



**DEGREE FINAL PROJECT**

# **A Study of Thermodynamic Properties using Molecular Dynamics**

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## 1. INTRODUCTION

Nowadays, the use of computing for the world of chemistry is essential to do all kinds of calculations, from any type of analytical formula for simple calculations, to physical simulations for complex calculations of systems. The use of computer programs to solve problems allows us to apply and develop the knowledge acquired throughout the grade and thus address more complex problems.

Molecular dynamics is one of the techniques that uses these programming tools. It is a simple way to study the behavior of thousands of atoms, allowing us to simulate condensed phases and observe the interactions between multiple molecules.

In this work, we will use it to be able to calculate, through a tool called LAMMPS, the thermodynamic properties known as enthalpy and heat capacities, of water, Carbon Dioxide and Methanol, we will compare these results with the values known in the bibliography and we will draw conclusions about the calculations made and the validity of these.

### 1.1 Thermodynamical variables

The thermodynamical variables that we are going to study are:

- **Temperature**

Temperature is a state variable. It is also an important concept in dynamics simulations. This macroscopic quantity is related to the microscopic description of simulations through the kinetic energy, which is calculated from the atomic velocities [1]

The temperature and the distribution of atomic velocities in a system are related through the Maxwell-Boltzmann probabilities:

$$f(v)dv = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(\frac{-mv^2}{2k_B T}\right) 4\pi v^2 dv \quad (1)$$

This formula expresses the probability  $f(v)dv$  that a molecule of mass  $m$  has a module of velocity between  $v$  and  $v + dv$  when the system is at temperature  $T$ , being  $k_B$  the Boltzmann constant.

The  $x$ ,  $y$ ,  $z$  components of the velocity vector follow Gaussian distributions:

$$g(v_x)dv_x = \left(\frac{m}{2\pi k_B T}\right)^{1/2} \exp\left(\frac{-mv_x^2}{2k_B T}\right) dv_x \quad (2)$$

From this distribution it follows that every components is zero on average:

$$\langle v_x \rangle = \int_{-\infty}^{\infty} v_x g(v_x) dv_x = 0 \quad (3)$$

This is expected, as atoms move with equal probability in both directions. The average kinetic energy associated with the motion in one direction is:

$$\left\langle \frac{1}{2} m v_x^2 \right\rangle = \frac{1}{2} m \int_{-\infty}^{\infty} v_x^2 g(v_x) dv_x = \frac{1}{2} k_B T \quad (4)$$

This is an example of the equipartition theorem, stating that each degree of freedom contributes  $\frac{1}{2} k_B T$  to the total kinetic energy. Consequently the total kinetic energy of  $N$  atoms is, on time average, given by:

$$K = \left\langle \sum_{i=1}^N \left( \frac{1}{2} m v_{x,i}^2 + \frac{1}{2} m v_{y,i}^2 + \frac{1}{2} m v_{z,i}^2 \right) \right\rangle = Nf \frac{1}{2} k_B T \quad (5)$$

Where  $Nf$  is the number of degrees of freedom. If all atoms move independently  $Nf$  equals  $3N$  because each atom has three velocity components (that is,  $v_x$ ,  $v_y$ , and  $v_z$ ). In most simulations, however, the total linear momentum is conserved (and usually set to zero). Consequently the number of degrees of freedom contributing to the kinetic energy is 3 less, that is,  $Nf = 3N - 3$ . In nonperiodic systems, in addition, the total angular momentum is also conserved (and again usually set to zero such that the system is not rotating). Hence in this case the number of degrees of freedom is less another 3,  $Nf = 3N - 6$ . In periodic systems the angular momentum is not conserved, as the cells impose a torque on one another.

The temperature is calculated utilizing this relation between the kinetic energy and the temperature:

$$T_{inst} = \frac{2}{k_B Nf} K_{inst} \quad (6)$$

Where  $K_{inst}$  is the total kinetic energy of the system at time  $t$ , that is:

$$K_{inst} = \sum_{i=1}^N \left( \frac{1}{2} m v_{x,i}^2 + \frac{1}{2} m v_{y,i}^2 + \frac{1}{2} m v_{z,i}^2 \right) \quad (7)$$

The time average of the instantaneous temperature is the thermodynamic temperature

## Pressure

Pressure is another basic thermodynamic variable that defines the state of a system. It is a familiar concept, defined as the force per unit area. Standard atmospheric pressure is 1.013 bar, where 1 bar=10<sup>5</sup> Pa. A single number for the pressure implies that pressure is a scalar quantity, but in fact, pressure is a tensor of the more general form [2]

$$P = \begin{pmatrix} P_{xx} & P_{xy} & P_{xz} \\ P_{yx} & P_{yy} & P_{yz} \\ P_{zx} & P_{zy} & P_{zz} \end{pmatrix} \quad (8)$$

Each element of the tensor is the force that acts on the surface of an infinitesimal cubic volume with edges parallel to the x, y, and z axes. The first subscript refers to the direction of the normal to the plane on which the force acts, and the second subscript refers to the component of the force.

In an isotropic situation, where forces are the same in all directions and there is no viscous force, the off-diagonal elements are zero and the diagonal elements are equal:

$$P = p \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = pI \quad (9)$$

where the scalar quantity p is the equivalent hydrostatic pressure.

Pressure is calculated through the use of the virial theorem. Like temperature, pressure is a thermodynamic quantity and is, strictly speaking, meaningful only at equilibrium. Thermodynamic pressure, thermodynamic temperature, volume, and internal virial can be related in the following way:

$$pV = Nk_B T + \frac{2}{3} \langle W \rangle \quad (10)$$

Where the virial W is defined as:

$$W = \frac{1}{2} \sum_{i=1}^N r_i \cdot f_i \quad (11)$$

With  $f_i$  being the force on atom i exercised by all other atoms. This force does not include external forces due to a container wall. The pressure effectively represents such external forces.

An instantaneous pressure function  $P_{instant}$  can be defined, so that thermodynamic pressure is the average of the instantaneous values:

$$P_{instant} = \frac{Nk_B T_{instant}}{V} + \frac{2}{3} \frac{W}{V} \quad (12)$$

Where  $T_{instant}$  is the instantaneous kinetic temperature, which is related to the instantaneous kinetic energy  $K$  of the system by equation (6). The instantaneous pressure function can thus be written as:

$$P_{instant} = \frac{2}{3V} (K + W) \quad (13)$$

As mentioned above, in general pressure is a tensor. The kinetic and virial terms in (10) can be generalized as:

$$P_{instant} = \frac{1}{V} \left[ \sum_{i=1}^N m_i v_i v_i^T + \sum_{i=1}^N r_i f_i^T \right] \quad (14)$$

In detail, the two terms on the right-hand side of the equation are:

$$\sum_{i=1}^N m_i v_i v_i^T = \begin{bmatrix} \sum_i m_i v_{ix} v_{ix}^T & \sum_i m_i v_{ix} v_{iy}^T & \sum_i m_i v_{ix} v_{iz}^T \\ \sum_i m_i v_{iy} v_{ix}^T & \sum_i m_i v_{iy} v_{iy}^T & \sum_i m_i v_{iy} v_{iz}^T \\ \sum_i m_i v_{iz} v_{ix}^T & \sum_i m_i v_{iz} v_{iy}^T & \sum_i m_i v_{iz} v_{iz}^T \end{bmatrix} \quad (15)$$

$$\sum_{i=1}^N r_i f_i^T = \begin{bmatrix} \sum_i r_{ix} f_{ix} & \sum_i r_{ix} f_{iy} & \sum_i r_{ix} f_{iz} \\ \sum_i r_{iy} f_{ix} & \sum_i r_{iy} f_{iy} & \sum_i r_{iy} f_{iz} \\ \sum_i r_{iz} f_{ix} & \sum_i r_{iz} f_{iy} & \sum_i r_{iz} f_{iz} \end{bmatrix} \quad (16)$$

where  $r_{ix}$ ,  $v_{ix}$ , and  $f_{ix}$  indicate the x components of the position, velocity, and force vectors of the  $i^{th}$  atom, respectively.

- **Internal and Total Energy**

Internal energy [3] ( $U$ ) of a body is that associated with the molecular activity of the body as indicated by its temperature  $T$  [K], and can be evaluated in terms of the heat required to change the temperature of the body having a specific heat capacity  $C$ , in absence of work, as follows:

$$\Delta Q = m \cdot C \cdot \Delta T = \Delta U \quad (17)$$

- **Enthalpy**

The value of enthalpy reflects the capability of a thermodynamic or steady flow system to release heat and perform work[3]. This involves the process of heat absorption or release during a reaction, which is the enthalpy change. The enthalpy change of a reaction highly influences the reaction types (endothermic, exothermic), phase transition (solid-liquid-gas), and other thermal phenomena. This also means the involvement of different types of enthalpy changes, such as the enthalpy of combustion, formation, or neutralization.

Mathematically it can be expressed as:

$$\Delta H = \Delta U + P\Delta V \quad (18)$$

- **Heat Capacity**

Heat capacity is the amount of heat required to change the temperature of a given amount of matter by 1 degree[3].

At constant pressure, heat supplied to the system contributes to both the work done and the change in internal energy, according to the first law of thermodynamics. The heat capacity is defined as:

$$C_p = \left( \frac{\partial Q}{\partial T} \right)_{P=cte} \quad (19)$$

From the first law of thermodynamics we can express  $\partial Q$  as a function of  $\partial U$ :

$$\partial Q = \left( \frac{\partial U}{\partial T} \right) dT + \left( \frac{\partial U}{\partial P} \right) dP + P \left[ \left( \frac{\partial V}{\partial T} \right) dT + \left( \frac{\partial V}{\partial P} \right) dP \right] \quad (20)$$

For constant pressure,  $dP = 0$ , so

$$C_p = \left( \frac{\partial Q}{\partial T} \right)_{P=cte} = \left( \frac{\partial U}{\partial T} \right) dT + P \left( \frac{\partial V}{\partial T} \right) dT \quad (21)$$

At constant volume, no expansion work is done, so the heat supplied contributes only to the change in internal energy. The heat capacity obtained this way is denoted  $C_v$ . The value of  $C_v$  is always less than the value of  $C_p$

$$C_v = \left( \frac{\partial Q}{\partial T} \right)_{V=cte} = \left( \frac{\partial U}{\partial T} \right)_V \quad (22)$$



The relationship between  $C_v$  and  $C_p$  is then:

$$C_p = C_v + \left( \left( \frac{\partial U}{\partial V} \right)_T + P \right) \left( \frac{\partial V}{\partial T} \right)_P \quad (23)$$

$C_p$  can also be expressed in terms of enthalpy, if we take into account that with a constant pressure:

$$dH_P = \left( \frac{\partial H}{\partial T} \right)_P dT, \quad \partial Q_P = dH_P, \quad C_p = \frac{\partial Q_P}{dT} = \left( \frac{\partial H}{\partial T} \right)_P \quad (24)$$

We can also calculate both  $C_p$  and  $C_v$  with fluctuation of its variables as follows[4]:

$$C_v = \frac{\langle U^2 \rangle - \langle U \rangle^2}{N_f k_B T^2} \quad C_p = \frac{H(P, T + \delta) - H(P, T - \delta)}{2\delta} \quad (25)$$

Where  $N_f$  is the number of degrees of freedom, and  $\delta$  is the value of the temperature fluctuation.

## 1.2 Statistical Thermodynamics

Macroscopic systems are an assembly of microscopic particles. Hence, it stands to reason that the behavior of a macroscopic system is determined by the properties of the microscopic particles it consists of. Statistical thermodynamics provides a quantitative link between the properties of the microscopic particles and the behavior of the bulk material.

It is a statistical theory because it uses statistics (and probabilities) and works with distributions of position and momenta. There can be a lot of particles in the system, statistic quantities such as expectation values have very little variance. Thus, for a large number of particles statistical thermodynamics is an extremely precise theory[5].

### 1.2.1 Quantum States

The quantum state (eigenstate)  $\Psi_s(x_k)$  of a single particle (atom or molecule)  $k$  is given for a system consists of  $N$  particles which do not interact with each other, by the time independent Schrödinger equation[6]:

$$\mathcal{E}_s \Psi_s(x_k) = \hat{h}_k \Psi_s(x_k) = \frac{\hbar^2}{2mk} \nabla_k^2 \Psi_s(x_k) + V_k(x_k) \Psi_s(x_k) \quad (26)$$

where  $\mathcal{E}_s$  is the associated energy eigenvalue.

$$E_j \Psi_j(x_1 \dots x_N) = \hat{H} \Psi_j(x_1 \dots x_N) = \sum_{k=1}^N \hat{h}_k \Psi_j(x_1 \dots x_N) \quad (27)$$

The energy levels are quantized, which means that only a certain value of energy is permitted

### 1.2.2 Molecular Partition Function

The partition function of the system (Q) can be expressed in terms of its constituents (q). Thus, for an ideal gas (independent and indistinguishable particles) we obtain:

$$Q = \frac{q^N}{N!}, E = E_{tras} + E_{rot} + E_{vib} + E_{elec}, q = q_{tras} + q_{rot} + q_{vib} + q_{elec} \quad (28)$$

So we have 4 different contributions, each of them can be calculated separately<sup>[4]</sup>:

$$E_{tras} = \frac{h^2 n_x^2}{8m a^2} \quad (29)$$

$$q_{tras} = \left( \frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2}} V \quad (30)$$

$$E_{rot} = hB J(J+1) \text{ where } B = \frac{h}{8\pi^2 I} \quad (31)$$

$$q_{rot} = \frac{\sqrt{\pi}}{\sigma} \frac{T^{3/2}}{\sqrt{\theta_A \theta_B \theta_C}} \text{ where } \theta_i = \frac{h^2}{8\pi^2 k_B I_i} \quad (\text{non linear}) \quad (32)$$

Where  $\sigma$  accounts of the identity plus all the symmetric rotation elements of the molecule. In addition, all the energy levels have been normalized with respect to the first one (which now is the zero of energy), thus making the partition function equal to 1 as long as T tends to zero.

$$E_{vib} = h \left( v + \frac{1}{2} \right) v_e \quad (33)$$

$$q_{vib} \cong \frac{e^{\frac{-hv_e}{2k_B T}}}{1 - e^{\frac{-hv_e}{k_B T}}} = \frac{1}{2 \sinh \left( \frac{hv_e}{2k_B T} \right)} \quad (34)$$

$$q_{ele} = g_0 + \sum_{s=1} g_s e^{-\beta \Delta \epsilon_s} \cong g_0 \quad (35)$$

Since we are talking about high energy excited states,  $E_{ele} = e^{-\beta \Delta \epsilon} \approx 0$

### 1.3 Classical Mechanics

There are different ways of obtaining the PES (Potential Energy Surface), but we are going to focus on the one that doesn't deal directly with electrons. The energy depends exclusively on the position of the nuclei, and it's based on parameters which are chosen to reproduce experimental data[7]. This method is used in systems of a great amount of atoms ( $\geq 10^4$ atoms), in order to estimate the effect of the condensed medium, such as the presence of enzymes, solvent molecules, etc.

The potential energy function will be split into two terms :

$$V = V_{intramolecular} + V_{intermolecular} \quad (36)$$

#### 1.3.1 Intramolecular terms (Bonded)

In their most general form, they can be broken down into: Bond + Angle + Dihedral + Improper (out-of-plane vibration)

- **Bonds**

The most common choice is the harmonic approximation[7]:

$$V_{bond} = \frac{1}{2}K(r - r_0)^2 \quad (37)$$

Where K is the bond strength constant, r is the actual distance between the two atoms defining the bond, and  $r_0$  is the value of the distance in the equilibrium:

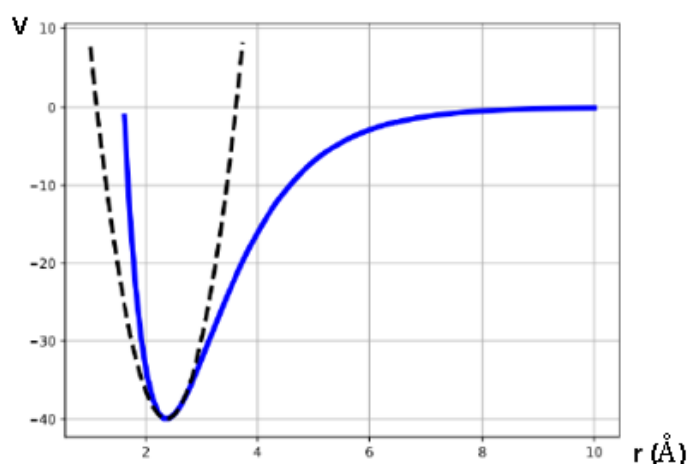


Image 1: Intramolecular term representation

This quadratic expression does not take into account the anomalies of small displacements with respect to the equilibrium position, since it is not able to reproduce the dissociation effect.

The alternative is to incorporate a Taylor Series:

$$V(r) = V(r_0) + \left(\frac{\delta V}{\delta r}\right)_{r=r_0} (r - r_0) + \frac{1}{2} \left(\frac{\delta^2 V}{\delta r^2}\right)_{r=r_0} (r - r_0)^2 + \frac{1}{3!} \left(\frac{\delta^3 V}{\delta r^3}\right)_{r=r_0} (r - r_0)^3 \dots \quad (38)$$

where  $V(r_0) = 0$  by definition (we take the bottom of the well as reference), and  $\left(\frac{\delta v}{\delta r}\right)_{r=r_0} = 0$  by minimum; or we can also make use of other expressions, such as the Morse potential:

$$V_{Morse} = D[1 - e^{-\alpha(r-r_0)}]^2 \quad (39)$$

- **Angles**

It is designed to mimic the energy of an angle between two bonds as it moves away from its equilibrium position. The harmonic expression is the most generally used[8]:

$$V_{angle}(\theta) = \frac{1}{2} K_\theta (\theta - \theta_0)^2 \quad (40)$$

The parameters are similar to those of the bonds: force constant ( $K_\theta$ ) associated with the bending motion, and the reference value of the angle ( $\theta_0$ ). Some force fields employ more complex polynomial expansions, but this is not common. Finally, a fictitious bond can also be added between the ends of the angle called Urey-Bradley term, with a low force constant and it is meant to avoid extreme deformations.

- **Torsions**

Since torsions are periodic in nature, a Fourier series is commonly used to adequately describe the energy[8]:

$$V_{dihedral}(\varphi) = \sum_i \frac{1}{2} V_i [1 + \cos(n_i \varphi - \delta_i)] \quad (41)$$

Where  $V_i$  is the force constant associated with the rotation and determines the associated energy barrier,  $n_i$  provides the periodicity, while the angle  $\delta_i$  (or phase) allows to shift the position of the energy minimum.

Different cosine functions can be combined to generate more complex behaviors (ie, a single dihedral but defined by several  $V_i/n_i/\delta_i$  terms).

- Improper

Improper torsion potentials are defined for groups of 4 bonded atoms where the central atom  $i$  is connected to the 3 peripheral atoms  $j, k$ , and  $l$ . Such group can be seen as a pyramid and the improper torsion potential is related to the distance of the central atom from the base of the pyramid. This potential is used mainly to keep molecular structures planar. As there is only one energy minimum the improper torsion term can be given by a harmonic function[8]:

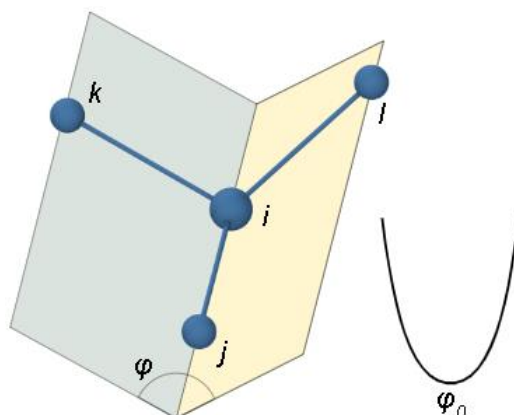


Image 2: Improper angles representation

Given by a harmonic function:

$$V_{improper} = k_{\phi}(\phi - \phi_0)^2 \quad (42)$$

Where the dihedral angle  $\phi$  is the angle between the planes  $i-j-k$  and  $i-j-l$

### 1.3.2 Intermolecular terms (Non-Bonded)

While bonded terms are used to define the covalent energy of a molecule (intramolecular), non-bonding terms are used to describe the interactions of atoms between different entities, or intermolecular (i.e., between atoms that are not directly related by bonds). In most force fields, where the charges of the atoms are non-polarizable (their charge does not vary depending on the environment) the equation of this term is usually split into:

$$V_{intermolecular} = V_{Electrostatic} + V_{Dispersive} \quad (43)$$

- **Electrostatics**

It corresponds to the electrostatic interaction between two charge distributions. In the simplest model this corresponds to the interaction between partial charges assigned to each atom:

$$V_{elec} = \frac{1}{4\pi\epsilon_0} \sum_{i,j} \frac{q_i q_j}{r_{ij}} \quad (44)$$

Where  $q_i$  and  $q_j$  are the partial charges associated with atoms  $i, j$  respectively (these charges are constant and do not change: they are parameters of the force field), and  $r_{ij}$  is the distance between both atoms. Generally the charges are obtained from quantum mechanics calculations, so that they reproduce to a large extent the electrostatic potential generated by the molecule (wave-function + nuclei) at chosen points around the molecule, and use the adequate parameters in order to reproduce macroscopical behaviors (for example, the TIP3P water molecule has a dipolar moment of 2.35D, much bigger than the experimentally observed for a water molecule of 1.85D).

