

MSN - 3D Thermostat Langevin Molecular dynamics

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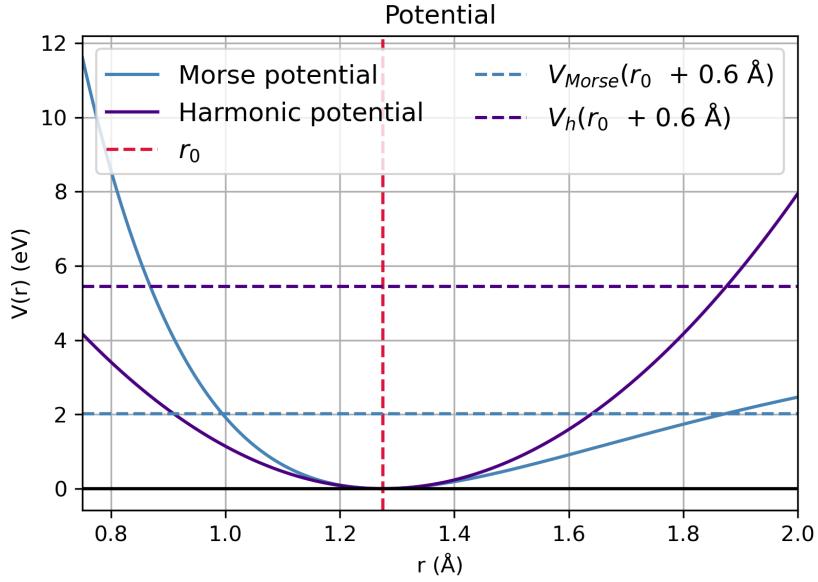


Figure 1: Morse (blue) and harmonic (indigo) potential around $r_0 = 1.275\text{\AA}$ the equilibrium radius of the molecule. We also showcase $V(r_0 + 0.6\text{\AA})$, since $r_0 + 0.6\text{\AA}$ is the initial radius we choose in the simulation presented in Figure 3.

1 Introduction

In this work, we simulate the movement of the diatomic molecule H-Cl in three dimensions, using the Langevin molecular dynamics method (LMD). To achieve this, we will first discuss simulating the H-Cl molecule without the Langevin thermostat, using the classical approach of MD. After verifying the consistency of our results and their coherence, we introduce the Langevin thermostat, placing the system in the canonical ensemble, where the temperature can be controlled. We vary the simulation parameters and interaction potentials and compare results. Furthermore, we verify the equipartition theorem of energy, and discuss the influence of thermostat parameters as well as coupling between energies.

2 Model

We consider two potential types, as described by equation 1. The first type (case 1) is a harmonic interaction potential; the second type is the Morse interaction potential.

$$V(r) = \begin{cases} \frac{1}{2}k(r - r_0)^2 & (\text{harmonic potential}) \text{ with } k = 2D\alpha \\ D(1 - e^{-\alpha(r - r_0)})^2 & (\text{Morse potential}) \end{cases} \quad (1)$$

Here, D and α are constant values, chosen with respect to the molecular system, with $D = 4.6141\text{eV}$ and $\alpha = 1.81\text{\AA}^{-1}$. The two types of interaction potential are showcased in Figure 1. We note that around the equilibrium radius of the molecule $r_0 = 1.275\text{\AA}$, the Taylor expansion of the Morse potential returns exactly the chosen expression of the harmonic potential at first order.

2.1 Classical MD

The molecular dynamics (MD) method is used to analyze the physical movements of atoms and molecules. Atoms in a system are treated as punctual masses in mutual interaction, which follow classical mechanics. The simulation is in the microcanonical ensemble. Each of the atoms $i \in [\text{H}, \text{Cl}]$ follows the following :

$$m_i \ddot{r}_i = f_i = -\frac{\partial V(r)}{\partial r_i} \quad (2)$$

with r_i being the position of an atom (Cl or H), f_i the external force and $U(r)$ (interatomic) interaction potential which depends on the position of the 2 atoms of our system (here, r is the relative distance between the two molecules). In three dimensions, the system is composed of 3×2 differential equations to solve. To do so, we used the Verlet algorithm which relies on the positions and velocities of the particles. The method requires the initial position and velocity of each particle. Only the first step does not use the Verlet update directly but instead relies on a Taylor expansion (cf. Table 2.1)

