initial conditions $q(0) = 1$, $p(0) = 0$ and plot the solutions of Eqs. (123) and (124) up to time $T = 10$. Compare the relative errors of the two integration schemes to the exact solution of Eq. (122). Which of the two integrators is more accurate?
- d) For the same values of the parameters given above plot the value of H as a function of t up to time $T = 10$. Plot H' as well for the symplectic integrator. Which of the two integrators has a long time drift in the energy estimate?
- e) Show that (124) can be obtained from (24).

²¹ M can be viewed as the Jacobian matrix of the transformation connecting position and momenta at time t to those at time $t + \Delta t$. The fact that $\det M = 1$ tells us that the transformation is volume preserving, i.e. it does not alter the volume of the two dimensional $x - p$ phase space.

13.3 Symplectic integrators (II)

Prove Eq. 29 for generic A and B . Show that working out this relation for a one dimensional single particle system with $A = D_V$ and $B = D_T$ one generates the Velocity Verlet algorithm.

Show that $\exp(\Delta t D_T)$ and $\exp(\Delta t D_V)$ preserve the volume in phase space²². You can do this by considering the three vectors $\vec{a} \equiv (q, p)$, $\vec{b} \equiv (q + \delta q, p)$ and $\vec{c} \equiv (q, p + \delta p)$. Under the action of the two exponential operators one maps these vectors into \vec{a}' , \vec{b}' and \vec{c}' . To prove that the volume is preserved one can show that $|(\vec{c}' - \vec{a}') \times (\vec{b}' - \vec{a}')| = \delta q \delta p$.

13.4 Falling springs

We consider a spring connecting two identical masses falling freely from a given height to the ground. To make the problem simpler we consider the system to be one dimensional: the spring is elongated in the same direction of the gravitational force (the vertical z -axis). We set the masses to $m = 1$, the spring constant to $K = 1$ and spring rest length $l = 1$. The spring is at rest at the beginning, with the particles set at positions $z = 5$ and $z = 6$. The particles are subject to a gravitational force towards the ground $F = mg$. We set $g = 10$. The ground corresponds to $z = 0$ and the collision is totally elastic: after each collision the velocity of each particle changes sign. Neglect the mutual interaction between the particles.

- Simulate the system with the velocity Verlet algorithm, taking care of the boundary condition at $z = 0$ when updating the positions of the particles. Test the algorithm for different values of Δt .
- Plot the trajectories of the two particles $z_1(t)$ and $z_2(t)$ as a function of time. Do the particles ever reach the initial height?
- Plot the total elastic E_{el} , gravitational E_{grav} and kinetic E_{kin} energy as a function of time. Check also that the total mechanical energy is conserved²³ during the simulation.
- Repeat the analysis of the potential and kinetic energies for a chain of N particles of equal masses connected by identical springs. Take as starting positions $z_1 = 5$, $z_2 = 6 \dots z_N = 4 + N$ and consider $N = 10$ and $N = 20$.
- We would like to study the effect of different thermostats on the system. For this purpose, repeat the previous step using a velocity rescaling (64) and a Berendsen thermostat (65), taking $\tau = 100\Delta t$ for the latter. Turn on the thermostat at $t = 0.25 t_{\text{total}}$ and then turn it off again at $t = 0.75 t_{\text{total}}$, where t_{total} is the total time of the simulation. Choose a temperature of $T = 10$.

²²Here “volume” is actually 2d surface as the phase space is two dimensional spanned by the coordinates q and p . In higher dimension we will have to handle higher dimensional volumes.

²³We know that the energy in the Velocity Verlet algorithm is conserved up to some order in Δt . However if your simulation is correct you should see no drift of the total energy in time.

13.5 Falling slinky (by Wout Laermans 2021)

A mesmerizing experiment in physics is the falling slinky. A nice video about it is provided by Veritasium ²⁴. It seems as if the bottom end of the slinky keeps floating in the air, just until the whole slinky has collapsed. One of the easiest ways to approximate such a falling slinky, is as collection of masses, connected by springs (very similar to falling springs).