- **Dispersive Terms: Lennard-Jones**

It simulates the effect of long-range dispersive forces and short-range repulsions[9]:

$$V_{disp} = \sum_{i,j} \frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^6} V_{LJ} = 4 \sum_{i,j} \epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] r_0 = \sigma 2^{1/6} \quad (45)$$

Where  $\epsilon_{ij}$  is the depth of the interaction well and  $\sigma_{ij}$  represents the point at which  $V_{LJ} = 0$

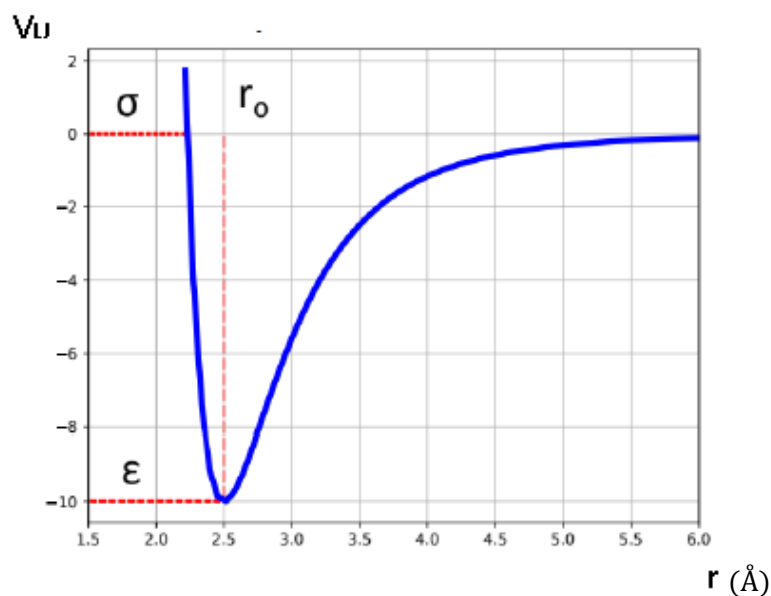


Image 3: Lennard-Jones Potential

In the case that the atoms  $i$  and  $j$  are of a different type/kind, the following rules of combination (geometric and arithmetic averages) are used:

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \quad (46)$$

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j) \quad (47)$$

Dispersive forces are the result of the combination of attractive forces between the dipoles of the molecules ( $B_{ij}$ ,  $n=6$ ), and the repulsive forces arising from the repulsions ( $A_{ij}$ ,  $n=9, \dots, 12$ ) between the electron shells, nucleus-nucleus...

A note of caution about intermolecular terms: any atoms related through a bond (1-2), as well as those involved in an angle (1-3) are not considered along the non-bonding  $V_{inter}$  calculation. Those atoms within a 1-4 relationship (dihedral and improper torsions) are included (usually scaled by a factor) to enrich the conformational equilibria (thus providing more realistic profiles than pure periodic terms):

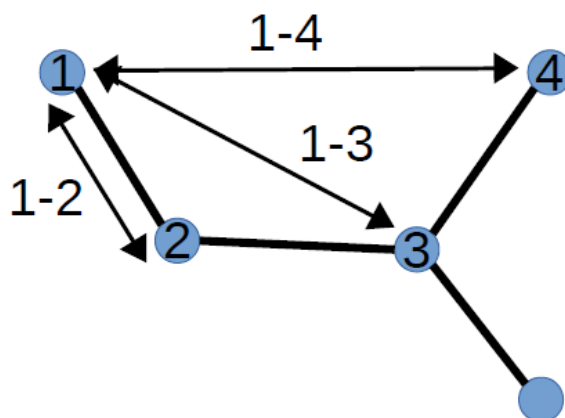


Image 4: Relations dihedrals and improper torsions involved

Finally, there are force fields which introduce more terms in the intermolecular potential (such as specific treatment for hydrogen bonds), but the standard is to rely on the two already discussed.

### 1.3.3 Periodic Boundaries

The aim of any simulation is to use models as much realistic as possible. This, in practice, summarizes to:

- number of molecules forming the system (limited by the computational power)
- number of microstates to be explored to render the averaged magnitudes (time of CPU)
- energy potential governing the model

There are techniques which allow to address the first problem, and simulate a “bulk”. For demonstrative purposes, a model consisting on  $10^4$  water molecules reduces to a spherical droplet of  $\sim 41.5 \text{ \AA}$  radius. Also, the outer molecules of the surface will experience an imbalance of forces leading to undesired effects such as Surface tension, evaporation, etc. The solution passes by applying Periodic Boundary Conditions (PBC), by surrounding the simulation cell with identical replicas. Although the total number of molecules does not increase, the molecules in the surface establish interactions in all directions:

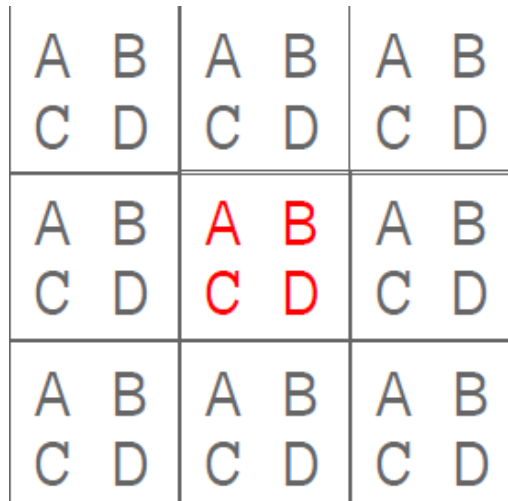


Image 5: PBC example

Cubic or Orthorhombic lattices are the most commonly used, but it is possible to use other geometries such as octahedrons, hexagonal prisms, etc.

Even so, there are still some problems:

- it is not possible to observe fluctuations with a wavelength longer than the size of the box.
- their use implies an artificial periodicity that may favor the appearance of "crystalline" structures.

Part of these problems can be avoided by using a large cell size, the others can be avoided by using minimum images and cutoffs

- Minimum Images and Cutoffs

The intermolecular terms calculations is done from the distance between pairs of atoms, and in general, this implies evaluate about  $\frac{N(N-1)}{2}$  pairs (being N the number of atoms). For big systems or by using PBC we end up calculating interactions between



distant pairs, which are usually irrelevant (for example, the Lennard-Jones potential decays to less than the 1% at distances larger than  $2.5 \sigma$ ).

One way to decrease the computational time is by means of the *minimum image convention*: only those interactions between a molecule and the closest replicas of the remaining original molecules are evaluated.

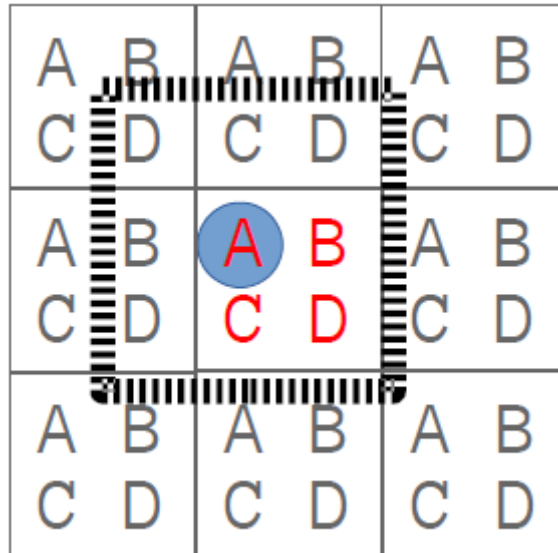


Image 6: Minimum Image for A

It can also be applied a truncation scheme: ie, a cutoff radius for pairwise interactions. It consists of canceling the interaction energy between particles that are at a larger distance than a certain value defined by the user ( $r_{cut}$ ).

For this purpose, we need to introduce the *lists of neighbors*:

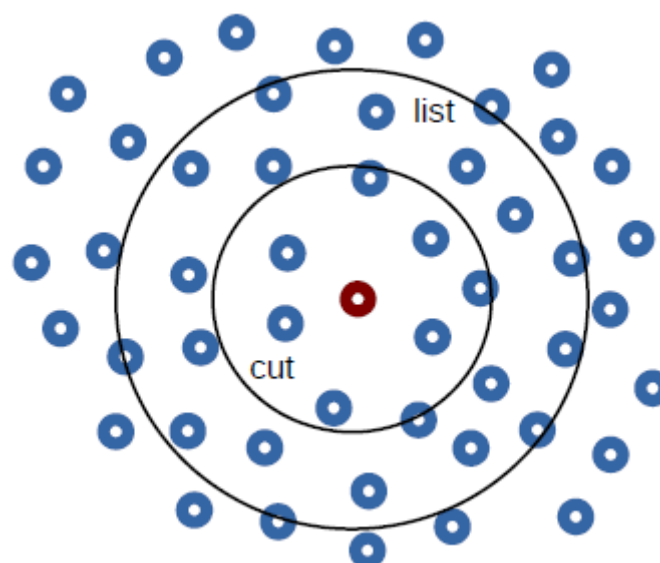


Image 7: List of Neighbors

These lists tell us which molecule/particle is close to the selected one. We need two different radii for efficiency:  $r_{list}$  is larger than  $r_{cut}$  so that molecules are allowed to move in and out of the cutoff radius and the calculation of pairs becomes efficient.

It is usually best to use a cutoff based on groups/fragments and not on atoms, to avoid abrupt variations due to the motion of the molecules around the cutoff (we make the whole group interact in the case that one of the atoms is inside the cutoff).

The main problem with truncated interactions is the discontinuities in the energy potential (and hence in the gradient) once the cutoff is exceeded:

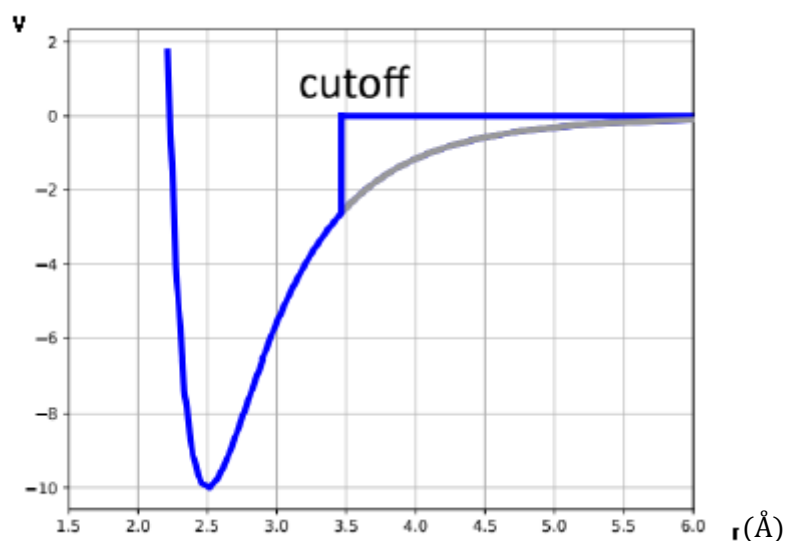


Image 8: Cutoff representation

Jumps in the potential (with discontinuities) are observed when the molecules move away from or towards each other during the simulation.

One way to avoid or smooth the effect of truncation is to use *smoothing* functions ranging from 0 to 1 as a function of distance. *Shift*-type functions apply to all interactions, while *switch*-type functions introduce an additional radius ( $r_{on}$ ) from which the smoothing is applied, so that the potential is multiplied by this value, obtaining a smoothing in the cutoff zone.

$$\gamma(r) = \begin{cases} \frac{(r_{off}^2 - r^2)^2 (r_{off}^2 + 2r^2 - 3r_{on}^2)}{r_{off}^2 - r_{on}^2} & \text{where } \begin{cases} r \leq r_{on} \\ r_{on} < r \leq r_{off} \\ r > r_{off} \end{cases} \end{cases} \quad (48)$$

Finally, there are other more sophisticated methods to evaluate electrostatic interactions such as Ewald Sums (in its most accepted variant: *Particle Mesh Ewald*, PME [10]), which takes advantage of the periodicity of the system to calculate the

interactions with the replicas (part directly, part in the reciprocal space). In these cases the unit cell to be replicated must be neutral to avoid convergence problems.

## 1.4 Molecular Dynamics

**Molecular dynamics (MD)** is a computer simulation method for analyzing the physical movements of atoms and molecules[11]. The atoms and molecules are allowed to interact for a fixed period of time, giving a view of the dynamic "evolution" of the system. In the most common version, the trajectories of atoms and molecules are determined by numerically solving Newton's equations of motion for a system of interacting particles, where forces between the particles and their potential energies are often calculated using interatomic potentials or molecular mechanical force fields.

There are two main families of MD methods, which can be distinguished according to the model (and the resulting mathematical formalism) chosen to represent a physical system. In the 'classical' mechanics approach to MD simulations molecules are treated as classical objects, resembling very much the 'ball and stick' model. Atoms correspond to soft balls and elastic sticks correspond to bonds. The laws of classical mechanics define the dynamics of the system[12].

The 'quantum' or 'first-principles' MD simulations, which started in the 1980s with the seminal work of Car and Parinello, take explicitly into account the quantum nature of the chemical bond. The electron density function for the valence electrons that determine bonding in the system is computed using quantum equations, whereas the dynamics of ions (nuclei with their inner electrons) is followed classically

Both position and velocity can be expressed as a Taylor series:

$$r(t + \delta) = r(t) + \delta \frac{dr(t)}{dt} + \frac{\delta^2}{2} \frac{d^2r(t)}{dt^2} + \dots \quad (49)$$

Where the first derivative corresponds to the velocities,  $v(t)$ , and the second to the accelerations,  $a(t)$ . Alternatively, the same result can be reached by integrating the equations of motion:

$$a = \frac{dv}{dt} \int_{v_0}^v dv = \int_{t=0}^t a dt \quad v(t + \delta) = v(t) + \delta a(t) \quad (50)$$

$$v = \frac{dr}{dt} \int_{r_0}^r dr = \int_{t=0}^t (v + at) dt \quad r(t + \delta) = r(t) + \delta v(t) + \frac{\delta^2}{2} a(t) \quad (51)$$

The initial velocities are obtained from a probability distribution function based on Maxwell-Boltzmann probability:

$$g(v_i) = \left( \frac{m_i}{2\pi k_B T_0} \right)^{\frac{1}{2}} e^{-\frac{m_i v_i^2}{2k_B T_0}} \quad \begin{array}{l} \text{gaussian} \\ \text{random} \\ \text{number} \end{array} \quad \mu = 0, \sigma = \sqrt{\frac{k_B T_0}{m_i}} \quad (52)$$

and are updated through instantaneous accelerations:

$$v(t + \delta) = v(t) + \delta a(t) \quad (53)$$

Finally, these can be obtained from Newton's second law of dynamics:

$$f_i = m_i a_i = -g_i = -\frac{\partial U}{\partial r_i} \quad (54)$$

These integrated equations of motion are used in different ways, giving rise to different algorithms.

Once the method of integration of the equations of motion has been selected, the next step is to determine the thermodynamic variables which will be controlled, thus defining the working *ensemble* (NVE, NVT, ...) [13].

We usually work under canonical collective conditions, in which number of particles (N), volume (V) and temperature (T) remain constant, which allows us to calculate the Helmholtz free energy. From a practical point of view, keeping N constant is implicit during the simulations (since no particle disintegrates). As far as the volume is concerned, it is also simple (or natural) if periodic boundary conditions are applied, or the external part of the model is kept "frozen" (immobile during the simulations). To keep the temperature constant we can resort to different approximations. In fact, the temperature can be related to the kinetic energy (K) of a system from the root mean square velocity expression:

$$v_{rms} = \langle v^2 \rangle = \left( \frac{3k_B T}{m} \right)^{1/2} \quad T = \frac{2}{N_f k_B} K \quad (55)$$

Where  $N_f$  is the number of degrees of freedom of the system (in Cartesians:  $3N$ ). Once the instantaneous temperature is known, the solution is to scale the velocities appropriately during the dynamics in order to keep the average temperature constant.

Finally, whatever the equations selected, during the dynamics could be necessary to eliminate the rotation and translation modes of the system (represented as a rigid solid). For this purpose, Eckart's conditions are applied to the gradient vector, in which both linear (translation) and angular (rotation) momentum cancel out:

$$\sum m_i(r_i - r_i^{mc}) = 0 \quad \sum m_i(r_i \wedge r_i^{mc}) = 0 \rightarrow g' = g - \sum_{i=1}^6 \left( \frac{\Lambda_i^T g}{\Lambda_i^T \Lambda_i} \right) \Lambda_i \quad (56)$$

$$\begin{cases} T_x \propto \sqrt{m}(1,0,0) \\ R_x \propto \sqrt{m}(0,-z,y) \end{cases}$$

Where  $r_i^{mc}$  is referred to the corresponding mass center of the system, and  $\Lambda_i$  are the resulting orthonormal set derived from the translations  $(T_x, T_y, T_z)$  and rotations  $(R_x, R_y, R_z)$ .

#### 1.4.1 Integration: Velocity-Verlet

The integration method that we are going to use to solve the equations of motion is the Velocity-Verlet method, which uses the velocities in each step, and these are updated using accelerations, but for this we need to use information from two different times to introduce stability and reducing the numerical error<sup>[14]</sup>:

$$r(t + \delta) = r(t) + \delta v(t) + \frac{\delta^2}{2} a(t) \quad v(t + \delta) = v(t) + \frac{\delta}{2} (a(t) + a(t + \delta)) \quad (57)$$

## 1.5 LAMMPS

LAMMPS is an open source classical molecular dynamics code that models ensembles of particles in a liquid, solid, or gaseous state. It can model atomic, polymeric, biological, solid-state (metals, ceramics, oxides), granular, coarse-grained, or macroscopic systems using a variety of interatomic potentials (force fields) and

boundary conditions. It can model 2D or 3D systems with sizes ranging from only a few particles up to billions[15].

LAMMPS can be built and run on single laptop or desktop machines. It will run in serial and on any parallel machine that supports the MPI message-passing library. This includes shared-memory multicore, multi-CPU servers and distributed-memory clusters and supercomputers. Parts of LAMMPS also support OpenMP multi-threading, vectorization, and GPU acceleration.

In the most general sense, LAMMPS integrates Newton's equations of motion for a collection of interacting particles. A single particle can be an atom or molecule or electron, a coarse-grained cluster of atoms, or a mesoscopic or macroscopic clump of material. The interaction models that LAMMPS includes are mostly short-ranged in nature; some long-range models are included as well.

LAMMPS uses neighbor lists to keep track of nearby particles. The lists are optimized for systems with particles that are repulsive at short distances, so that the local density of particles never becomes too large.

## 2. OBJECTIVES

The purpose of this paper, as stated before, is to calculate the thermodynamical variables aforementioned (U, Cp, Cv, H) utilizing LAMMPS, and compare them to the ones on the bibliography (Cp, Cv and density extracted from the National Institute of Standards and Technology chemistry webbook Library).

We will be studying  $CO_2$ ,  $MeOH$  and  $H_2O$ ; particularly for  $H_2O$ , we'll look at 4 different sets of parameters due to its importance in biological systems. With this, we'll see if the type of conformation taken into account by the LAMMPS software has an influence on the outcome.

This study will be done under a fixed pressure with changing temperatures, specifically 1 atm for the pressure and a temperature varying from 290 to 310 in increments of 5 K and a rigid model will also be taken into account when doing the calculations.