Verlet	Taylor (2nd order)
$r_i(t + \delta t) = 2r_i(t) - r_i(t - \delta t) + \frac{(\delta t)^2}{m_i} f_i(t) + o(\delta t^4)$	$r_i(\delta t) = r_i(0) + \delta t v_i(0) + \frac{\delta t^2}{2m_i} f_i(0) + o(\delta t^3)$
$v_i(t) = \frac{r_i(t + \delta t) - r_i(t - \delta t)}{2 \delta t} + o(\delta t^2)$	$v_i(\delta t) = v_i(0) + \frac{\delta t}{m_i} f_i(0) + o(\delta t^2)$

Table 1: Verlet algorithm.

Temperature and pressure are computed using the generalized equipartition theorem. But it is not easy to control these two physical quantities. To address this issue, we use an adapted version of MD.

2.2 Langevin method

The Langevin method is an adapted version of MD that introduces a random force R in the differential equation of particle movement, which is due to random collisions with surrounding molecules. The method also takes into account the viscous damping $-m_i \gamma v$ with m_i the mass of one of the atoms, v_i the respective velocity, and γ the viscous coefficient. In this context, $\frac{1}{\gamma}$ is exactly the thermal exchange characteristic time with the thermostat. By default, we choose $\gamma = 5.10^{11} s^{-1}$ and choose the timestep accordingly $\delta t = 0.1 ps = 10^{-16} s$. While for some simulations we let one or the other vary if necessary, we conserve $\delta t \ll 1/\gamma$ in order to obtain accurate simulations. The equation of the motion of the atom i in the H-Cl molecule is therefore:

$$m_i \ddot{r}_i = f_i - m_i \gamma v_i + R_i \quad (3)$$

At thermal equilibrium, the equipartition theorem must be verified, meaning each quadratic degree of freedom contributes an average energy of $\frac{1}{2} k_B T$. For a free particle in three dimensions, there are three translational degrees of freedom, so the mean kinetic energy is

$$\langle E \rangle = \frac{3}{2} k_B T.$$

The random force satisfies the fluctuation–dissipation relation. It is not correlated:

$$\langle R(t_0)R(t+t_0) \rangle = 2m\gamma k_B T \delta(t)$$

3 Simulation of the H-Cl

To simulate the molecule, a first approach is to introduce the reduced mass μ and modeled the two-atom system as a single particle of this effective mass, thereby reducing the problem to the study of one object of interest instead of two. We assume for now there is no thermostat for the system, as we will discuss later the implementation of a thermostat.

3.1 Reduced mass approach

With this approach, it is therefore possible to model our problem with the Hamiltonian of our system and using reduced masses of the two atoms. The Hamiltonian is (in the case of the Morse-type potential):

$$\hat{H} = \frac{\hat{p}_H^2}{2m_H} + \frac{\hat{p}_{Cl}^2}{2m_{Cl}} + D \left[e^{-\alpha(|r_H - r_{Cl}| - r_0)} - 1 \right]^2 \quad (4)$$

Through a change of variables, one can express the following:

$$\left\{ \begin{array}{lcl} \hat{r}_{rel} & = & \hat{r}_H - \hat{r}_{Cl} \\ \hat{R} & = & \frac{m_H \hat{r}_H + m_{Cl} \hat{r}_{Cl}}{m_H + m_{Cl}} \\ \hat{P} & = & \hat{p}_H + \hat{p}_{Cl} \\ \hat{p} & = & \frac{m_{Cl} \hat{p}_H - m_H \hat{p}_{Cl}}{m_H + m_{Cl}} \\ \mu & = & \frac{m_{Cl} m_H}{m_{Cl} + m_H} \\ M & = & m_{Cl} + m_H \end{array} \right.$$

With this parameterization, one obtains the following expression:

$$\hat{H} = \underbrace{\frac{\hat{P}^2}{2M}}_{H_1} + \underbrace{\frac{\hat{p}^2}{2\mu}}_{H_2} + \underbrace{D \left[e^{-\alpha(r_{rel} - r_0)} - 1 \right]^2}_{H_3} \quad (5)$$