- a) The first step of the simulation is to find the initial configuration. You can take a collection of 10 masses, each with mass $m = 1$, connected by springs with rest length $l_0 = 1$ and spring constant $k = 1$ and the gravitational constant $g = 10$. The upper mass can be taken at a height of 500, the next at 499 and so on. Then, use the velocity Verlet algorithm to find the equilibrium positions. The upper mass is fixed at a height of 500 (so the speed $v = 0$ at all times). Without friction, the system would oscillate forever. Therefore, you can lower the speed of every mass by 10% at every time step to mimic friction. Since you are only interested in the equilibrium positions (not the trajectory itself), the time step does not have to be so small ($\Delta t = 0.1$ is fine). In order to know when you have reached equilibrium, you can check for example when the speed of the lowest mass becomes smaller than 10^{-7} (with such a high friction, the system is overdamped, which is why you can be sure this gives equilibrium.)
- b) The next step is to find the trajectories of the masses. Lower the time step to $\Delta t = 0.001$ and drop the whole slinky (no friction anymore). Plot the trajectories. Do you observe that the bottom mass keeps almost stationary just until the mass above it starts falling? What about the center of mass, which trajectory does it make before the slinky hits the ground and why?
- c) What happens if you would attach a heavy mass at the bottom of the slinky? Would the bottom end still be stationary just until the whole slinky collapsed? Change the bottom mass to 10 and repeat the experiment.

13.6 Testing Kramers' theory

In section 9.2 we derived an analytical expression for the rate at which a system can cross an energetic barrier in order to minimize its energy. In order to test this result, we are going to simulate the one-dimensional problem of a particle of mass $m = 1$, which feels the following potential

$$V(x) = -6\Delta V \left(\frac{x^3}{3} + \frac{x^2}{2} \right)$$

From Fig. 8 we see that this potential has a local minimum (well) at $x = -1$ next to a local maximum at $x = 0$ (barrier). This means that a particle initially placed at $x = -1$ will have to cross an energetic barrier of height ΔV in order to minimize its energy.²⁵

²⁴<https://www.youtube.com/watch?v=eCMmmEEy000>

²⁵Note that in this case the reaction coordinate x is just the position of the particle.

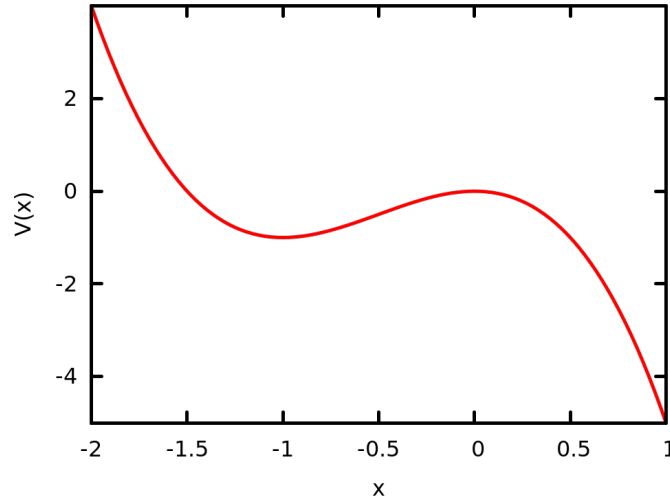


Figure 8: Energetic landscape of the barrier-crossing problem for $\Delta E = 1$. The energy has two local extrema, one at $x = -1$ (well) and one at $x = 0$ (top of barrier).

- a) If the energetic barrier is sufficiently high, the particle will practically remain fully confined within the potential well. This will provide it with enough time to equilibrate, so that the probability of finding it at x will follow the Boltzmann distribution $p(x) \sim e^{-V(x)/k_B T}$ within the well, while it will be $p(x) = 0$ beyond the barrier. To test this statement, place the particle at $x = -1$ with zero velocity, take $\Delta V = 10$ and run a sufficiently long simulation using the Langevin integrator (105) for $T = 0.25$ and $\gamma = 1$. One can then determine $p(x)$ by regularly collecting the position of the particle during the simulation and calculating the histogram at the end.
- b) We would like to verify the theory of section 9.2. For this purpose, simulate a system of many (at least 10^4) such non-interacting particles using the Langevin integrator for $\Delta V = 1$ and $\gamma = 1$. Place initially all particles at the bottom of the well with zero velocity. At every step of the simulation check which particles have crossed the barrier (e.g. satisfy the condition $x > 0.5$) and re-initialize them.²⁶ Vary the temperature around $T = 0.5$, plot the barrier-crossing rate and compare with the exponential dependence of Kramers' formula (116) by choosing the axes accordingly.