As for the water models, we will be studying 4 different types of approach to the way that we treat the initial data:

**Model 1)** PIP3P water model

**Model 2)** PIP3P water model with Ewald summation [16]

**Model 3)** PIP3P water model with a CHARMM force field [\[17\]](#)

**Model 4)** SPC/E [\[18\]](#)

### 3. METHODOLOGY

The first thing we have to do is define a box forming our model. For this we will need the values of a bunch of variables, such as atomic number, bond length, dihedral angles, etc. We will be using the following parameters:

For each model, we will need specific parameters, for this we will use our  $CO_2$  input as an example:

C	6	0.055855	2.757
O	8	0.159860	3.033

 (1)

C	-0.00790	0.02878	0.01780	0.6512
O	-0.71622	0.69226	-0.64615	-0.3256
O	0.70035	-0.63498	0.68153	-0.3256

 (2)  
(3)

C O	1282.462	1.149
-----	----------	-------

 (4)

O C O	147.5997	180
-------	----------	-----

 (5)

0.040824
3259

 (6)

(1) LJ parameters for the atoms involved ( $Z$ ,  $\epsilon$  (kcal/mol),  $\sigma$  (Å))

(2) Example of a geometry of a molecule (x, y, z coordinates)

(3) Partial charges of the atoms

(4) Bonded parameters ( $K$  (kcal/mol Å<sup>2</sup>),  $r_0$ )

(5) Angle parameters ( $K_\theta$  (kcal/mol rad<sup>2</sup>),  $\theta$  (degree))

(6) In order, molar density of the molecule and number of atoms for the cubic system

In this case, there are two bonds but they are equivalent so we only have to define one of them. The dimensions of the initial boxes that we are going to use will be (28x63x63) for CO<sub>2</sub>, (47x47x47) for H<sub>2</sub>O and (60x60x60) for MeOH.

After this, we prepared a code to introduce our simulation into LAMMPS to calculate the variables utilizing NVT and NPT processes. We will be using 4 inputs:

- 1) Setup/ NPT balance
- 2) NPT production
- 3) NVT balancing
- 4) NPT production

1) The setup/balancing for NPT input that we ended up using is this:

<b>units</b>	<b>real</b>	}	this part defines the type of system, using real units and a periodic boundary
<b>boundary</b>	<b>p p p</b>		
<b>atom_style</b>	<b>full</b>		

<b>pair_style</b>	<b>lj/cut/coul/long 12</b>	}	This indicates the type of interaction pairwise, specifying that we have Lennard-Jones with long range coulomb interaction
<b>kpspace_style</b>	<b>pppm 1.0e-4</b>		

<b>pair_modify</b>	<b>mix arithmetic</b>	}	This specifies the combination rules to follow (arithmetic). We then define the style/equations of bonds, angles and dihedrals present on the molecules.
<b>bond_style</b>	<b>harmonic</b>		
<b>angle_style</b>	<b>harmonic</b>		
<b>dihedral_style</b>	<b>fourier</b>		
<b>special_bonds</b>	<b>charm</b>		

<b>variable</b>	<b>temp equal 300</b>	}	We specify the value of all needed variables, such as temperature, pressure, number of steps and the rate at which the output gives us information
<b>variable</b>	<b>pres equal 1</b>		
<b>variable</b>	<b>nstp equal 1000000</b>		
<b>variable</b>	<b>fout equal 10</b>		

<b>read_data</b>	<b>../00.data</b>	→	We read the initial data
------------------	-------------------	---	--------------------------



```
thermo      1
thermo_style multi
minimize    1.0e-4 1.0e-6 1000 10000
```

} We minimize the energy of the system by adjusting atom coordinates, stopping when we reach the local energy minimum

```
neigh_modify every 1 delay 0 check yes
```

→ update the interaction tables

```
velocity    all create ${temp} 31416
reset_timestep 0
```

} generates an ensemble of random velocities at a specified temperature

```
thermo      ${fout}
thermo_style custom step temp enthalpy density vol
fix         1 all langevin ${temp} ${temp} 100 31416
fix         2 all nph iso ${pres} ${pres} 1000
run         ${nstp}
```

} This prints the thermodynamic info that we specify, setting a fix to take into account the Langevin temp control and constant pressure conditions

```
write_data  01.data
write_dump  all xyz 01.xyz modify sort id element X
```

} Write all the data and the coordinates of X atoms

2)The NPT production input would be:

```
units      real
```

```
boundary   p p p
```

```
atom_style full
```

```
pair_style lj/cut/coul/long 12
```

```
kspace_style pppm 1.0e-4
```

```
pair_modify mix arithmetic
```

```
bond_style harmonic
```

```
angle_style harmonic
```

```
dihedral_style harmonic
```

```
special_bonds charmm
```

```
variable   temp equal 300
```

```

variable    pres equal 1
variable    nstp equal 1000000
variable    fout equal 10

```

```

read_data   @@@@

```

```

neigh_modify every 1 delay 0 check yes

```

```

velocity    all create ${temp} 31416

```

```

variable    avrH2 equal enthalpy^2
variable    avrH  equal enthalpy
variable    avrT  equal temp
variable    avrD  equal density
variable    avrV  equal vol

```

} We define all of the,  
variables that we are  
going to calculate

```

fix         nptH2 all ave/time 1 ${nstp} ${nstp} v_avrH2
fix         nptH  all ave/time 1 ${nstp} ${nstp} v_avrH
fix         nptT  all ave/time 1 ${nstp} ${nstp} v_avrT
fix         nptD  all ave/time 1 ${nstp} ${nstp} v_avrD
fix         nptV  all ave/time 1 ${nstp} ${nstp} v_avrV

```

} Update the variables as the  
code processes the data

```

thermo      ${fout}

```

```

thermo_style custom step temp enthalpy v_avrH2 density vol

```

```

fix         1 all npt temp ${temp} ${temp} 100 iso ${pres} ${pres} 1000

```

```

run         ${nstp}

```

```

print       "=====
print       "<H2>: $(f_nptH2)_(kcal/mol)^2"
print       "<H> : $(f_nptH) _kcal/mol"
print       "<T> : $(f_nptT) _K"
print       "<D> : $(f_nptD) _g/cm^3"
print       "<V> : $(f_nptV) _ang^3"
print       "=====

```

} We print all of the information  
calculated by the program

**write\_data** lammps.data

**write\_dump** all xyz lammps.xyz modify sort id element X

3)The NVT setup would be:

**units** real

**boundary** p p p

**atom\_style** full

**pair\_style** lj/cut/coul/long 12

**kpace\_style** ppm 1.0e-4

**pair\_modify** mix arithmetic

**bond\_style** harmonic

**angle\_style** harmonic

**dihedral\_style** harmonic

**special\_bonds** charmm

**variable** temp equal 300

**variable** nstp equal 1000000

**variable** fout equal 10

**read\_data** @@@@

**neigh\_modify** every 1 delay 0 check yes

**velocity** all create \${temp} 31416

**reset\_timestep** 0

```

thermo      ${fout}
thermo_style custom step temp etotal
fix        1 all nvt temp ${temp} ${temp} 100.0
run        ${nstp}

```

} Similar to the 1) setup, we take into account a constant volume and print all of the variables

```

write_data  lammmps.data
write_dump  all xyz lammmps.xyz modify sort id element X

```

4)The NVT production input would be:

```

units      real
boundary   p p p
atom_style  full
pair_style  lj/cut/coul/long 12
kspace_style  ppm 1.0e-4

```

```

pair_modify  mix arithmetic
bond_style   harmonic
angle_style  harmonic
dihedral_style harmonic
special_bonds charmm

```

```

variable    temp equal 300
variable    nstp equal 1000000
variable    fout equal 10

```

```

read_data   @@@@

```

```

neigh_modify every 1 delay 0 check yes

```

```

velocity    all create ${temp} 31416

```

```

reset_timestep 0

```

```

variable    avrE equal etotal
variable    avrE2 equal etotal^2
variable    avrT equal temp
fix         nvtE all ave/time 1 ${nstp} ${nstp} v_avrE
fix         nvtE2 all ave/time 1 ${nstp} ${nstp} v_avrE2
fix         nvtT all ave/time 1 ${nstp} ${nstp} v_avrT

```

} We define the energy,  
average energy and  
average temperature.

```

thermo      ${fout}
thermo_style custom step temp etotal v_avrE2
fix         1 all nvt temp ${temp} ${temp} 100.0
run         ${nstp}

```

```

print       "=====
print       "<E2>: $(f_nvtE2)_(kcal/mol)^2"
print       "<E> : $(f_nvtE) _kcal/mol"
print       "<T> : $(f_nvtT) _K"
print       "=====

```

} We print the values of the square  
of the energy, the energy and the  
temperature

```

write_data  lammps.data
write_dump  all xyz lammps.xyz modify sort id element X

```

## 4. RESULTS AND OBSERVATIONS

In the following graphs we will see in orange a running average of the thermodynamical variable shown in the header, this is done for both NPT and NVT conditions. We will only be showing the graphs for 300 K for conciseness sake and the corresponding model for all of them, all of the other temperatures will be represented in the annex.

CO<sub>2</sub>

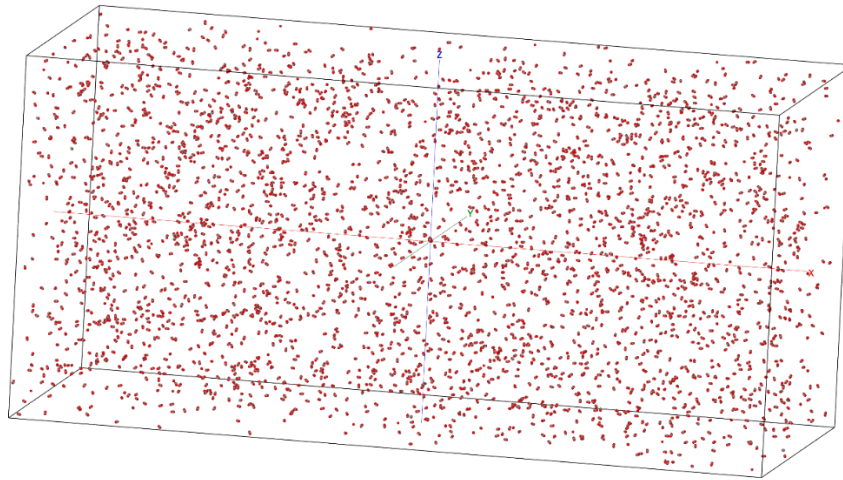


Image 9: CO<sub>2</sub> model (63x28x28)