To better understand how the molecule evolves in three dimensions over time and to see whether the equipartition theorem is verified, we compute the kinetic, potential, translational, vibrational, and rotational energies. In the expression above, H_1 represents the translational energy of the center of mass, H_2 corresponds to the kinetic energy associated with vibration and rotation, and H_3 denotes the vibrational potential energy. Here, the degrees of freedom of the fictional particle are more restrictive, therefore we do not expect to obtain the same mean energy as if we were simulating the full 3D system with both particles. H_2 becomes:

$$H_2 = \underbrace{\frac{\mu \dot{r}_{rel}^2}{2}}_{\text{vibrational energy}} + \underbrace{\frac{\mathbf{L}^2}{2\mu r_{rel}^2}}_{\text{rotational energy}} \quad (6)$$

The first term corresponds to the kinetic vibrational energy and the second is kinetic rotational energy, where we introduce \mathbf{L} the angular momentum operator. In order to compute the position and velocity of the center of mass, we used the Verlet algorithm (1967) with the following parameters:

- Relative position (r_{rel}) of the center of mass
- Velocity of the center of mass (v calculated from r_{rel}).
- Derivative of the Morse potential as the external force
- Reduced mass (μ)

However, while this parameterization is theoretically very practical, as mentioned beforehand it reduces the effective number of degrees of liberty. When attempting to verify the equipartition theorem, one cannot compute all the energies necessary to recover all degrees of freedom. To address this issue, we revise our approach, considering that each particle has three coordinates for their position ((x, y, z)) and three for their velocity ((v_x, v_y, v_z) but also in spherical coordinates). We discuss expressions of the energies in the following section. This is the 3D approach.

3.2 In 3D

We now use cartesian lab coordinates for the position and speed of the diatomic system (3 for each). In the following section, we will assume the following initial conditions:

- The molecule starts at $r_{Cl} = (0, 0, 0)$, $r_H = (r_{init}, 0, 0)$, where $r_{init} = r_0 + 0.6\text{\AA}$ (if there is no thermostat, following potential shown in Figure 1) or $r_{init} = r_0$ (if we set a thermostat). A change of coordinates can fall back on other initialization parameters for (r_{Cl}, r_H) , hence this is a 1 degree of freedom parameter.
- The initial speed is null for both atoms.
- $\gamma = 5.10^{11}\text{s}^{-1}$ unless stated otherwise.
- The thermostat is set to be $T = 500K$ if one adds a thermostat.
- It follows that the initial energy of the molecule is always given by $E = V(||r_{init}||)$, whether V is the harmonic or Morse potential.

The total kinetic energy of a diatomic molecule can be decomposed into translational, rotational, and vibrational components, as explained above. M and μ are defined in section 3.1. We note by subscript $i \in [\text{H}, \text{Cl}]$ the molecule, such that for example v_i is the speed of one or the other atom. The subscript CM denotes the center of mass quantity q associated to the molecule, where:

$$q_{CM} = \frac{m_H q_H + m_{Cl} q_{Cl}}{m_H m_{Cl}} \quad (7)$$

with m_H and m_{Cl} being respectively the mass of the hydrogen (H) and the chlorine atom (Cl), and q_H and q_{Cl} being physical quantity (position or speed for instance) of respectively the atom of hydrogen or chlorine. We showcase the movement of the atom in 3D space in Figure 2.