13.7 Overdamped harmonic oscillator

The solution of the Fokker-Planck equation for an overdamped harmonic oscillator with potential energy $V(x) = kx^2/2$

$$\frac{\partial P(x, t)}{\partial t} = D \frac{\partial^2 P(x, t)}{\partial x^2} + \frac{\partial}{\partial x} \left[\frac{kx}{\gamma} P(x, t) \right]$$

²⁶Replenishing the particles in this way eventually leads to a constant current of barrier-crossing particles.

with initial condition $P(x, 0) = \delta(x - x_0)$ is

$$P(x, t) = \left(\frac{\Omega e^{\Omega t}}{4\pi D \operatorname{sh} \Omega t} \right)^{1/2} \exp \left[-\frac{\Omega}{4D} \frac{(x e^{\Omega t/2} - x_0 e^{-\Omega t/2})^2}{\operatorname{sh} \Omega t} \right]$$

where we defined $\Omega \equiv Dk/k_B T$.

- a) Show that in the limit $k \rightarrow 0$ the above expression for $P(x, t)$ reduces to the solution of a free diffusion equation.
- b) Show that in the limit $t \rightarrow \infty$ and $k > 0$ the above expression for $P(x, t)$ reduces to the known expression from equilibrium statistical mechanics.
- c) Using the overdamped integrator (Eq. (88)) calculate the trajectories of a large number for independent simulations (say $\sim 10^3$) with fixed x_0 and obtain $P(x, t)$ for some fixed values of t as $t/\Omega = 10^{-2}, 10^{-1}, 1, 10$ and show that your results match the analytical expression given above.

13.8 Lennard-Jones fluid

In this problem we are going to simulate a group of N particles of mass $m = 1$ that are confined to move within a cubic box of width $L = 10$. The particles interact with each other through a Lennard-Jones potential

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

where we choose $\sigma = \epsilon = 1$. For computational efficiency we are going to truncate this potential at $r = R_c = 2.5$ and shift it as follows

$$V(r) = \begin{cases} V_{\text{LJ}}(r) - V_{\text{LJ}}(R_c), & r \leq R_c \\ 0, & \text{else} \end{cases}$$

The appropriate pair-interaction style that implements this in LAMMPS is `lj/cut`. In order to shift the potential, you will have to use the command `pair_modify`.

The initialization of the simulation is performed as follows. First define the simulation box using the command `region`, create it using the command `create_box` and then generate N atoms randomly within the box with the command `create_atoms`. We would like to have periodic boundary conditions, but since this is the default choice in LAMMPS you will not need to specify it explicitly.

Note that there is a chance, especially for large N , that two or more particles are initially very close to each other. Owing to the Lennard-Jones repulsion term r^{-12} , this can lead to extremely high forces which may in turn lead to missing particles and LAMMPS giving an error. In order to avoid this, you can first perform an energy

minimization using the command `minimize`.²⁷ Then you can initialize the velocities of the particles according to the Maxwell-Boltzmann distribution for an initial temperature T and set at the same time the total momentum equal to zero using the command `velocity` with the appropriate options.