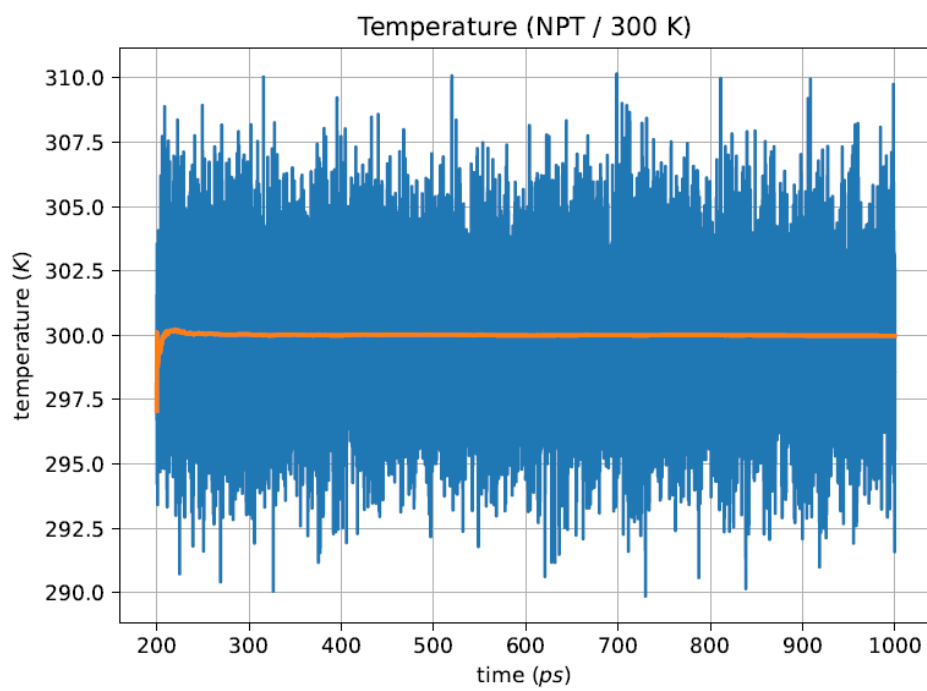


Image 10: NPT temperature at 300K for CO<sub>2</sub>

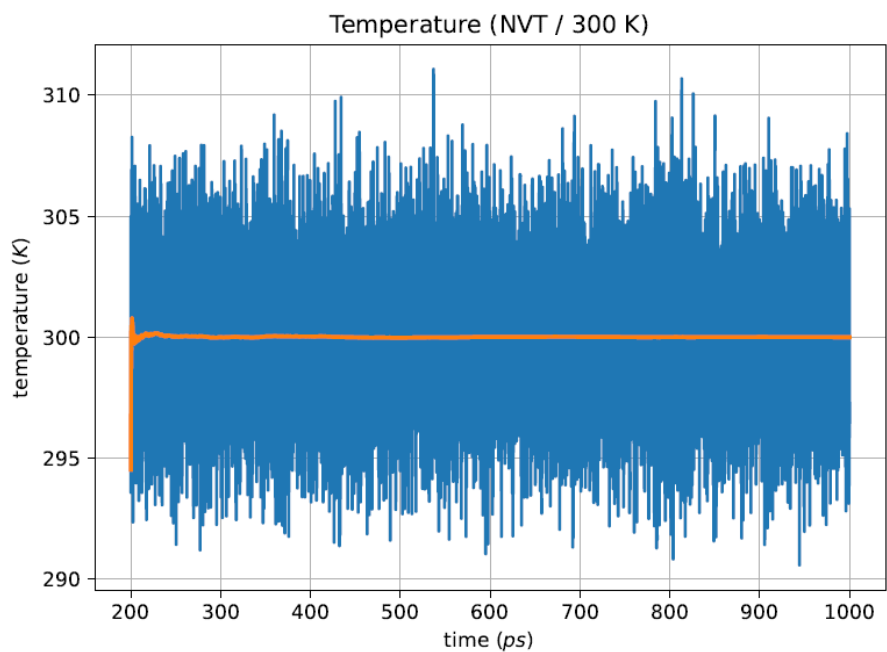


Image 11:NVT temperature at 300K for CO<sub>2</sub>

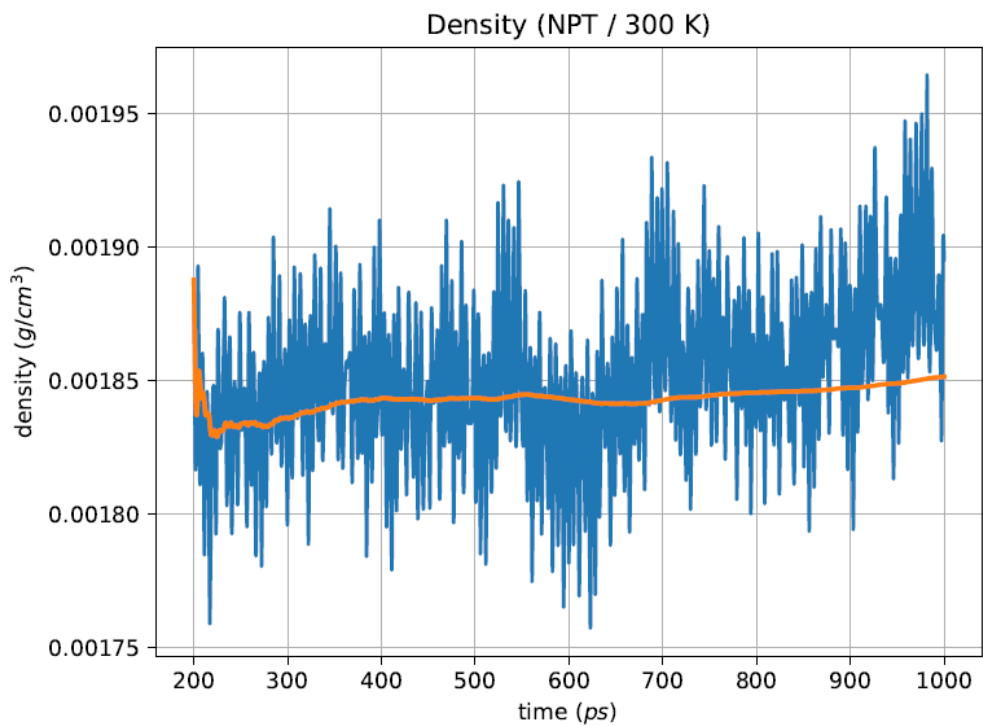


Image 12:NPT density at 300K for CO<sub>2</sub>

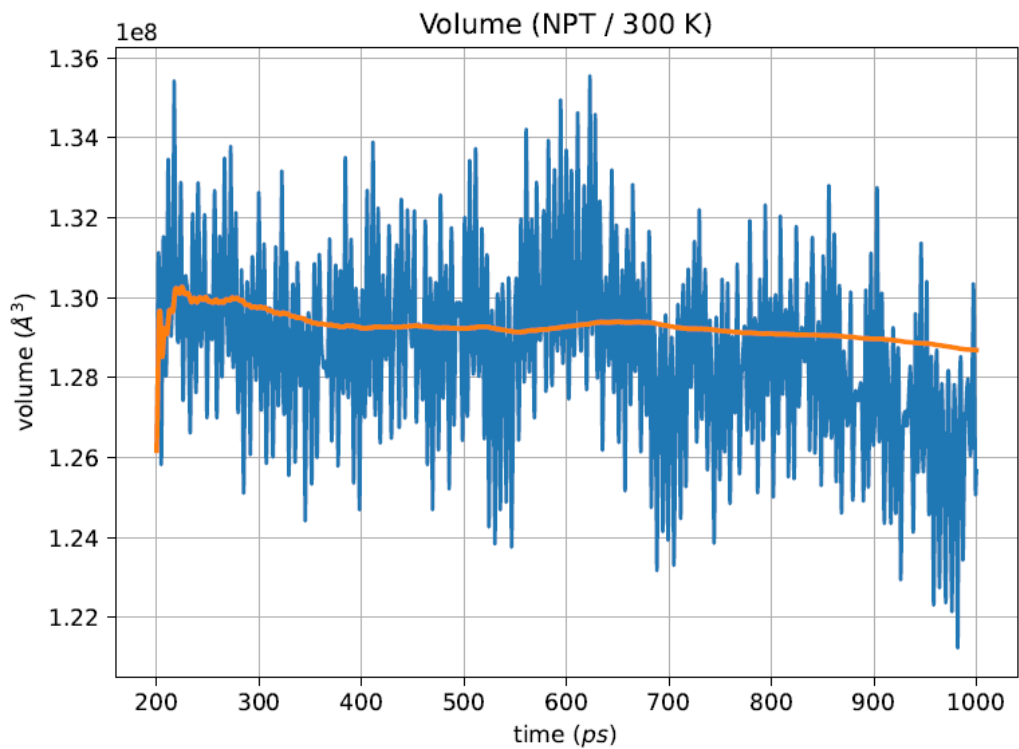


Image 13: NPT volume at 300K for  $CO_2$

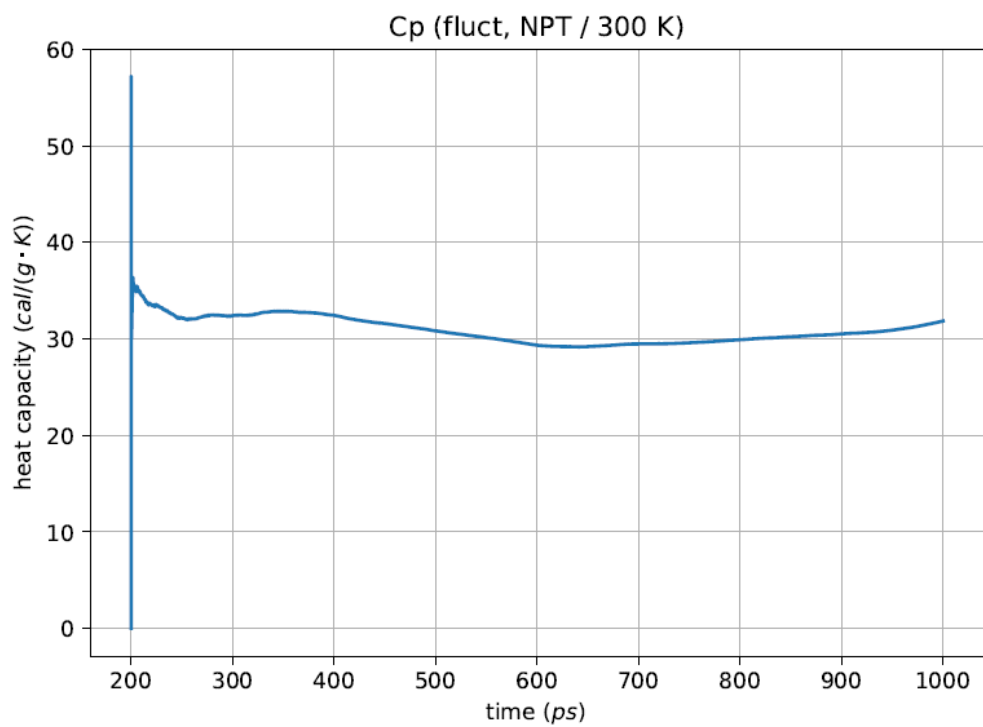


Image 14:  $C_p$  at 300K for  $CO_2$



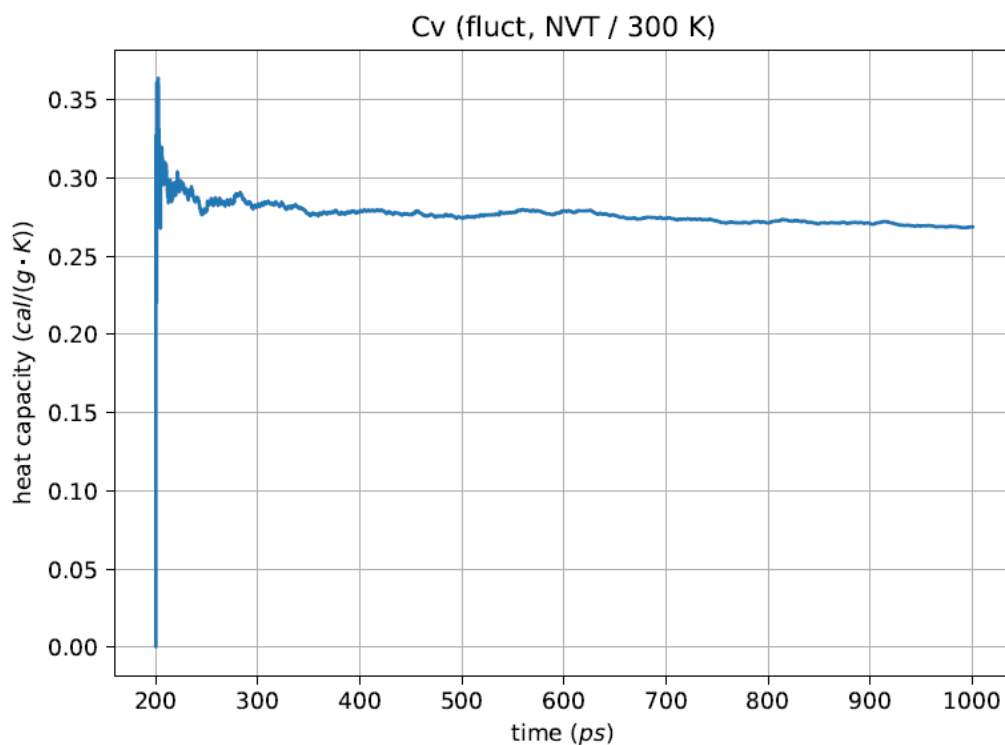


Image 15:Cv at 300K for  $CO_2$

## MeOH

### Parameters

**C 6 0.0780 3.6527**

**O 8 0.1921 3.1449**

**Hx 1 0.0460 0.4000**

**H 1 0.0240 2.3876**

**O 0.70790 0.00000 0.00000 -0.65**

**C -0.70790 0.00000 0.00000 -0.04**

**H -1.07320 -0.76900 0.68520 0.09**

**H -1.07310 -0.19471 -1.01130 0.09**

**H -1.06320 0.97861 0.33120 0.09**

**Hx 0.99360 -0.88040 -0.29800 0.42**

**C H 322.00 1.1110**

**C O 428.00 1.4200**

O Hx 545.00 0.9600

O C H 45.90 108.89

C O Hx 57.50 106.00

H C H 35.50 108.40

H C O Hx 1 0.1800 3 0.00

24.486

3185

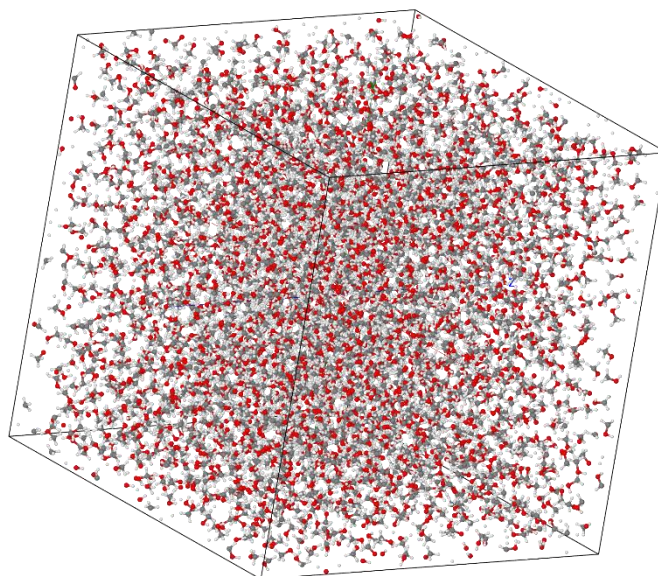


Image 16:MeOH model (60x60x60)

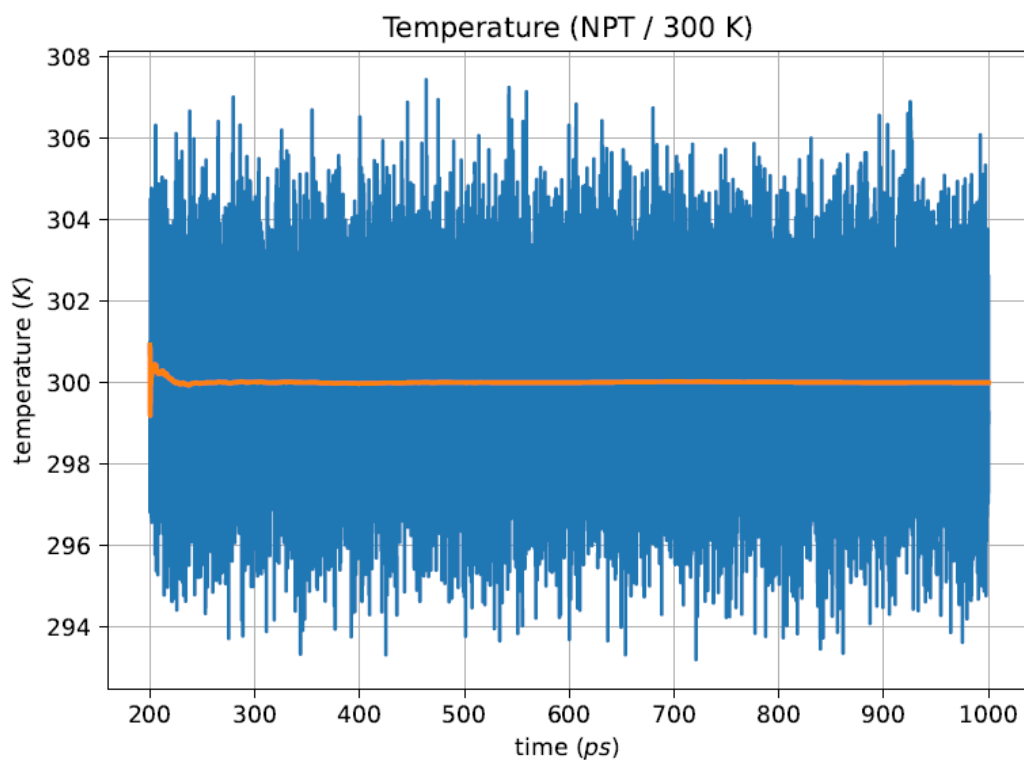


Image 17:NPT temperature at 300K for *MeOH*

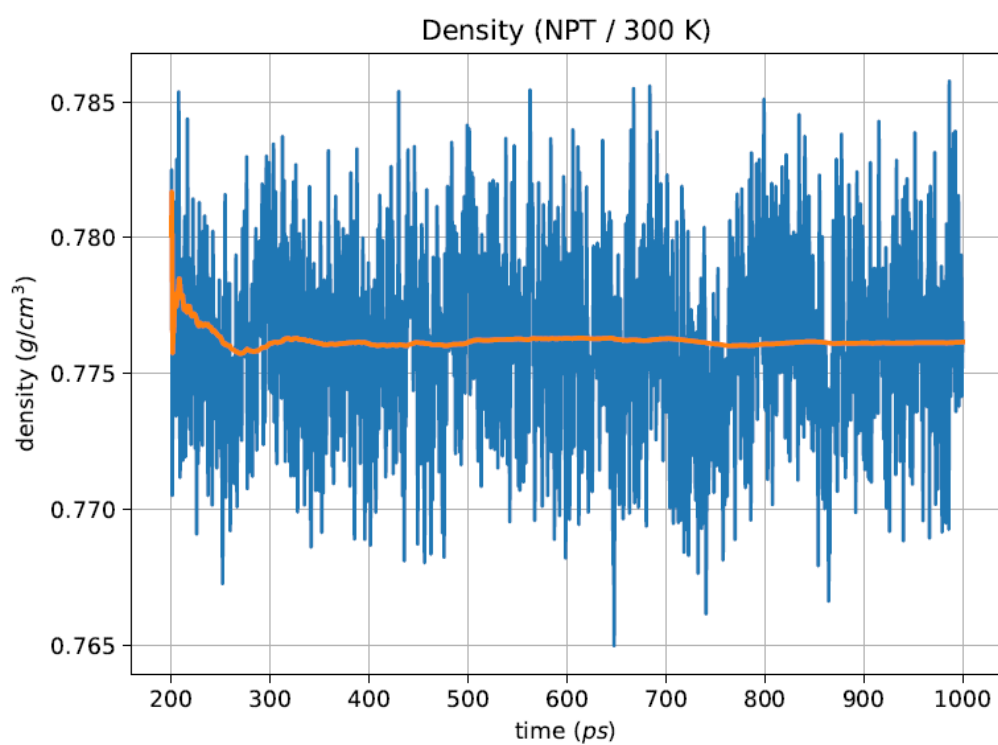


Image 18:NPT density at 300K for *MeOH*

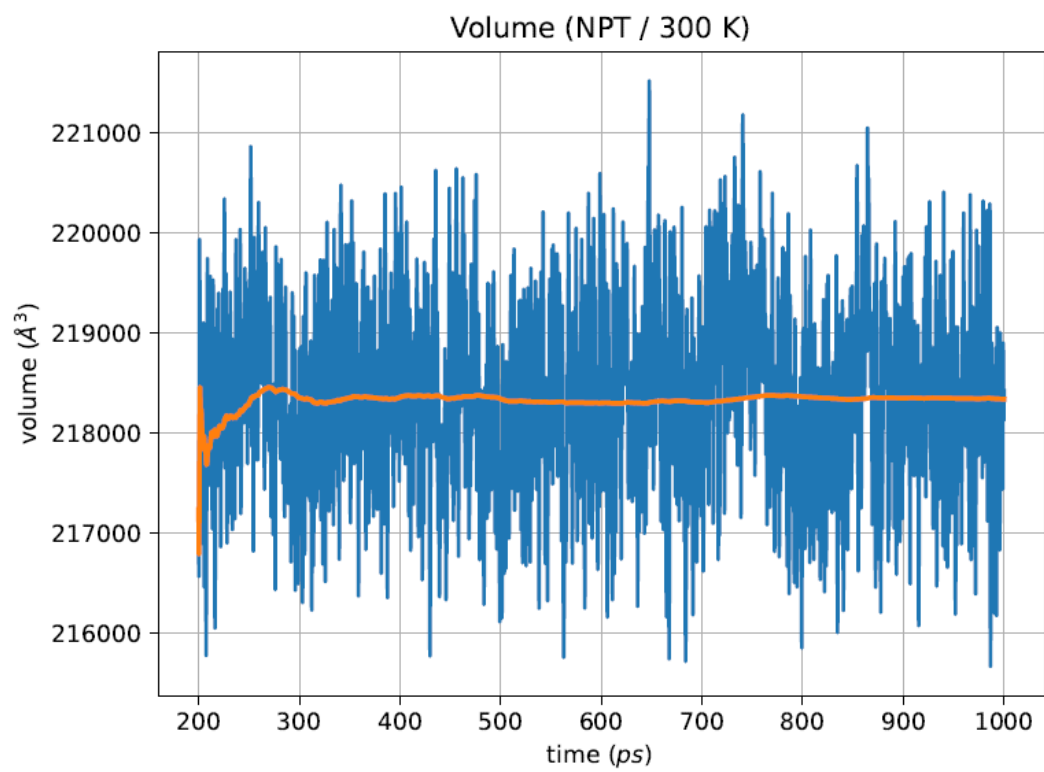


Image 19:NPT Volume at 300K for *MeOH*

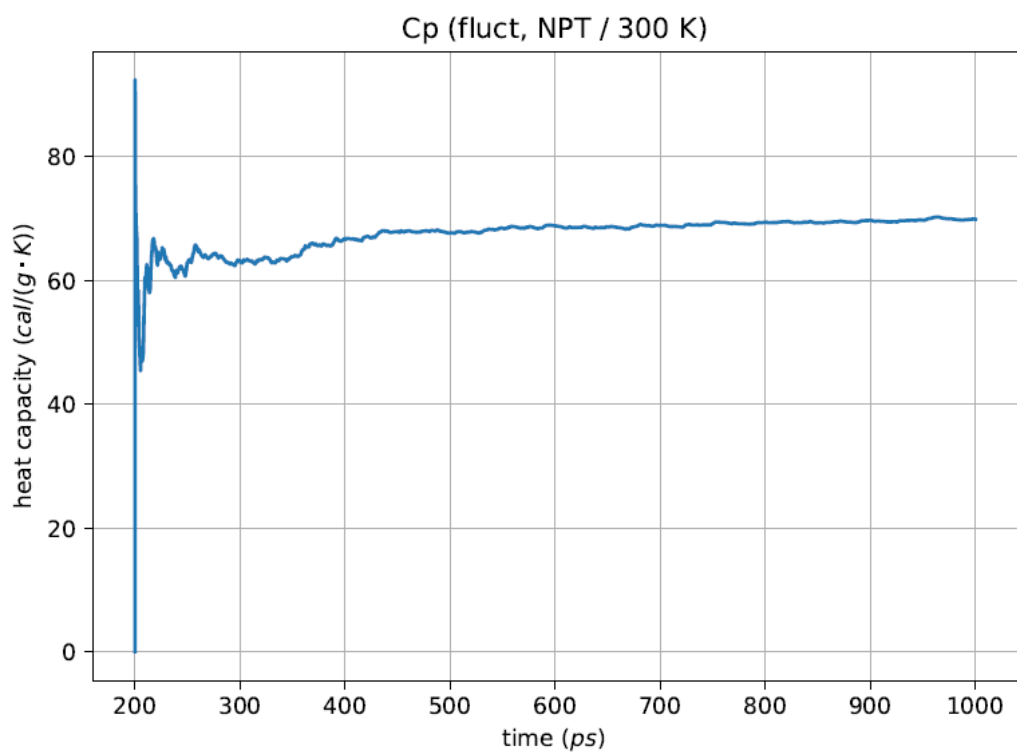


Image 20:Cp at 300K for *MeOH*

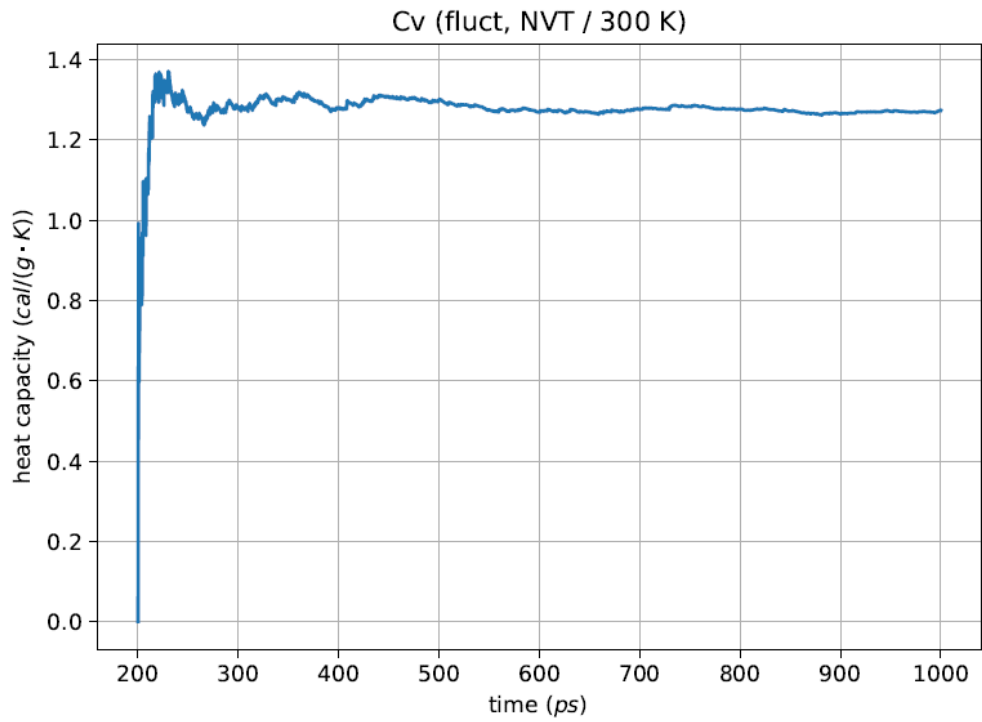


Image 21: Cv at 300K for *MeOH*

Now, we will be showing the results for MeOH utilizing a **rigid model**::