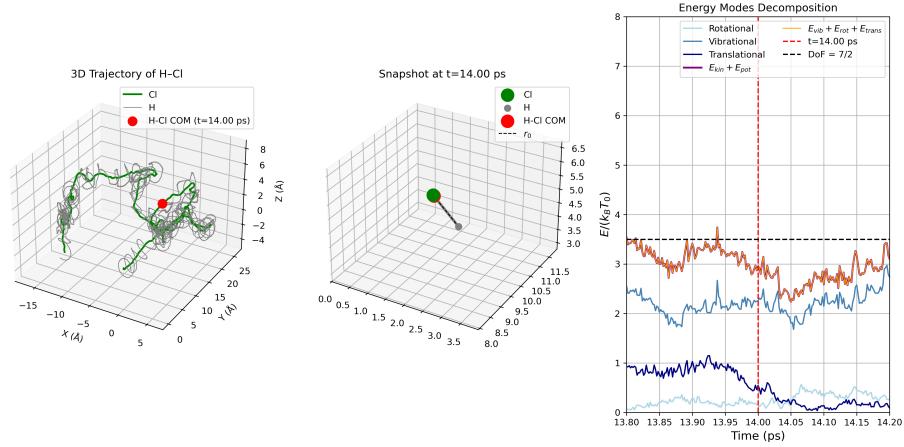


Figure 2: a) Showcasing the molecule trajectory (both H, Cl) in 3D space, as well as the position of the Center of Mass (COM) at the chosen time frame. We note that due to the ratio of masses $m_H/m_{Cl} \ll 1$, the center of mass basically coincides with the green trajectory at all times. b) The molecule at the chosen timeframe $t = 14\text{ps}$ in 3D, with the r_0 distance overlaid between the two molecules (black, dotted), the COM (red), H (gray) and Cl (green). c) The energy distribution between modes around $t = 14\text{ps}$

Translational energy. The translational energy corresponds to the motion of the center of mass.

$$E_{\text{trans}} = \frac{1}{2} M V_{\text{CM}}^2 \quad (8)$$

where the center-of-mass velocity is the 3D vector written with equation 7.

Rotational energy. The rotational energy is associated with the angular momentum of the relative motion:

$$E_{\text{rot}} = \frac{\mathbf{L}^2}{2I} \quad (9)$$

We define the moment of inertia I and \mathbf{L} the angular momentum:

$$\mathbf{L} = \mu (\mathbf{r}_H - \mathbf{r}_{Cl}) \times (\mathbf{v}_H - \mathbf{v}_{Cl}) \quad \text{and} \quad I = \mu |\mathbf{r}_H - \mathbf{r}_{Cl}|^2 \quad (10)$$

Vibrational energy. The vibrational energy is related to the radial (bond-stretching) motion:

$$E_{\text{vib, kin}} = \frac{1}{2} \mu v_{\text{rad}}^2 \quad (11)$$

with the radial velocity defined as:

$$v_{\text{rad}} = (\mathbf{v}_H - \mathbf{v}_{Cl}) \cdot \frac{(\mathbf{r}_H - \mathbf{r}_{Cl})}{|\mathbf{r}_H - \mathbf{r}_{Cl}|} \quad (12)$$

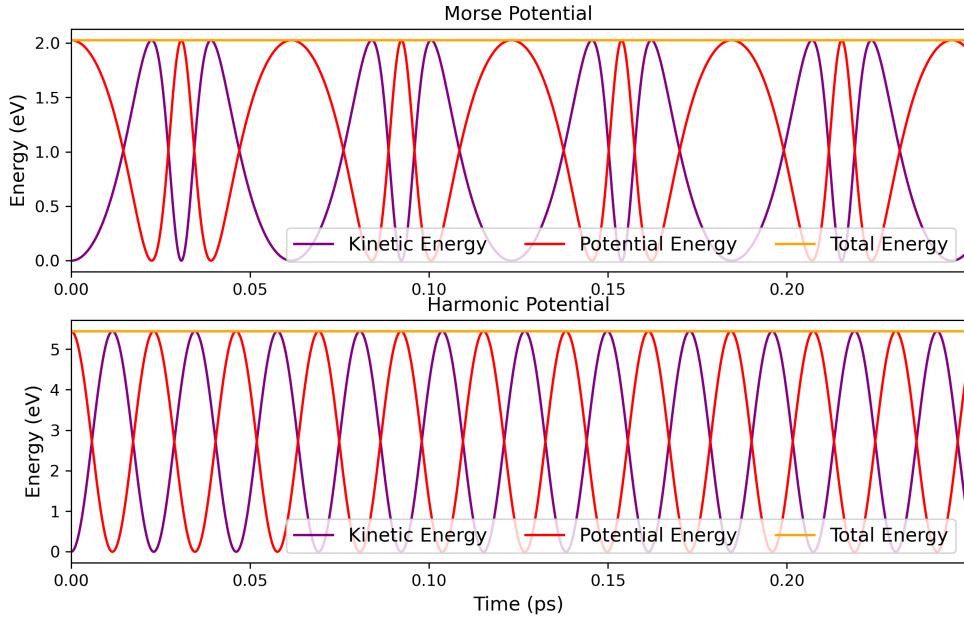


Figure 3: Comparing kinetic and potential energies for the Morse potential and the Harmonic potential in the case of no thermostat. We use the same offset value as shown in Figure 1 and see that we recover the initial potential energy (equal to the total mechanical energy per energy conservation, since initial speed is null) that is shown in dotted lines on that plot, for both the Harmonic potential and the Morse potential. One can also see how the approximation of a Taylor series expansion for the potential breaks down if the initial "pinch" is such that we no longer have $|r_0 - r_{\text{eq}}| \ll 1$: the oscillations lose their initial periodicity.