- a) Run an NVE time integration²⁸ (`fix nve`) with time-step $\Delta t = 5 \times 10^{-3}$ and particle density $\rho = N/L^3 = 0.3$. Choose $T = 2$ as an initial temperature and plot the total energy as a function of time in order to verify that it is conserved. For the calculation of the kinetic and potential energy you will need to use the commands `compute ke` and `compute pe` respectively. **Once the system has equilibrated compute the velocity distribution $p(v_\alpha)$ where v_α is any component of the velocity vector of a particle. Show that the distribution is Gaussian and obtain a fit of the temperature from it. Does this match the initial value $T = 2$?**
- b) Turn on a Nosé-Hoover thermostat for $T = 2$, using an NVT time integration (`fix nvt`) instead of NVE, and repeat the simulation. Plot the kinetic energy as a function of time and compare with the expression $\langle K \rangle = 3Nk_B T/2$ obtained from the equipartition theorem.
- c) The Nosé-Hoover thermostat should reproduce the fluctuations of the canonical ensemble. Verify that by calculating the variance of the kinetic energy from simulations and compare it to the variance which you get from the canonical ensemble in Statistical mechanics.²⁹ **Calculate the velocity distribution $p(v_\alpha)$ as done in a).**
- d) Repeat the previous simulation for different values of the particle density within the range $0 < \rho \leq 0.2$. Plot the pressure P of the system as a function of the density and compare with both the ideal gas law $P = \rho k_B T$ and its first correction $P = \rho k_B T(1 + b_2 \rho)$ coming from the virial expansion.³⁰ Do you observe a deviation

²⁷Note that with this command LAMMPS does not perform an actual time-integration, but rather “artificially” drive the system into a state of minimum energy.

²⁸NVE means that the number of particles N , the volume V of the simulation box and the total energy E are kept constant during the integration.

²⁹Hint: in the canonical ensemble the component v_x , v_y and v_z of the particles velocities are Gaussian distributed with zero average and variance $\langle v_x^2 \rangle = k_B T/m$. We want to calculate the variance of the kinetic energy $\sigma_K^2 \equiv \langle K^2 \rangle - \langle K \rangle^2$ with

$$K = \frac{m \vec{v}_i^2}{2}$$

To obtain the variance of K we note that this is composed by the sum of $3N$ independent components of velocities then the variance is the sum of variances

$$\sigma_K^2 = 3N \frac{m^2}{4} \sigma_{v_x^2}^2 = 3N \frac{m^2}{4} (\langle v_x^4 \rangle - \langle v_x^2 \rangle^2)$$

We finally note that for a Gaussian variable $\langle v_x^4 \rangle = 3\langle v_x^2 \rangle^2$.

³⁰The second virial coefficient b_2 is given by the formula

$$b_2 = -\frac{1}{2} \int d\vec{r} \left(e^{-V(r)/k_B T} - 1 \right)$$

for larger values of ρ ? Note that, in order to extract the pressure of the system using `compute pressure`, you will first need to obtain the current temperature with the command `compute temp`.

e) Optional: Calculate numerically the third virial coefficient

$$b_3 = -\frac{1}{3} \int d\vec{r} \int d\vec{r}' f(r) f(r') f(|\vec{r} - \vec{r}'|)$$

where $f(r) \equiv e^{-\beta V(r)} - 1$, and compare the previous result with the second correction $P = \rho k_B T (1 + b_2 \rho + b_3 \rho^2)$ to the ideal gas law.

13.9 Langevin dynamics of Gaussian polymers

A Gaussian polymer consists of a series of $N+1$ successive beads which are connected by N harmonic springs, similarly to what is shown in Fig. 9. The corresponding potential energy is

$$V_{\text{bond}} = \frac{3k_B T}{2a^2} \sum_{i=1}^N d_i^2$$

where d_i is the length of each spring, $k_B = 1$ is the Boltzmann's constant, T is the temperature and a is the equilibrium bond length.³¹ For the implementation of this potential in LAMMPS one needs to use the `harmonic` bond-interaction style with the appropriate parameters.

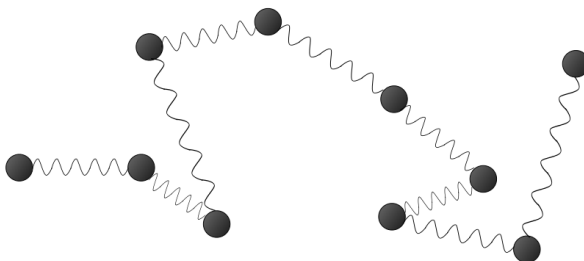


Figure 9: Bead-and-spring representation of a Gaussian polymer.