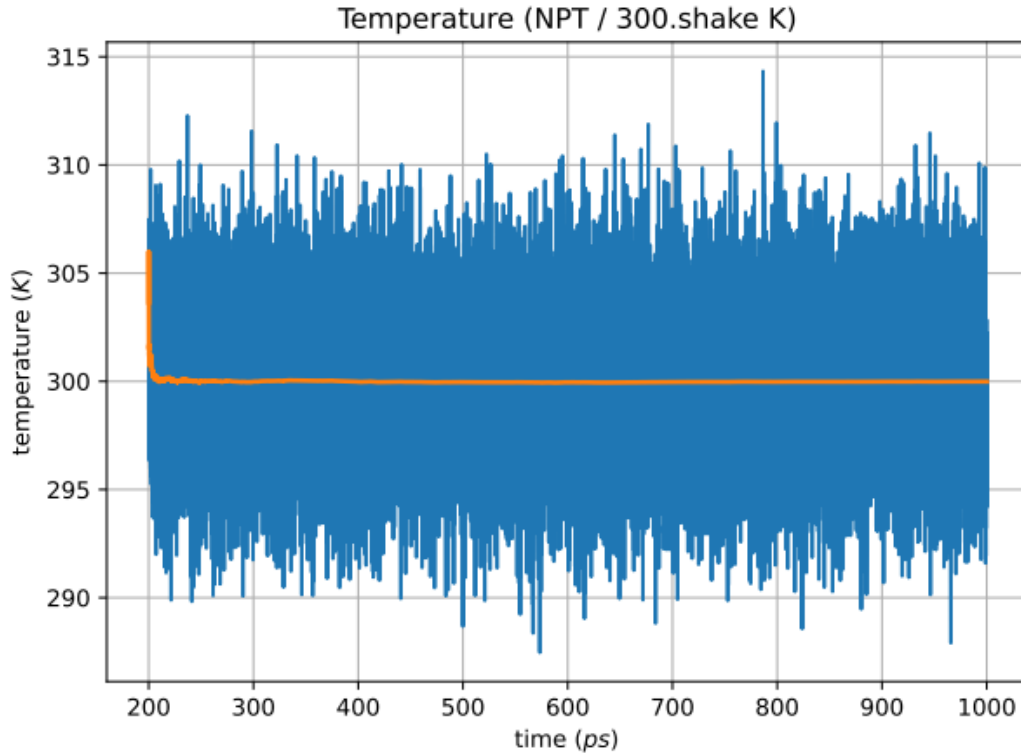


Image 22:NPT temperature at 300K for rigid *MeOH*

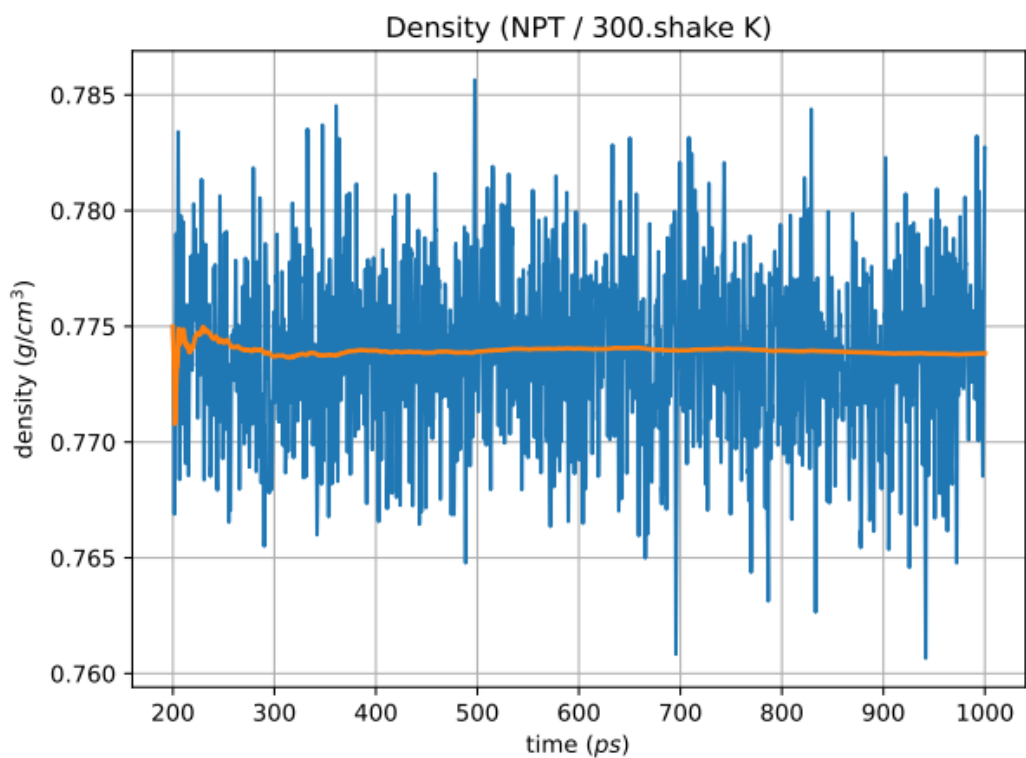


Image 23:NPT density at 300K for rigid *MeOH*

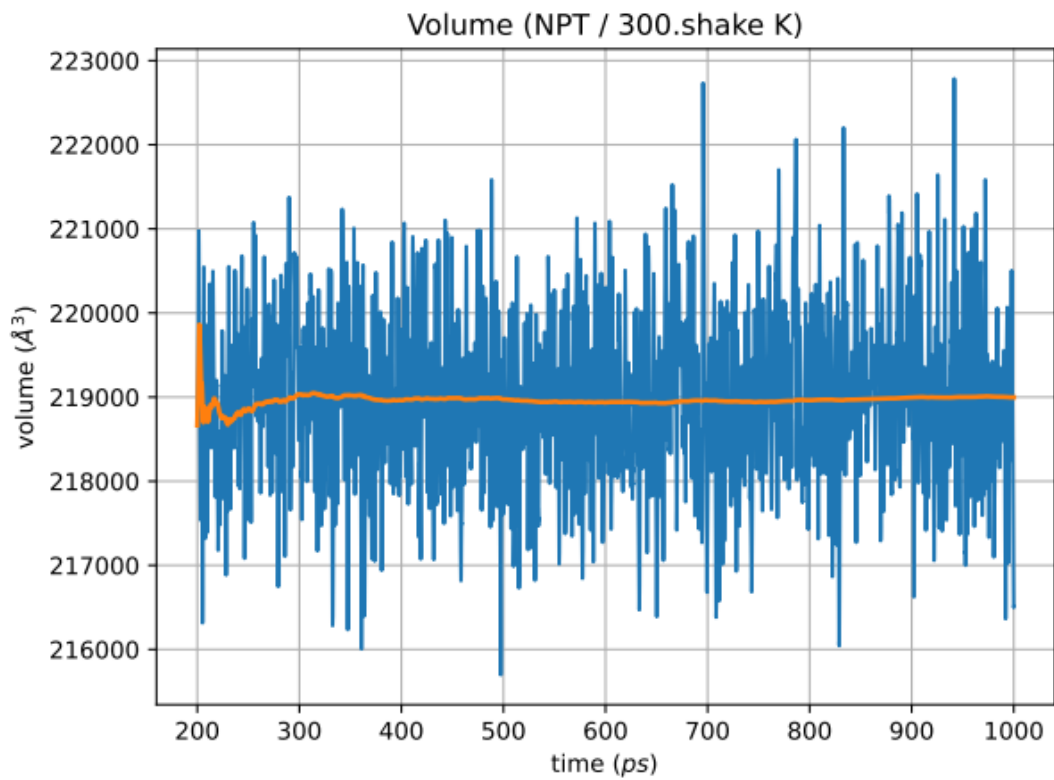


Image 24:NPT volume at 300K for rigid *MeOH*

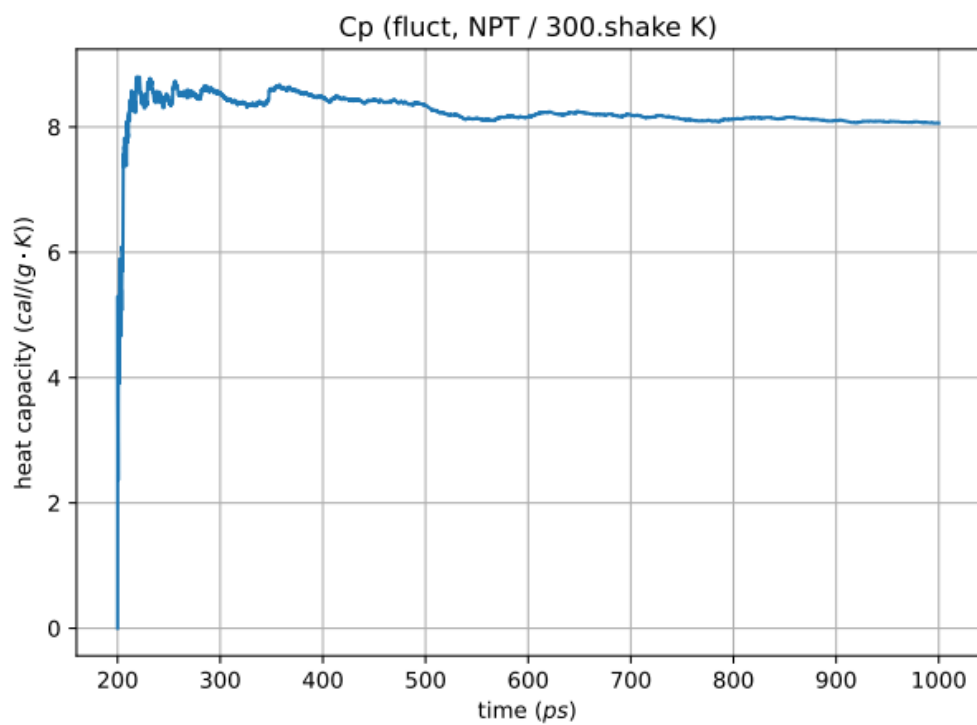


Image 25:Cp at 300K for rigid *MeOH*

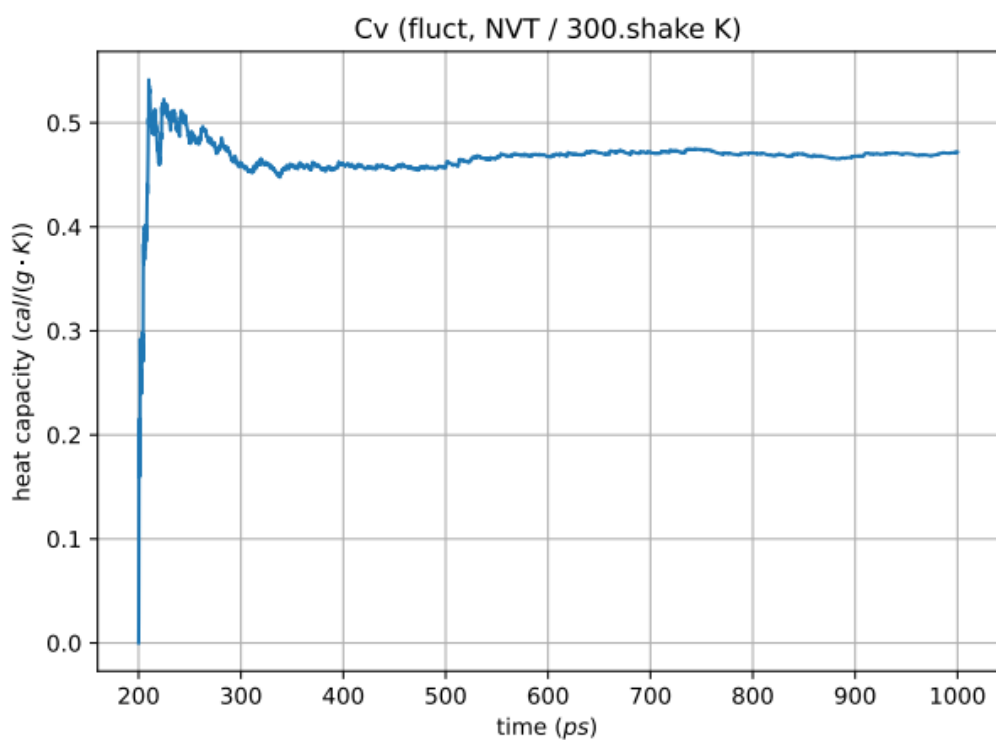


Image 26:Cv at 300K for rigid *MeOH*

## H<sub>2</sub>O

For the H<sub>2</sub>O, we will only show the first model, all of the other ones will be discussed in the annex. With that said, the results are:

### Parameters

O 8 0.102 3.188

H 1 0.000 0.000

O 0.000000 0.000000 0.000000 -0.834

H 0.900000 0.000000 0.000000 0.417

H -0.225340 0.871330 0.000000 0.417

H O 450.0 0.9572

H O H 55.0 104.52

55.31734

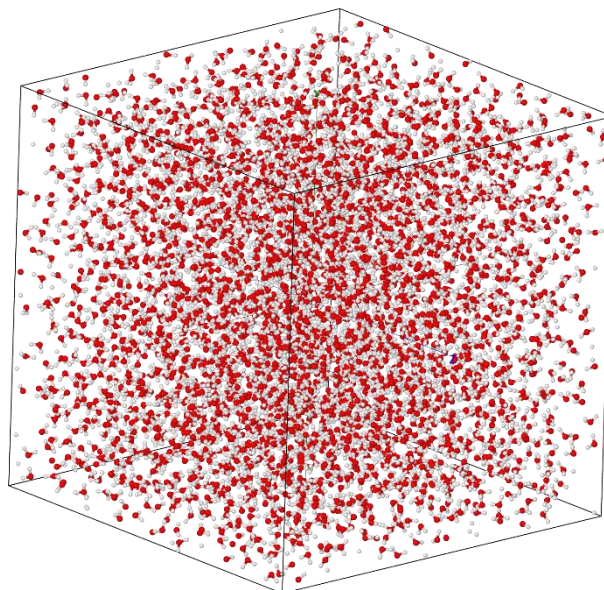


Image 27: Water model (47x47x47)