To this, we append the vibrations due to the potential energy, which simply is $E_{\text{pot}} = V(r)$. Therefore, the vibrational energy of the system can be described as:

$$E_{\text{vib}} = E_{\text{vib, kin}} + E_{\text{pot}} \quad (13)$$

3.2.1 No thermostat

In the case of no thermostat, we can compare the energies we obtain to the initial potential energy set in Figure 1 for both the Morse and Harmonic potential. Far away from the $\|r - r_0\| \ll 1$ regime, the potentials behave very differently, as showcased in Figures 3, 4. We compare the kinetic and potential energy evolutions in Figure 3.

One can still decompose the energetic contribution in order to verify the equipartition theorem. We expect the molecule to only contribute to the vibrations of the energy modes, since the molecule has no reason to be out-of-axis (no random impulse for rotations, no initial transverse speed). In Figure 4, we showcase this effect. In fact, the speed of the atoms is at all times aligned with the intermolecular bond and therefore the kinetic energy is perfectly equal to the vibrational kinetic energy.

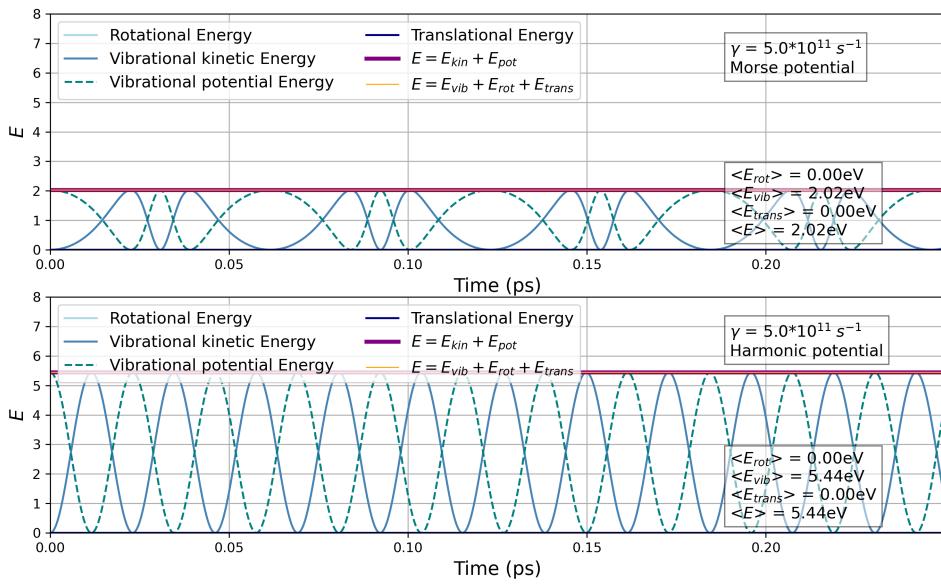


Figure 4: Decomposition of $E_{vib,kin}$, E_{rot} , E_{trans} and E_{pot} (in eV). No global translation of the molecule is shown (the center of mass speed is at all times null) and no rotation (there is no projection of speed outside of the molecular bond axis). Therefore, only vibrations contribute to energy. The initial conditions remain the same as Figure 1. The sum of all modes still recovers the total energy, as expected; and the total energy is equal to the initial potential energy (since there is no initial speed in this case).