The student has to solve one of the following problems, which focus on various properties of such a polymer. All $N + 1$ beads have equal mass $m = 1$ and all N springs have an equilibrium length of $a = 1$. The system follows Langevin dynamics, which can be implemented in LAMMPS using two successive fixes, namely the `nve` and `langevin` ones. For the latter the user has to specify a damping parameter, which is defined as the inverse of the friction coefficient γ appearing in the Langevin equation (68), which we will set here $\gamma = 1$. You will also need to turn off the sorting of atoms with the command `atom_modify sort 0 0.0`.³²

which you can calculate numerically. For $T = 2$ one finds $b_2 \simeq -0.772$.

³¹Although the minimum energy of this potential is at $r_i = 0$, one can show that for finite temperature the equilibrium bond length is $r_i = a$.

³²You will need to do this whenever a simulation does not take pair interactions into account, otherwise an error will occur.

- a) Systems that follow Langevin dynamics typically perform diffusive motion. For instance, the Gaussian polymer is expected to undergo regular diffusion $\langle r_{\text{cm}}^2(t) - r_{\text{cm}}^2(0) \rangle \sim t$, where r_{cm} is its center of mass. However, if one focuses on a single bead of such a polymer, he or she will first observe an anomalous diffusion of the form $\langle r_i^2(t) - r_i^2(0) \rangle \sim \sqrt{t}$ at short time-scales, owing to the presence of the springs. At longer times the diffusion of the whole polymer will dominate, thus leading to an ordinary diffusion $\langle r_i^2(t) - r_i^2(0) \rangle \sim t$.

In order to verify the above statement, run simulations (about 10^7 time-steps for $\Delta t = 0.02$ and $\gamma = 1$) at $T = 1$ for a polymer consisting of $N = 200$ springs and plot the mean squared displacement of a bead as a function of time in a logarithmic scale, after letting the system equilibrate.

Hint: You can write a script that initializes the polymer as a random walk that performs jumps of length a , in order to reduce the equilibration times. Moreover, the mean squared displacement can be calculated and averaged over all beads with the compute `msd`. The current time-step of the simulation is automatically stored by LAMMPS in the variable `step`.

- b) One can make the system more realistic by introducing a resistance to bending. In order to simulate such a stiff polymer, one needs to introduce an angle energy term of the form³³

$$V_{\text{bend}} = \frac{\kappa_b}{a} \sum_{i=1}^{N-1} [1 - \cos(\theta_i - \pi)]$$

where κ_b is the bending rigidity and θ the angle formed by three successive beads. This can be implemented in LAMMPS using the `cosine/delta` angle-interaction style with the appropriate parameters (angles in degrees).

Run simulations for $\kappa_b = 5$, $\Delta t = 0.01$, $N = 100$ and for different temperatures within the range $0.25 \leq T \leq 1.5$. Let the system equilibrate (about 10^5 steps) and then calculate the mean bending angle $\langle \cos(\theta - \pi) \rangle$. Plot it together with the theoretical expression

$$\langle \cos(\theta - \pi) \rangle = \frac{1}{\tanh(\kappa_b / ak_B T)} - \frac{ak_B T}{\kappa_b}$$

Hint: An easy way to get $\langle \cos(\theta - \pi) \rangle$ in LAMMPS is to first obtain the energy V_{bend} of every angle interaction with the `angle/local` compute, then average it along the polymer using the compute `reduce` and store it in a variable rearranging the terms appropriately.

- c) Simulate the stretching of a Gaussian polymer by applying two opposite forces F at the two ends. Set $T = 1$, $\Delta t = 0.02$ and $N = 100$, let the system equilibrate (roughly 10^5 steps) and plot the average squared extension $\langle z^2 \rangle$ as a function

³³Notice that the minimum energy corresponds to $\theta_i = \pi$, i.e. a completely straight configuration.

of the magnitude of the force within the range $0 \leq F \leq 3$. Compare with the analytical expression

$$\langle z^2 \rangle = \frac{Na^2}{3} + \frac{N^2a^2}{9} \left(\frac{Fa}{k_B T} \right)^2$$

Hint: In order to apply a force on a single particle in LAMMPS, one needs to define a group consisting of the particle and then use the fix `addforce` on it. Moreover, for the calculation of the extension you will need the coordinates of the first and last bead, which LAMMPS stores automatically in the variables `x[1]`, `x[101]` etc.