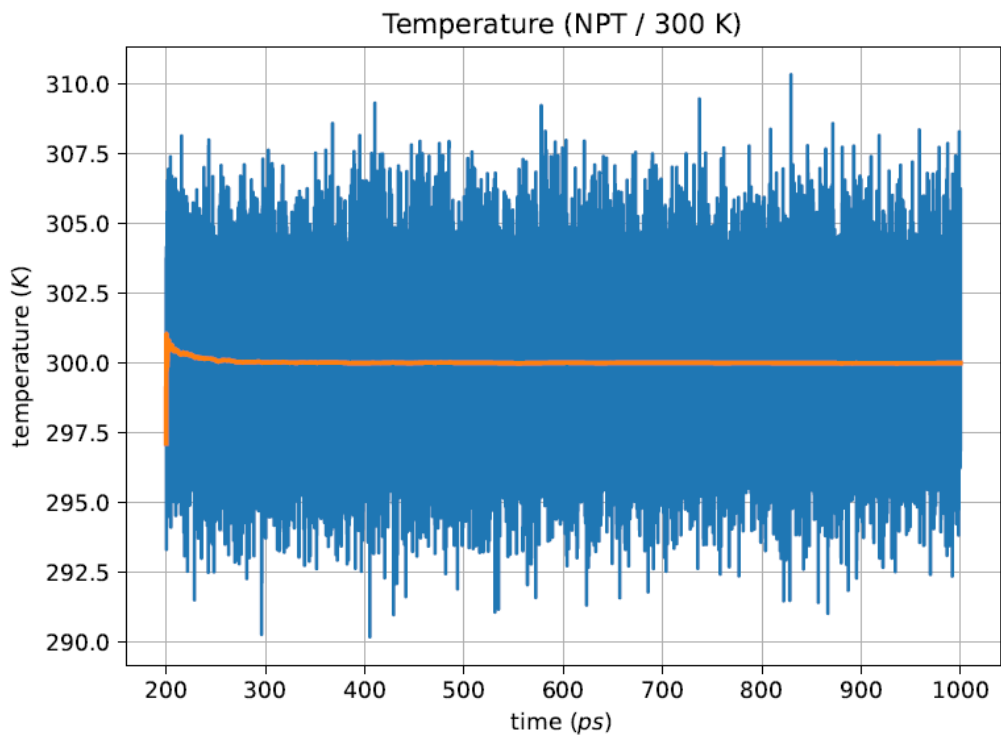


Image 28:NPT temperature at 300K for  $H_2O$  model 1

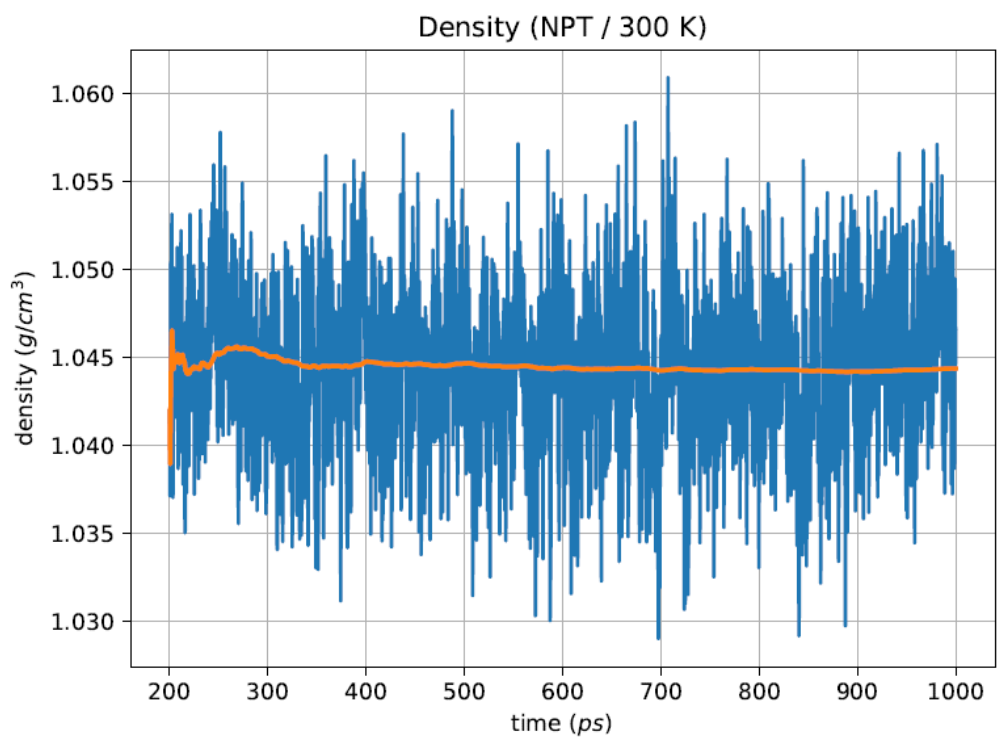


Image 29:NPT density at 300K for  $H_2O$  model 1

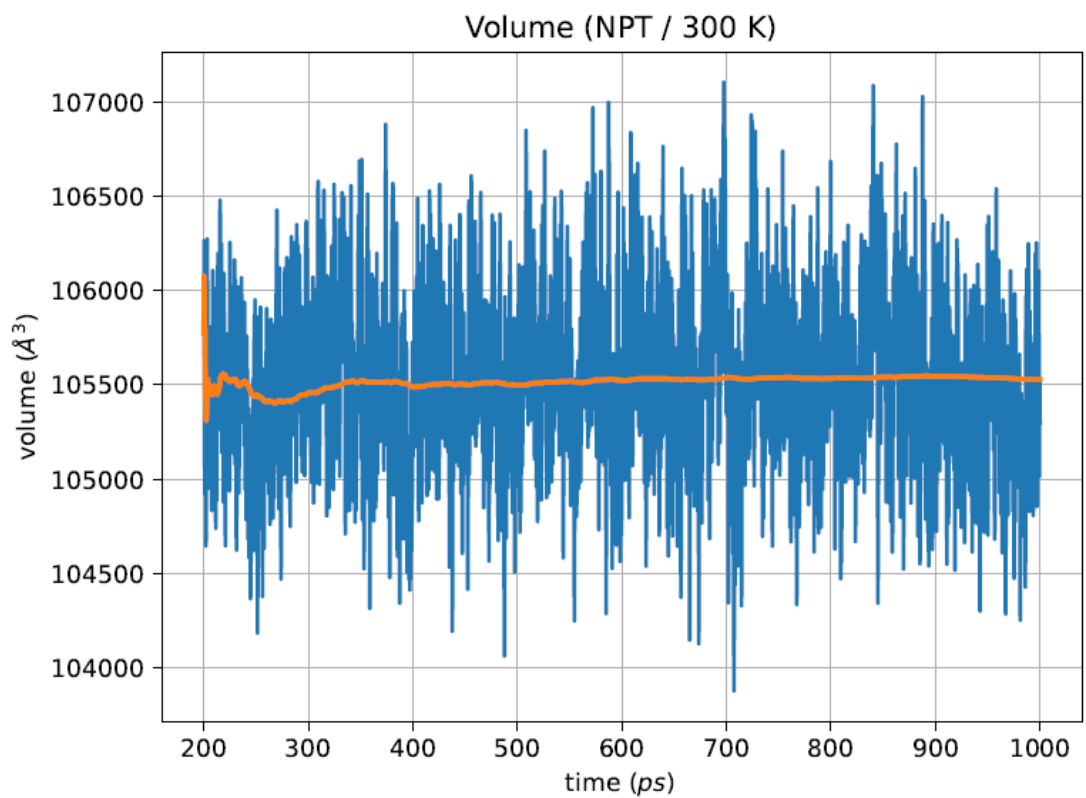


Image 30:NPT volume at 300K for  $H_2O$  model 1

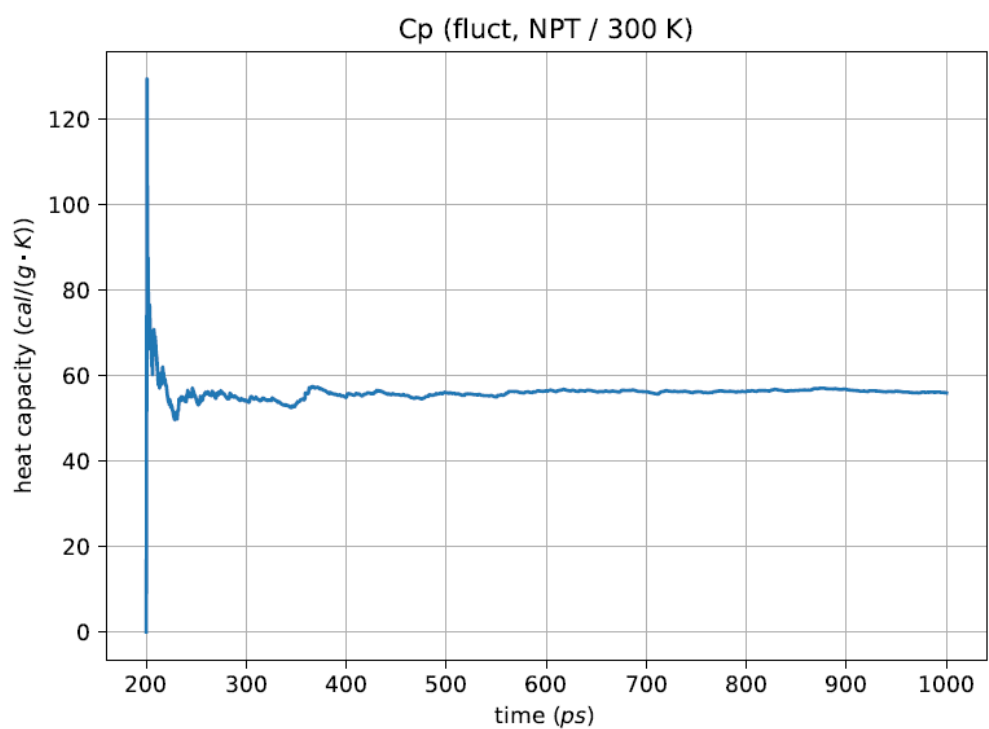


Image 31:Cp at 300K for  $H_2O$  model 1

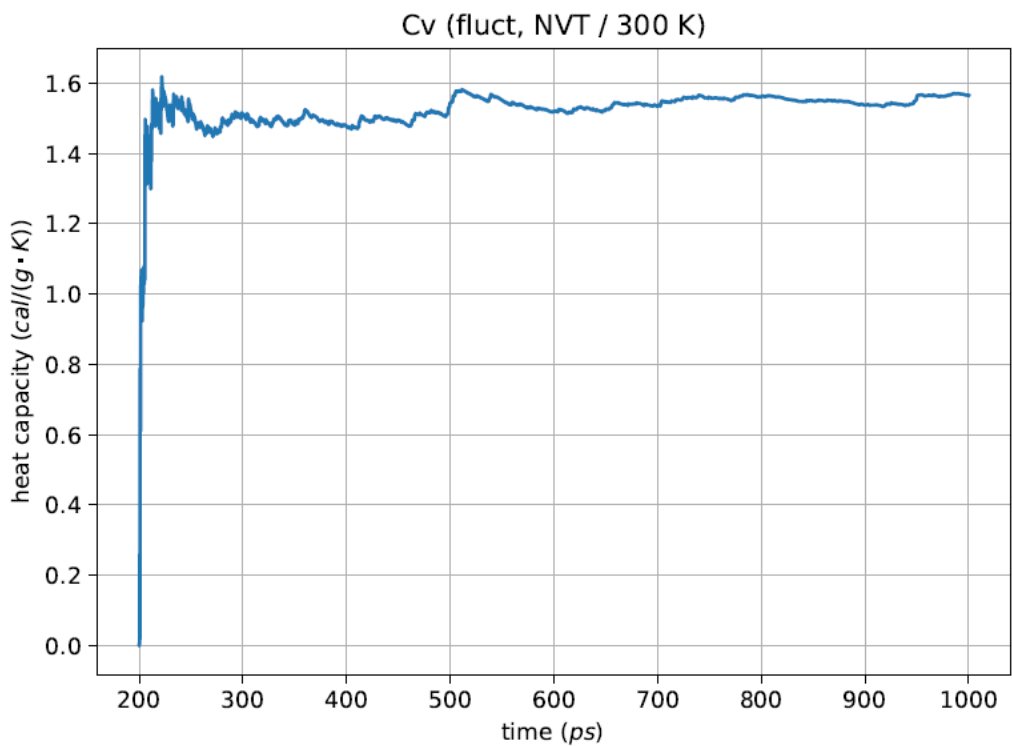


Image 32: Cv at 300K for  $H_2O$  model 1

As for the water with the **rigid model**:

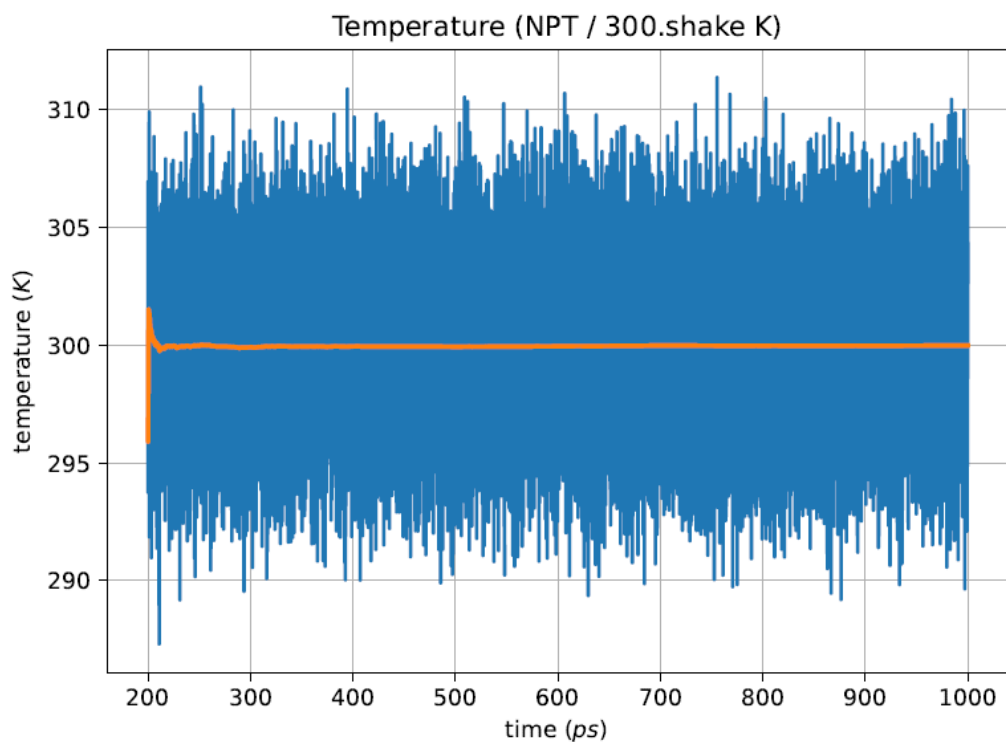


Image 33:NPT temperature at 300K for rigid  $H_2O$  model 1

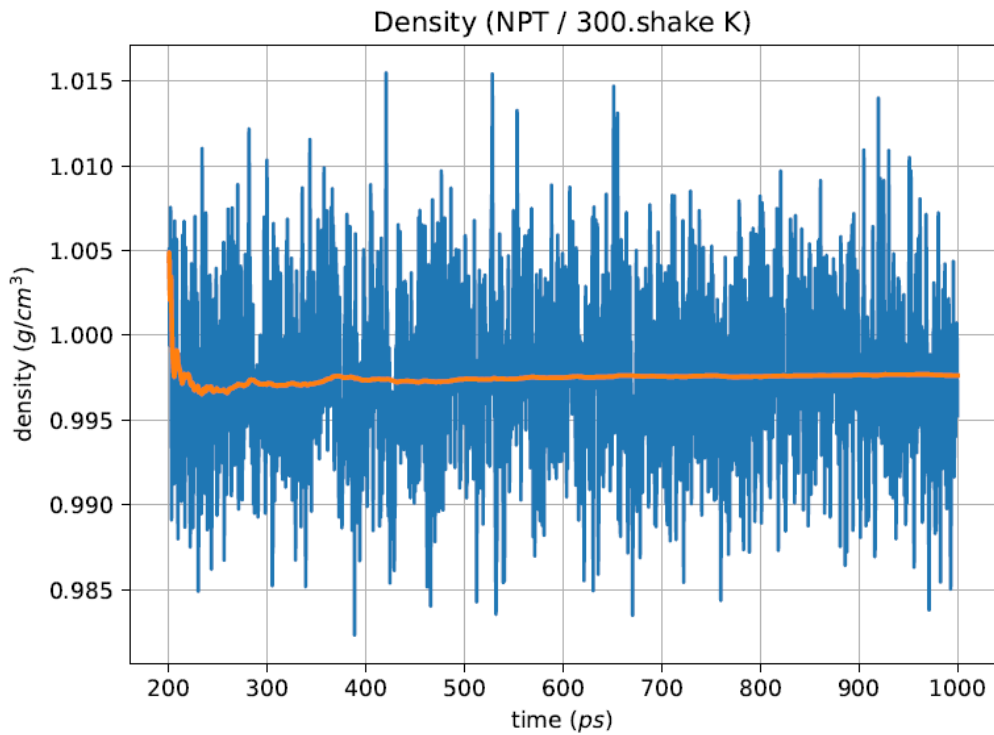


Image 34:NPT density at 300K for rigid  $H_2O$  model 1

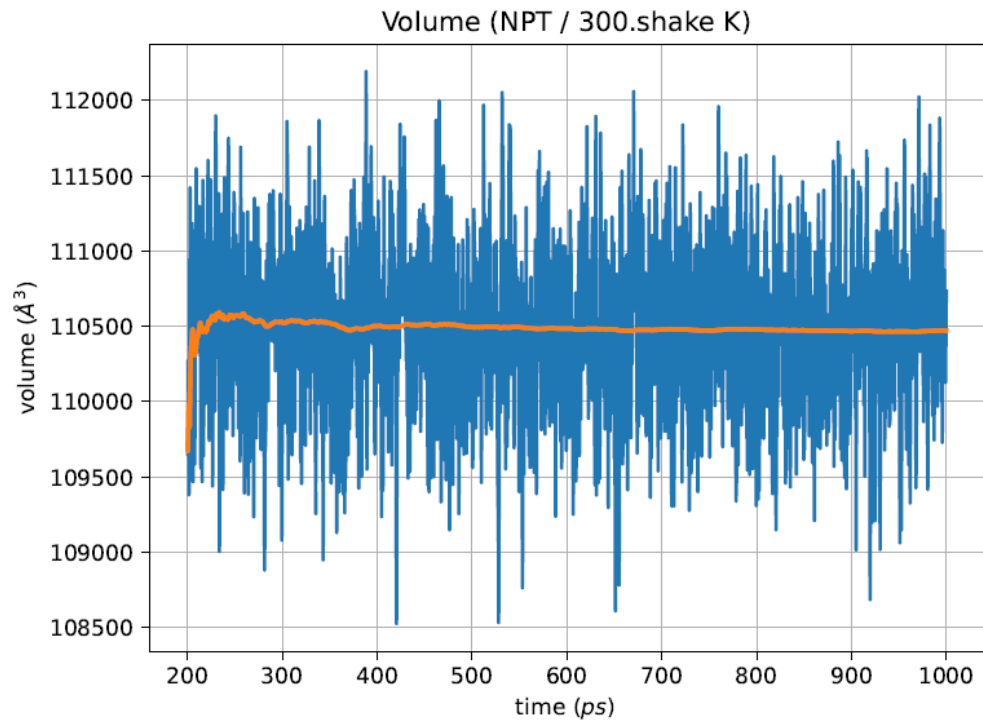


Image 35:NPT volume at 300K for rigid  $H_2O$  model 1

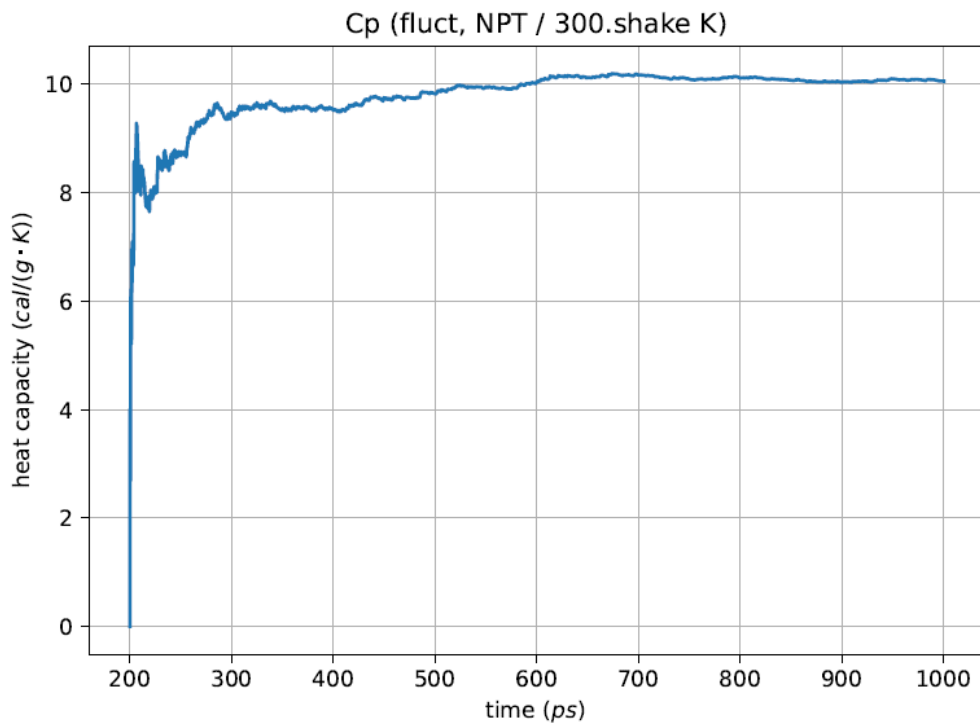


Image 36:Cp at 300K for rigid  $H_2O$  model 1

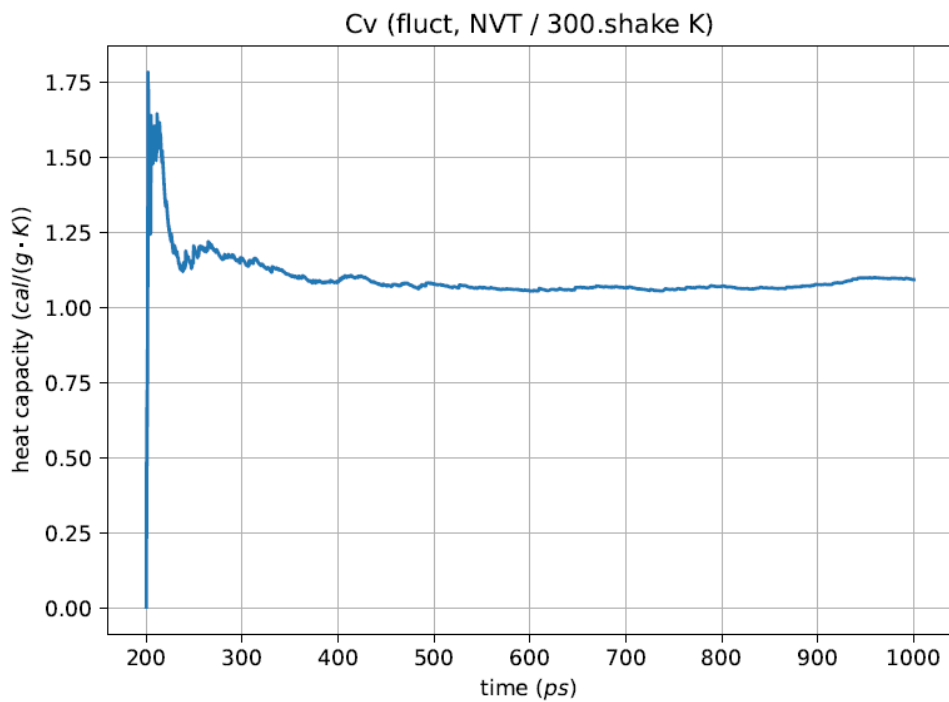


Image 37:Cv at 300K for rigid  $H_2O$  model 1

Now, we represent the derived magnitudes obtained from each dynamic system:

Table 1: Results of Cp and Cv for  $CO_2$  in cal/g K

T (K)	Cp (fluctuation)	Cp* ( $\Delta T$ )	Cp (experimental)	Cv (fluctuation)	Cv* ( $\Delta T$ )	Cv (experimental)
290	21.469	-	0.201	0.267	-	0.155
295	90.003	0.3304	0.203	0.257	0.279	0.156
300	32.651	0.3538	0.204	0.266	0.326	0.158
305	1.444	0.3267	0.205	0.270	0.284	0.159
310	43.642	-	0.206	0.262	-	0.160

\* calculated for  $\Delta T=10$

Table 2: Results of Cp and Cv for  $MeOH$  in cal/g-K

T (K)	Cp (fluctuation)	Cp* ( $\Delta T$ )	Cp (experimental)	Cv (fluctuation)	Cv* ( $\Delta T$ )	Cv (experimental)
290	72.216	-	0.594	1.231	-	0.493
295	71.251	1.394	0.601	1.254	1.277	0.499
300	69.689	1.413	0.608	1.276	1.547	0.506
305	68.376	1.432	0.616	1.235	1.562	0.513
310	65.788	-	0.624	1.238	-	0.520

\* calculated for  $\Delta T=10$

Table 3: Results of Cp and Cv for  $H_2O$  in cal/g·K (**model 1**)

T (K)	Cp (fluctuation)	Cp* ( $\Delta T$ )	Cp (experimental)	Cv (fluctuation)	Cv* ( $\Delta T$ )	Cv (experimental)
290	57.469	-	1.001	1.565	-	0.996
295	53.925	1.575	0.999	1.533	1.521	0.992
300	55.182	1.587	0.999	1.565	1.605	0.987
305	53.472	1.568	0.999	1.491	1.581	0.982
310	53.375	-	0.999	1.492	-	0.977

\* calculated for  $\Delta T=10$

Table 4: Results of Cp and Cv for  $H_2O$  in cal/g·K (**model 2**)

T (K)	Cp (fluctuation)	Cp* ( $\Delta T$ )	Cp (experimental)	Cv (fluctuation)	Cv* ( $\Delta T$ )	Cv (experimental)
290	54.377	-	1.001	1.410	-	0.996
295	54.222	1.442	0.999	1.401	1.457	0.992
300	54.088	1.452	0.999	1.371	1.613	0.987
305	52.622	1.449	0.999	1.382	1.471	0.982
310	52.59	-	0.999	1.380	-	0.977

\* calculated for  $\Delta T=10$

Table 5: Results of Cp and Cv for  $H_2O$  in cal/g·K (**model 3**)

T (K)	Cp (fluctuation)	Cp* ( $\Delta T$ )	Cp (experimental)	Cv (fluctuation)	Cv* ( $\Delta T$ )	Cv (experimental)
290	56.395	-	1.001	1.365	-	0.996
295	56.244	1.408	0.999	1.372	1.406	0.992
300	53.318	1.399	0.999	1.345	1.387	0.987
305	49.305	1.395	0.999	1.333	1.339	0.982
310	48.439	-	0.999	1.309	-	0.977

\* calculated for  $\Delta T=10$

Table 6: Results of Cp and Cv for  $H_2O$  in cal/g·K (**model 4**)

T (K)	Cp (fluctuation)	Cp* ( $\Delta T$ )	Cp (experimental)	Cv (fluctuation)	Cv* ( $\Delta T$ )	Cv (experimental)
290	55.919	-	1.001	1.539	-	0.996
295	57.561	1.559	0.999	1.537	1.563	0.992
300	54.752	1.545	0.999	1.546	1.549	0.987
305	53.493	1.547	0.999	1.446	1.533	0.982
310	51.977	-	0.999	1.529	-	0.977

\* calculated for  $\Delta T=10$



Table 8: Results of Cp and Cv for *MeOH* in cal/g-K (**rigid model**)

T (K)	Cp (fluctuation)	Cp* ( $\Delta T$ )	Cp (experimental)	Cv (fluctuation)	Cv* ( $\Delta T$ )	Cv (experimental)
295	8.524	-	0.601	0.481	-	0.499
300	8.159	0.659	0.608	0.473	0.797	0.506
305	8.255	-	0.616	0.469	-	0.513

\* calculated for  $\Delta T=10$

Table 9: Results of Cp and Cv for *H<sub>2</sub>O* in cal/g-K (**rigid model**) at 300 K

Model	Cp (NPT)	Cp* ( $\Delta T$ )	Cp (experimental)	Cv (NVT)	Cv (experimental)
1	10.133	1.152	1.001	1.089	0.996
2	9.722	1.058	0.999	0.933	0.992
3	10.704	1.026	0.999	0.922	0.987
4	11.675	1.122	0.999	1.070	0.982

\* calculated for  $\Delta T=10$

Table 10: Results of density for  $CO_2$  in  $g/cm^3$

T (K)	Density (NPT)	Density (experimental)
290	0.00193	0.00186
295	0.00188	0.00183
300	0.00185	0.00180
305	0.00184	0.00177
310	0.00180	0.00173

Table 11: Results of density for  $MeOH$  in  $g/cm^3$

T (K)	Density (NPT)	Density (experimental)
290	0.7862	0.7939
295	0.7813	0.7892
300	0.7764	0.7845
305	0.7708	0.7798
310	0.7653	0.7751

Table 12: Results of density for  $H_2O$  in  $g/cm^3$

T (K)	Density model 1 (NPT)	Density model 2 (NPT)	Density model 3 (NPT)	Density model 4 (NPT)	Density (experimental)
290	1.051	1.022	1.043	0.993	0.998
295	1.048	1.018	1.039	0.991	0.997
300	1.044	1.014	1.036	0.990	0.996
305	1.041	1.011	1.032	0.988	0.994
310	1.037	1.006	1.025	0.987	0.993

## 5. CONCLUSIONS

We are trying to use LAMMPS to calculate the variables known as  $C_p$ ,  $C_v$  and density of the systems described above, and compare them to their experimental value.