3.2.2 Appending the thermostat

We now discuss the effect of adding a thermostat at temperature T_0 to the system. In this scenario, we now expect the random force discussed in the model to add more components to the speed, such that there is a global translation of the molecule in space as well as rotations. This in turn should decompose the global energy differently : we study this decomposition in Figure 5

Degrees of freedom. The degrees of freedom are described hereafter, as well as their contribution to the energy of the system:

- 3 degrees of freedom with the translational kinetic energy (one in each direction in 3D space), contributing for $\frac{3}{2}k_B T$ to the total energy of the system. E_{trans} is described in equation 8
- 2 degrees of freedom due to vibrations, that one can further decompose into vibrations due to the potential (E_{pot}) and intrinsic kinetic vibrations ($E_{vib, kin}$), as described in equation 13 and 11. Both contribute with $\frac{1}{2}k_B T$, for a total contribution of $k_B T$.
- 2 degrees of freedom due to rotational kinetic energy, also contributing for a total of $k_B T$ to the energy, as showcased in equation 9

With this, we find that the total energy of the system is $E = \frac{f}{2}k_B T$, where $f = 7$ is the number of degrees of freedom of the molecule. We verify that the total mechanical energy of the system can be either decomposed in its potential and kinetic energies, or in the $E_{rot} + E_{trans} + E_{vib}$ energy modes, as showcased in Figure 5. Moreover, if one averages energy over long periods of time in the steady state solution, we can also verify that we obtain:

$$\frac{\langle E \rangle}{k_B T_0} \approx \frac{7}{2} \quad (14)$$

Temperature. Using the expression of the total energy by modes, one can find the temperature of the system with:

$$T \approx \frac{2\langle E_{tot} \rangle}{7k_B} \quad (15)$$

Here, we use a sliding window mean of $\langle E_{tot} \rangle$ to average the energy values beyond the statistical fluctuations and get rid of the high-frequency modes. In Figure 6, we notice we recover the ratio $T/T_0 \approx 1$ after stabilization of the simulation, on the larger time scales.

Once the equipartition theorem is verified, we introduced the Langevin thermostat, therefore adding the random forces of collisions and γ with $\frac{1}{\gamma}$ being the characteristic time, as explained in section 2.2. From now, the simulations are in the Langevin thermostat.

4 Influence of γ

$\frac{1}{\gamma}$ represents the characteristic time of exchange with the defined thermostat. We expect, for a system at "T = 0K" (figuratively, we place the H-Cl molecule in the equilibrium position with no speed, therefore no initial energy), that the system progressively gains a mean energy of $\frac{7}{2}k_B T$ at a rate of γ . This also gives insights on the relevant δt timestep to choose for the simulation.

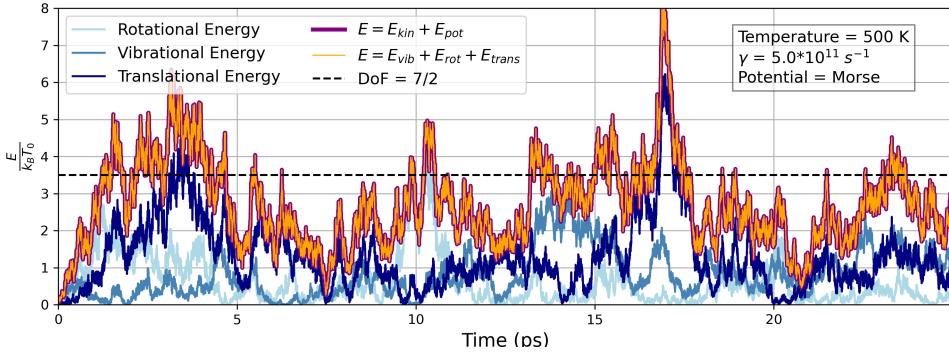


Figure 5: Verifying the decomposition of energies into (E_{vib}), translational (E_{trans}) and rotational (E_{rot}) energies. By superposition of the orange and purple curves, we see the total mechanical energy computed as $E_m = E_{pot} + \frac{1}{2} \sum_{i \in [H, Cl]} m_i(v_{ix}^2 + v_{iy}^2 + v_{iz}^2)$ is equal to the sum of the energies with modes $E_{rot} + E_{trans} + E_{vib}$. The energies are made dimensionless by dividing by $k_B T_0$ where T_0 is the thermostat temperature. We overlay in black the value obtained for the number of degrees of freedom of the system, $dof = \frac{7}{2}$. When computing the mean energy of the system over long periods of time, we recover the dof value.