As we can see on the graphs of Temperature, volume and density, with the running average represented with an orange line, the variation is very low at the end, that's why we can see almost a flat line, which means we have successfully obtained an equilibrated system and can evaluate the data.

As for the results, the model falls apart on the attempts of calculating the  $C_p$  and  $C_v$  using the fluctuation method. As we can see on tables 1-8, none of the models can successfully, predict either the  $C_p$  and  $C_v$  of the system. However, on table 9, we can see that for the rigid model of water we obtain a value pretty close to the experimental one, meaning that, with this method, we can approximately know the  $C_v$  of a rigid system of water, being model 3 the one with less error.

If we calculate it taking into account two sets of data (utilizing eq. 25), the results improve for all models, giving us some better results for both variables ( $C_p$  and  $C_v$ ), but still we cannot accurately say that we predict the real value.

As for the rigid models, we can see a great improvement on the  $C_p$  values, giving us values close to the experimental ones (Table 9) in the water models case and an improvement on the MeOH (Table 8). The water model that has a closer value is, again, model 3.

As for the densities, as we can see on tables 10-12, we can accurately predict the density of all systems, this time model 4 being the one closer to the experimental value

As we depicted before, we have shown that Molecular Dynamics is able to calculate, with some amount of precision, the values of both density and  $C_v$  of a system, but for some reason we are not able to accurately estimate the value of  $C_p$ . Whilst we don't know why it happens, we can appreciate an improvement when we use rigid models, this can mean that we are not taking into account enough parameters to make our initial model, and thus, giving us an error in the  $C_p$ .