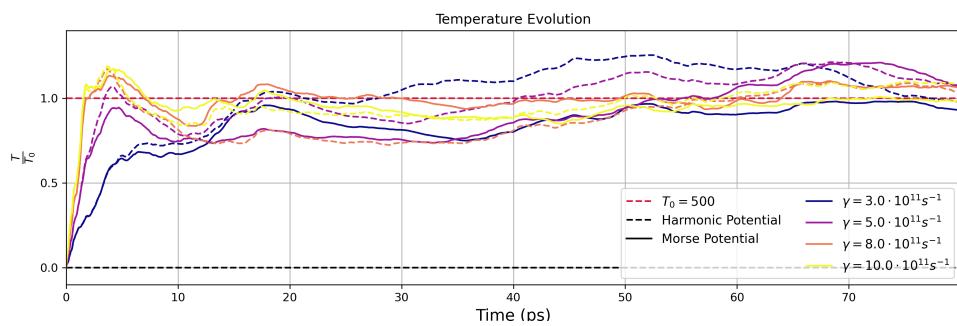


Figure 6: Evolution of relative temperature for a thermostat $T_0 = 500K$ with different values of γ over 80ps. Dotted lines represent the harmonic potential, while the full lines correspond to the Morse interaction potential. We observe there is variance around the requested temperature, that we attribute to statistical fluctuations, since there does not seem to be strong correlations between the lines. We note the same random seed was used for each simulation, resulting in the same draws for the force amplitude in the Langevin scenario.

In Figure 6, we show the rolling mean temperature of the system for various values of γ . We find that the system stabilizes around the equilibrium temperature for long times, and the slope of evolution is described by γt at the beginning ($t \ll N_{steps}\delta t$), akin to an RC circuit in electronics. We show the results for the harmonic and Morse potentials at different values of γ .

5 Influence of subsampling

We discuss the influence of δt our timestep when comparing to a fixed value γ . Concretely, we observe different regimes (these regimes were probed through dichotomy over convergence on the δt values), and display them in figure 7

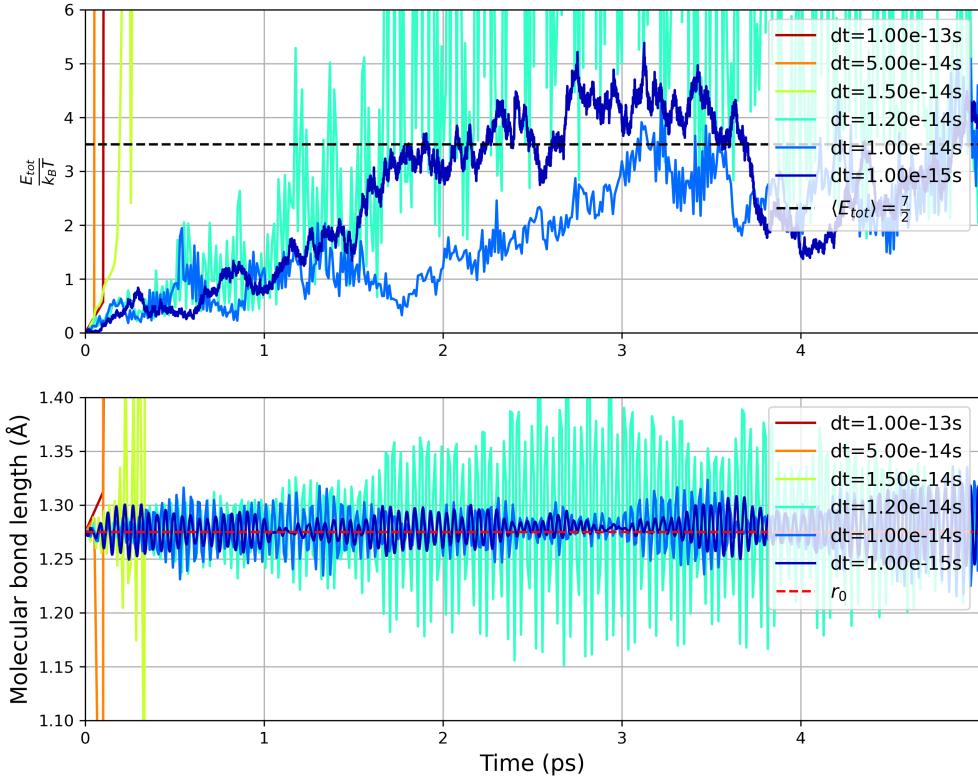


Figure 7: The influence of δt on convergence of the simulation. Top : Total energy E (normalized by $k_B T_0$), with $\frac{7}{2}$ for reference. Bottom : molecular bond length (\AA), with r_0 for reference (red, dotted). Here, $\gamma = 3.10^{11}\text{s}^{-1}$.

For δt divergent simulations for steps above 10ps, and different divergent regimes :

- Larger amplitude (cyan, $\delta t=12\text{ps}$)
- Starts okay, diverges (green, $\delta t=15\text{ps}$)
- Fully divergent (orange, red, $\delta t > 50\text{ps}$)

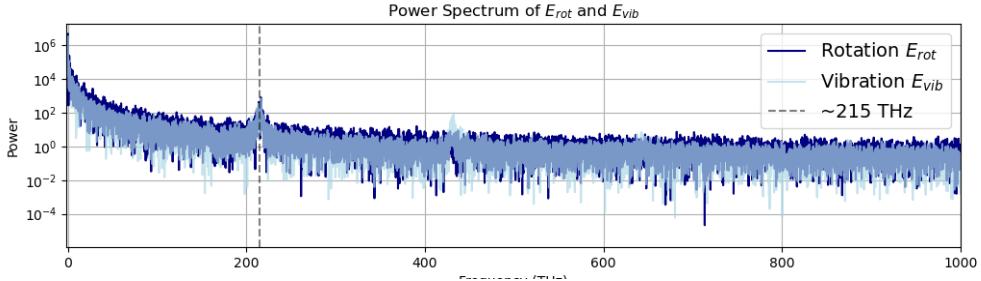


Figure 8: Power spectrum (Fast Fourier Transform, FFT) of E_{rot} and $E_{vib,kin}$. Around ~ 215 THz, we notice a second frequency peak, finding the vibration frequency f_{vib} . It is interesting to note that we can read higher order harmonics of f_{vib} on the vibration power spectrum at ~ 430 THz, ~ 645 THz and even ~ 860 THz, but these are not seen on the E_{rot} power spectrum.

Therefore, one must always pick δt sufficiently small such that $\gamma t \ll 1$ (at least of order 10^{-4} s to be safe).

6 Rotation-vibration coupling

In this section, we study the coupling between the rotational and vibrational movements of the molecule. We remind that the Hamiltonian corresponding to kinetic vibrational energy and the rotational energy can be expressed as:

$$H_2 = \frac{\mu \dot{r}_{rel}^2}{2} + \frac{\mathbf{L}^2}{2\mu r_{rel}^2} \quad (16)$$

We notice both quantities depend on r_{rel} : they are not independent, and therefore there is a coupling between rotational and vibrational movements of the molecule, since inertia depends on r_{rel} as well. To assess their coupling, we perform a power spectrum analysis of the energies $E_{vib,kin}$ and E_{rot} and find results showcased in Figure 8.

During a rotation of the molecule, the molecule typically undergoes many vibrations (this can be seen in figure 2). Therefore, the relative distance r_{rel} fluctuates at frequency f_{vib} (and multiples). Because the total angular momentum $\mathbf{J} = \mathbf{I} \cdot \boldsymbol{\omega}$ of a molecule is constant in time, but \mathbf{I} depends on r_{rel} , necessarily \mathbf{J} must also fluctuate in f_{vib} . Finally, because E_{rot} inherently depends on \mathbf{J} , we find that the E_{rot} fluctuates at the same periodicity, which hints at strong coupling between the two : the frequency peaks overlap in the power spectrum around ~ 215 THz in figure 8. Moreover, we see the following higher order harmonics of f_{vib} in the power spectrum of E_{vib} , but do not see them for E_{rot} , which is expected, since vibrations happen at a much higher frequency than E_{rot} .

7 Conclusion

The code used for this analysis is made publicly available at github.com/jeanchdjdev/md-langevin. In this work, we have investigated the effects of the thermostat on a diatomic H-Cl molecule, recovering the equipartition energy theorem, and investigated how the molecule behaves at different values of the thermal exchange coefficient γ . In order to improve this work, further upgrades could

look at simulating larger molecules, or multiple sets of molecules at once. It would also be interesting to modify the effects of the initial conditions on the simulation, such as initial radius or speed, since this sets an initial energy and therefore temperature.

References

- [1] Marc Hayoun, Hichem Dammak, *Simulation numérique des ensembles statistiques*, Chapitre 4, p49-53 (2025), Programme Ingénieur CentraleSupélec