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## 7. ANNEX

### 1.- CO<sub>2</sub>

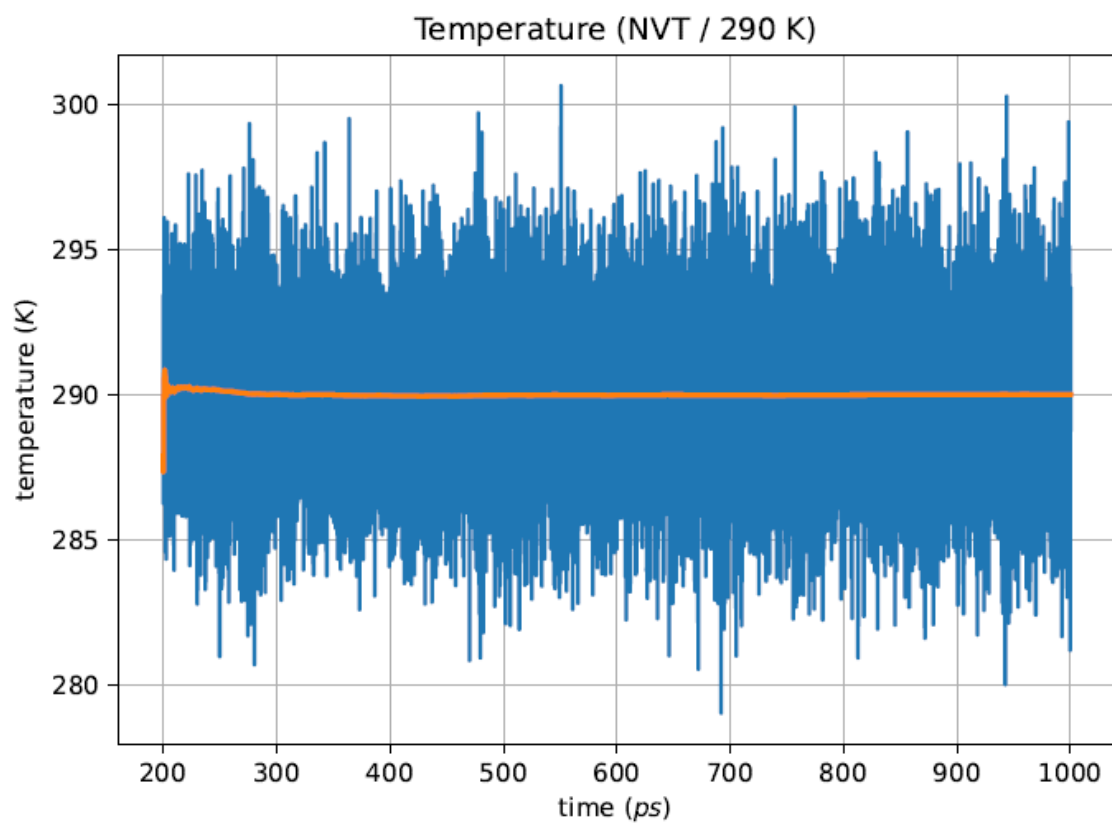


Image A.1:NPT temperature at 290 K for CO<sub>2</sub>

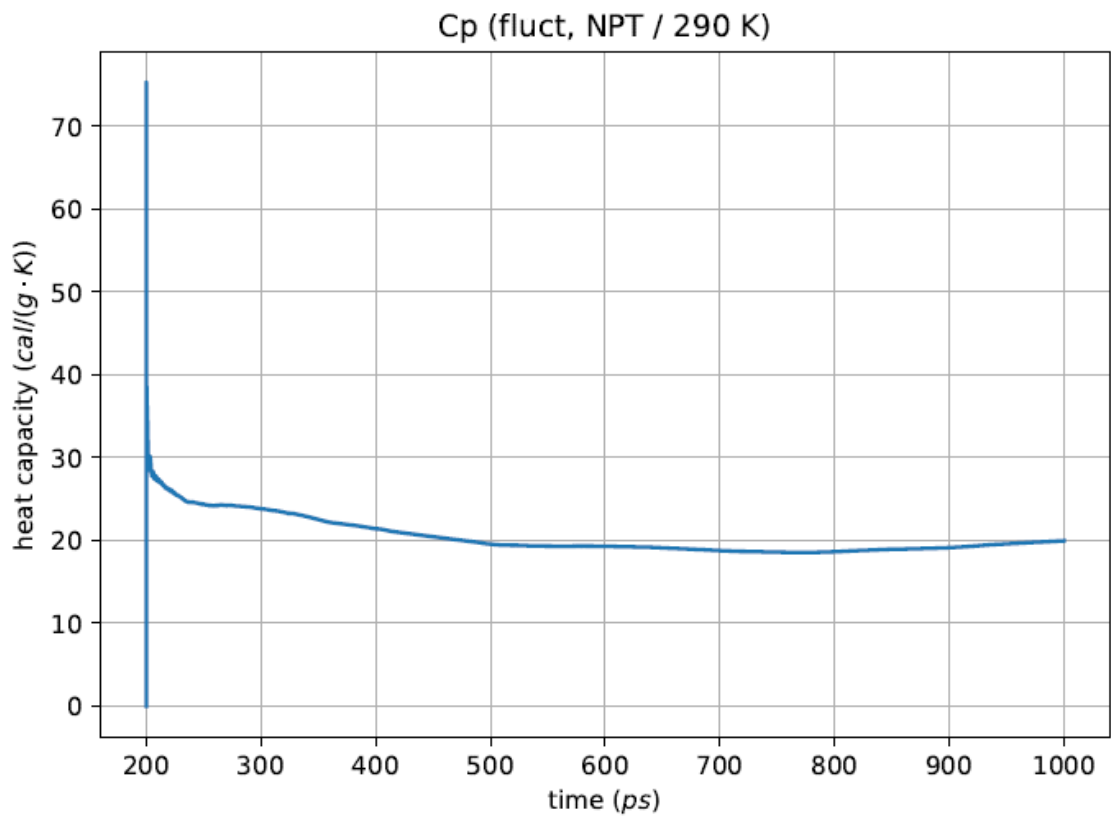


Image A.2 :Cp at 290 K for CO<sub>2</sub>

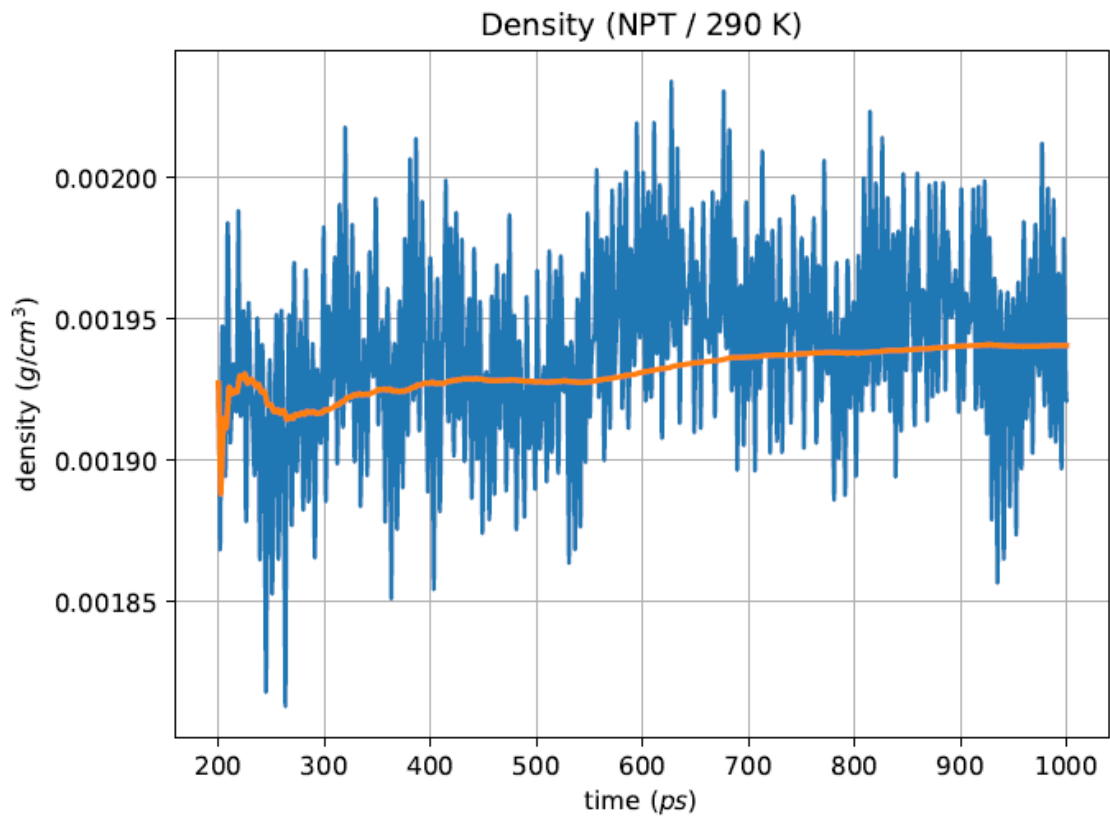


Image A.3:NPT Density at 290K for CO<sub>2</sub>



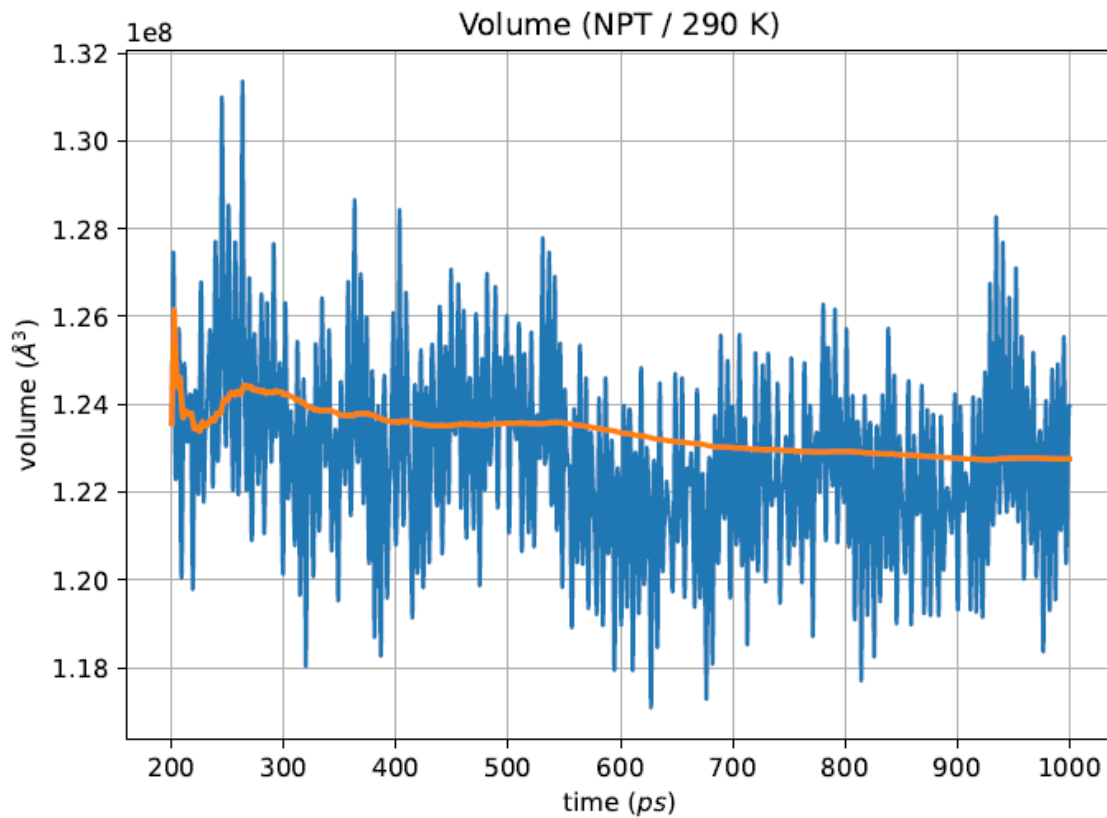


Image A.4:NPT Volume at 290K for CO<sub>2</sub>

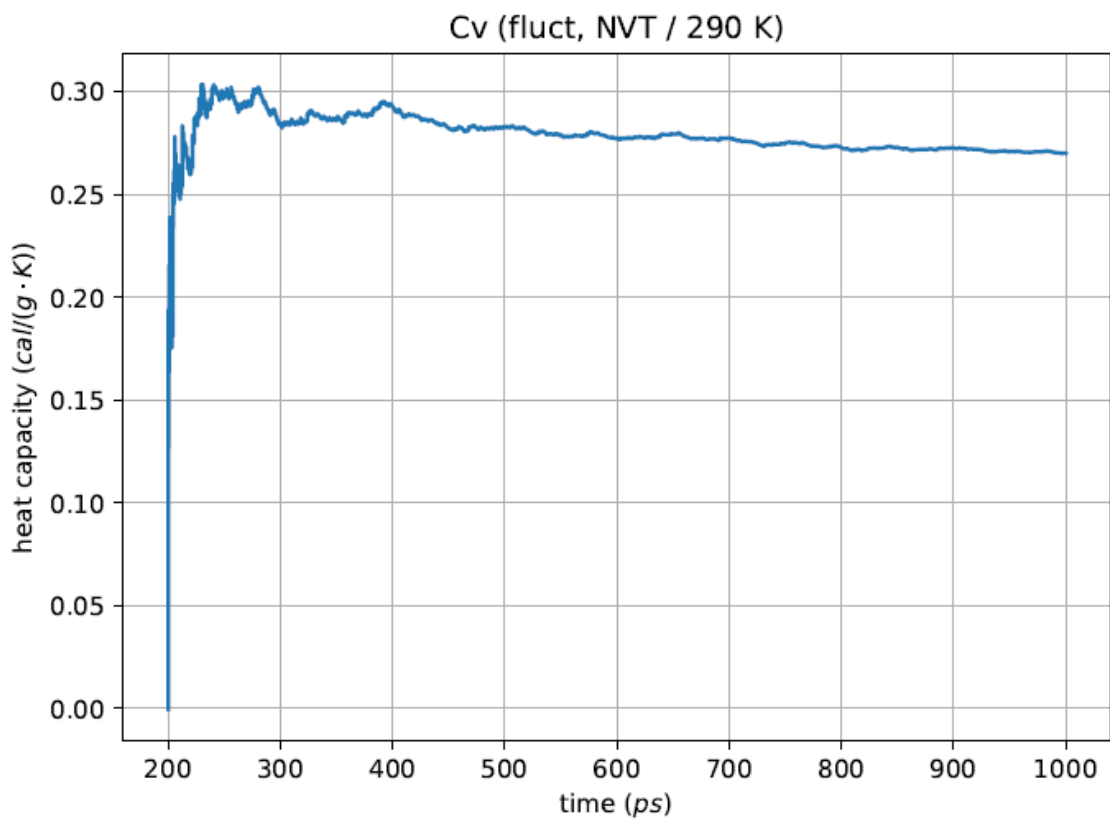


Image A.5:Cv at 290K for CO<sub>2</sub>

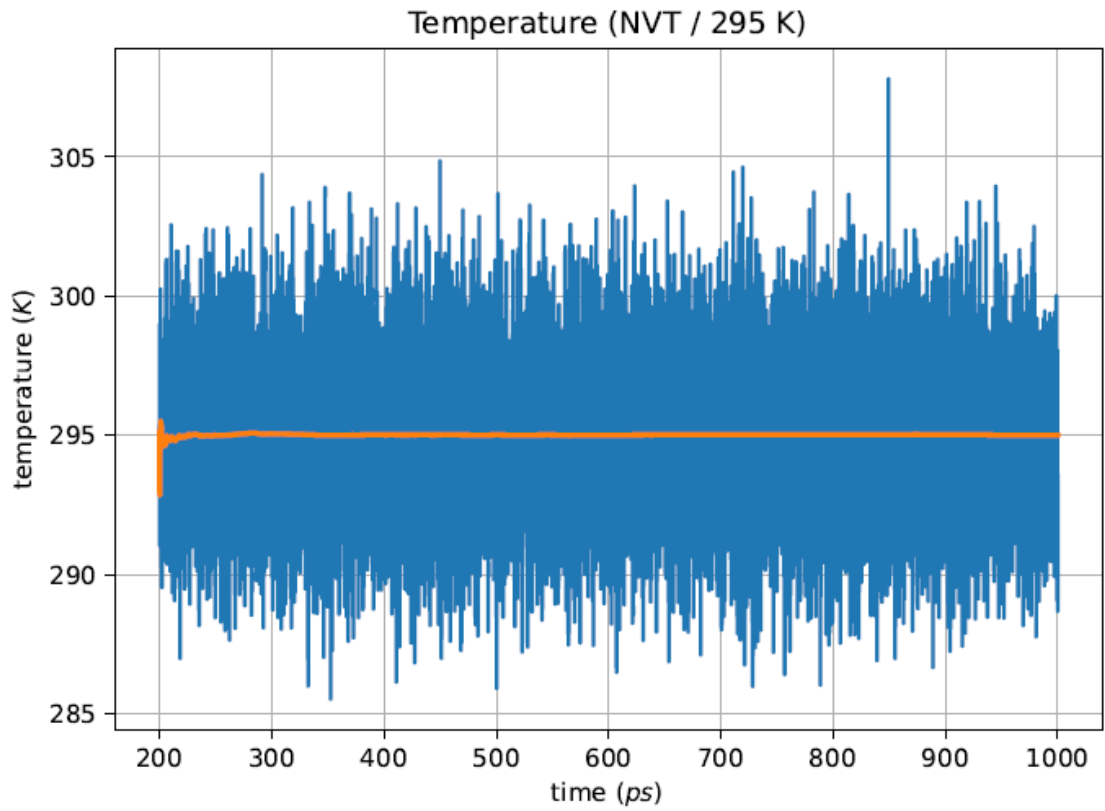


Image A.6: NPT temperature at 295K for CO<sub>2</sub>

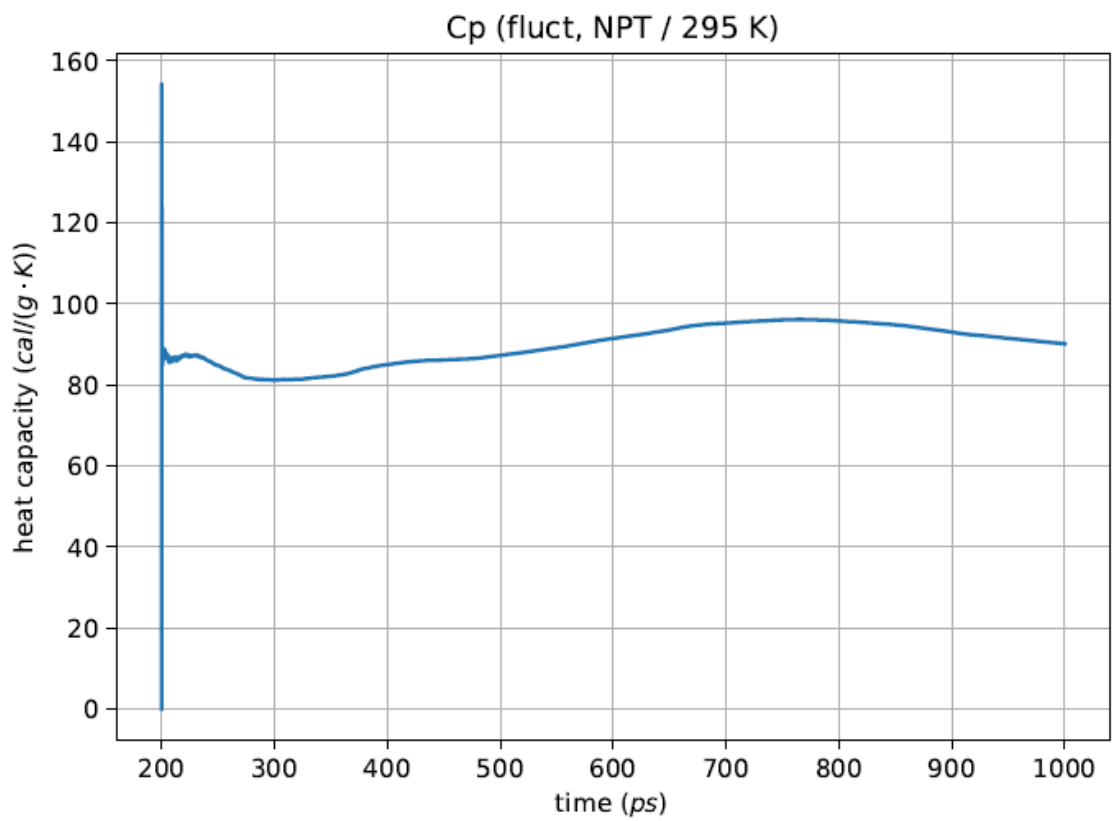


Image A.7: Cp at 295K for CO<sub>2</sub>

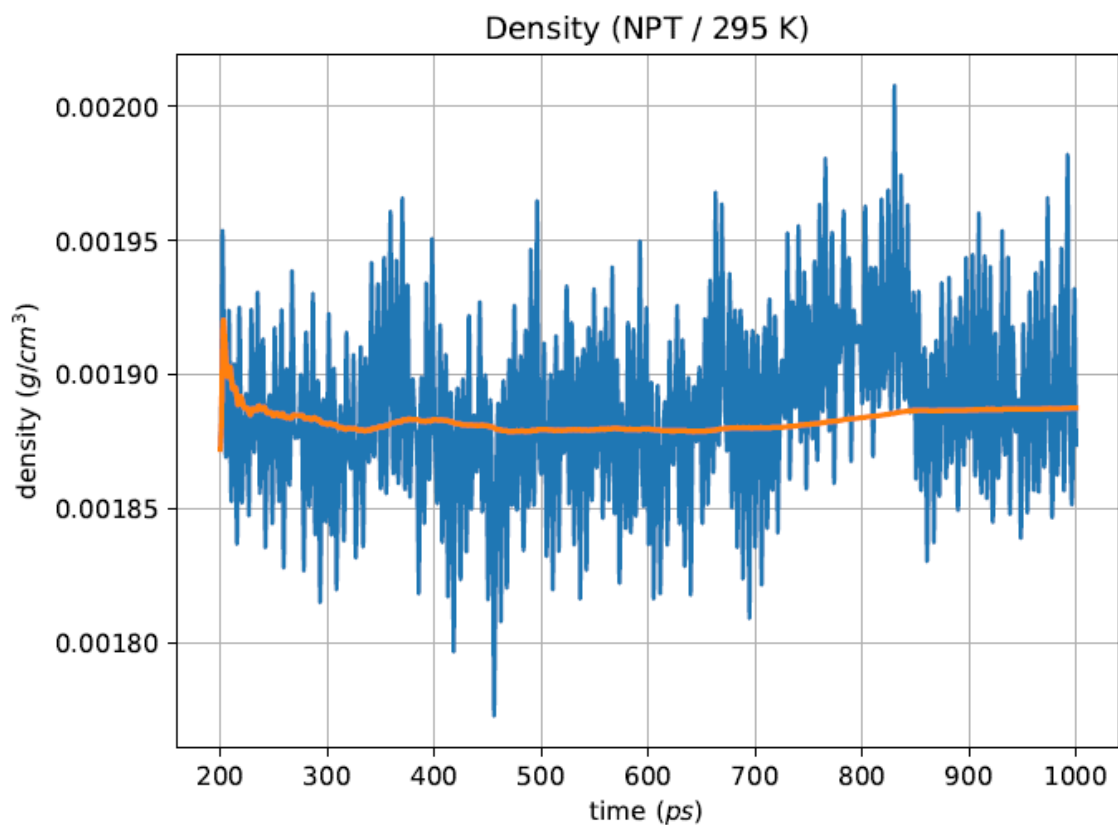


Image A.8:NPT density at 295K for CO<sub>2</sub>

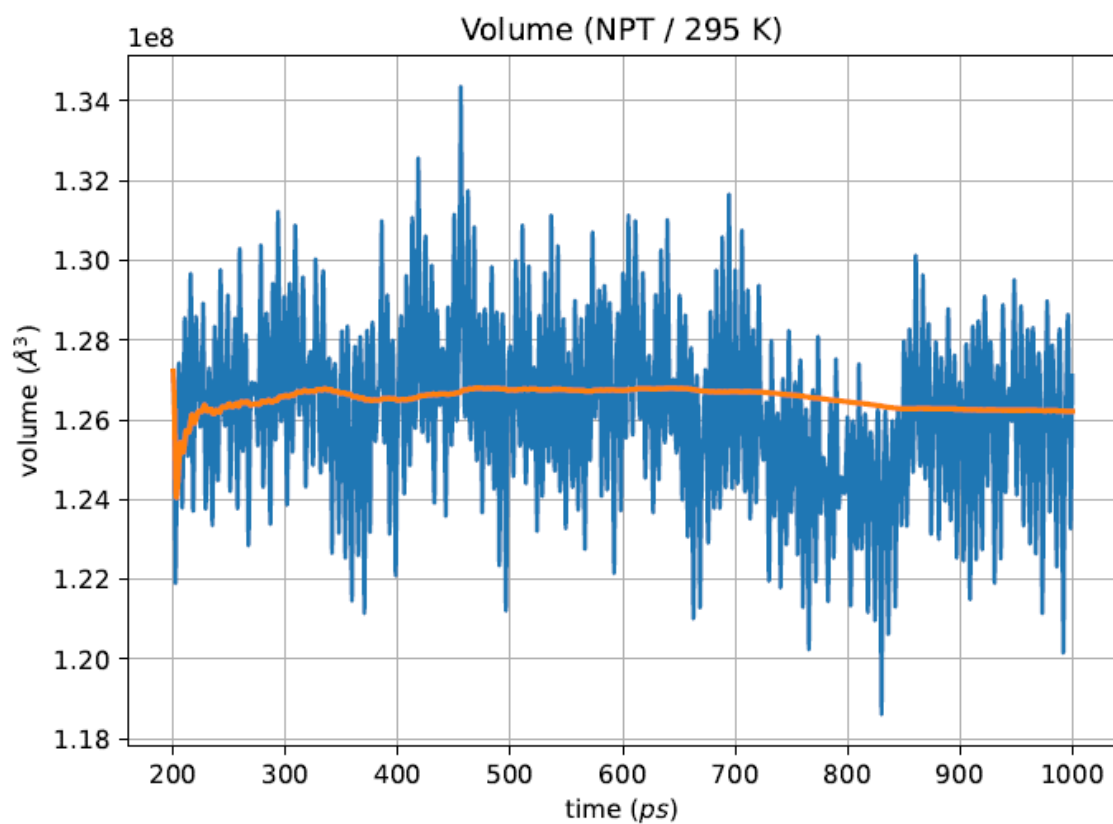


Image A.9:NPT Volume at 300K for CO<sub>2</sub>

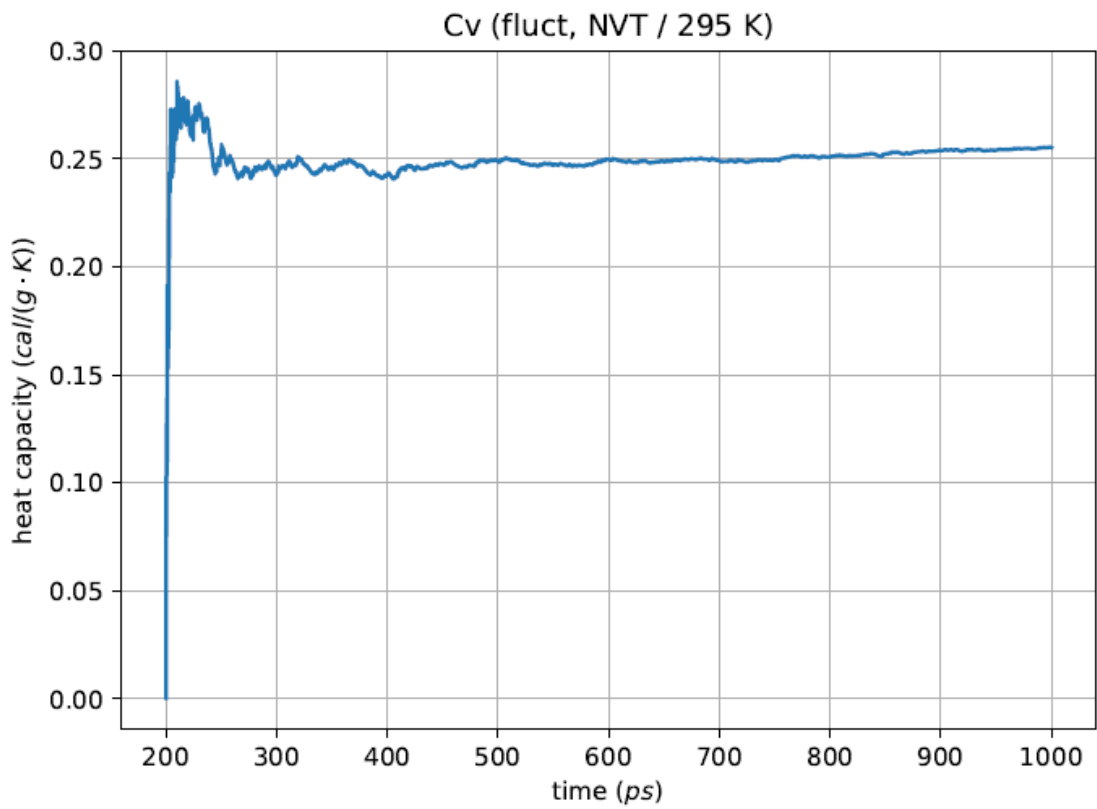


Image A.10:  $C_v$  at 295K for  $\text{CO}_2$

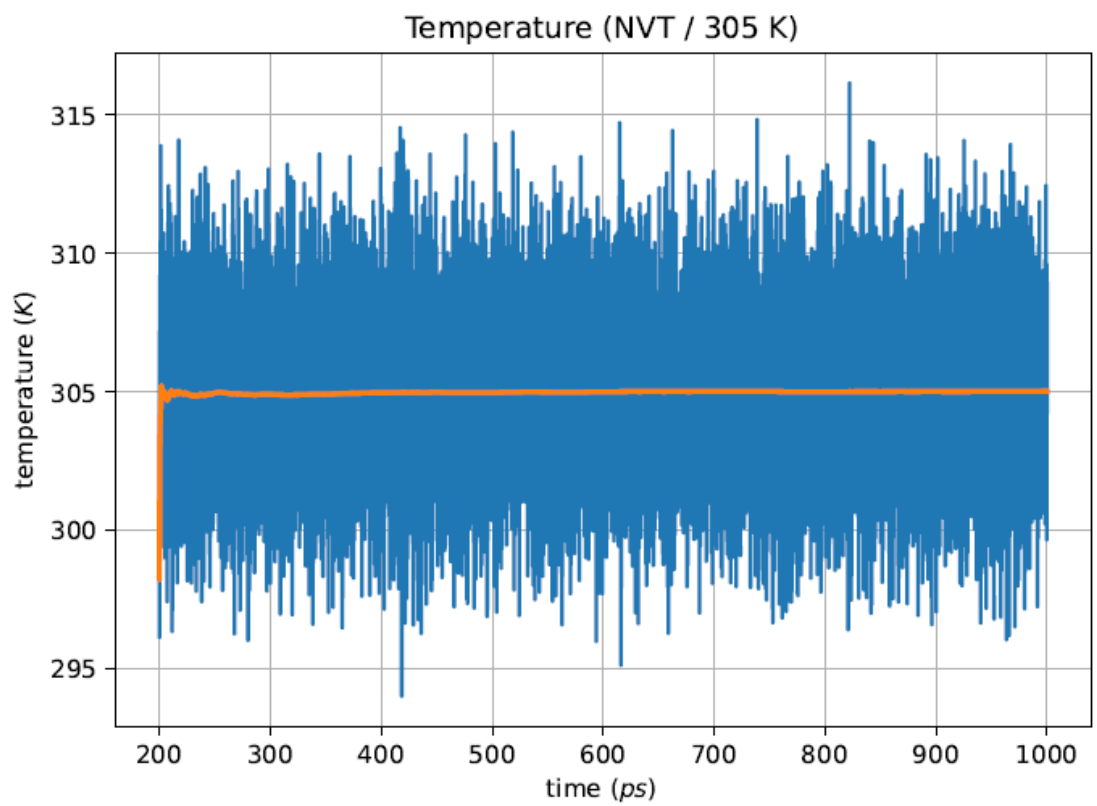


Image A.11: NPT temperature at 305K for  $\text{CO}_2$

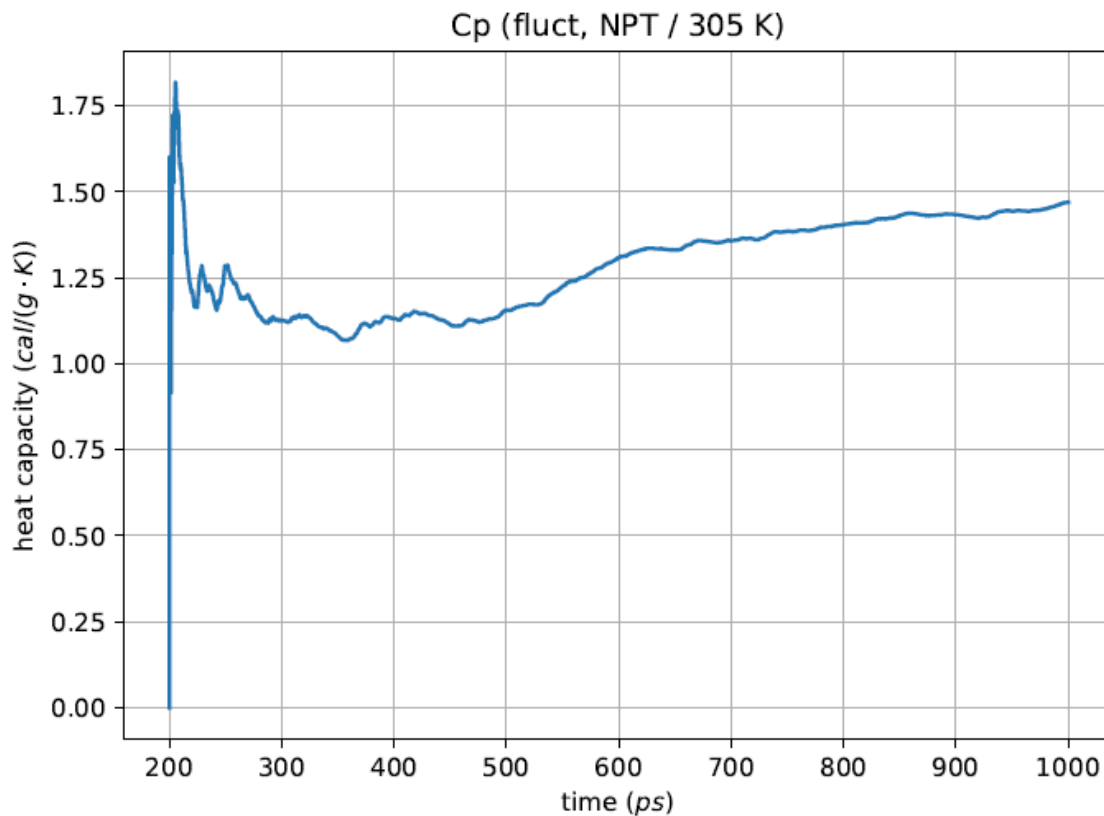


Image A.12:Cp at 305K for CO<sub>2</sub>

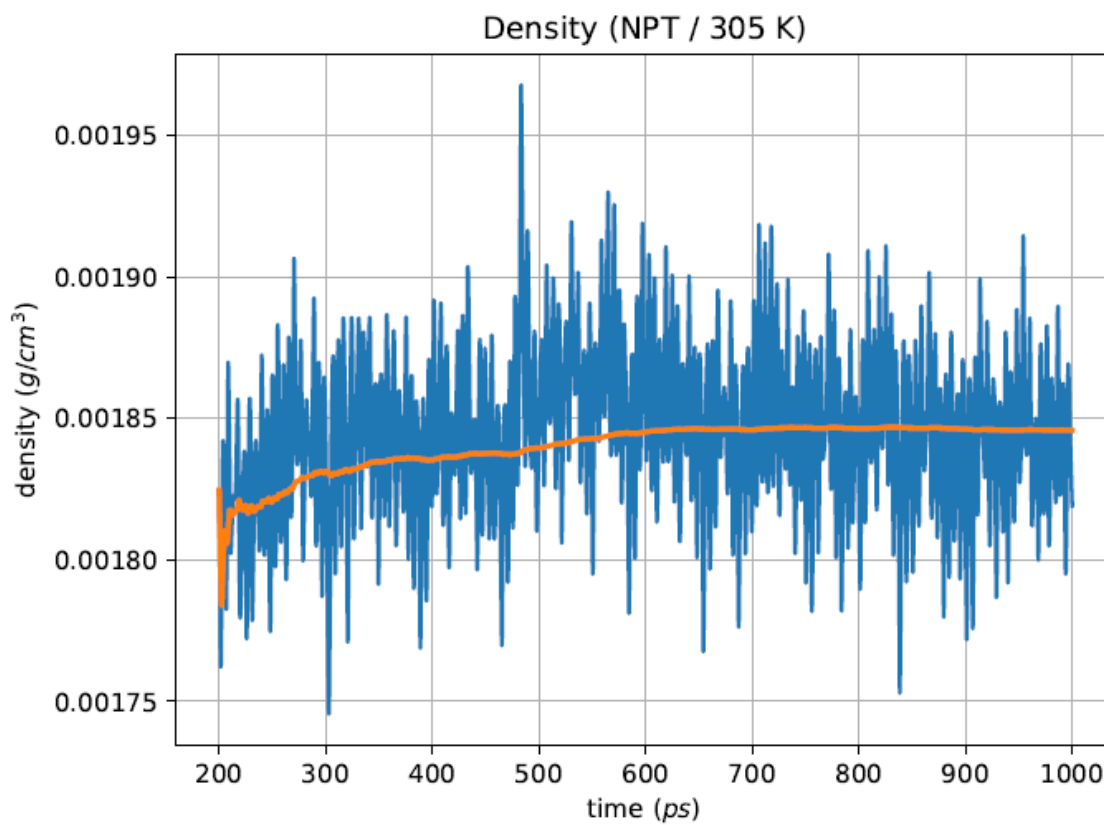


Image A.13:NPT Density at 300K for CO<sub>2</sub>

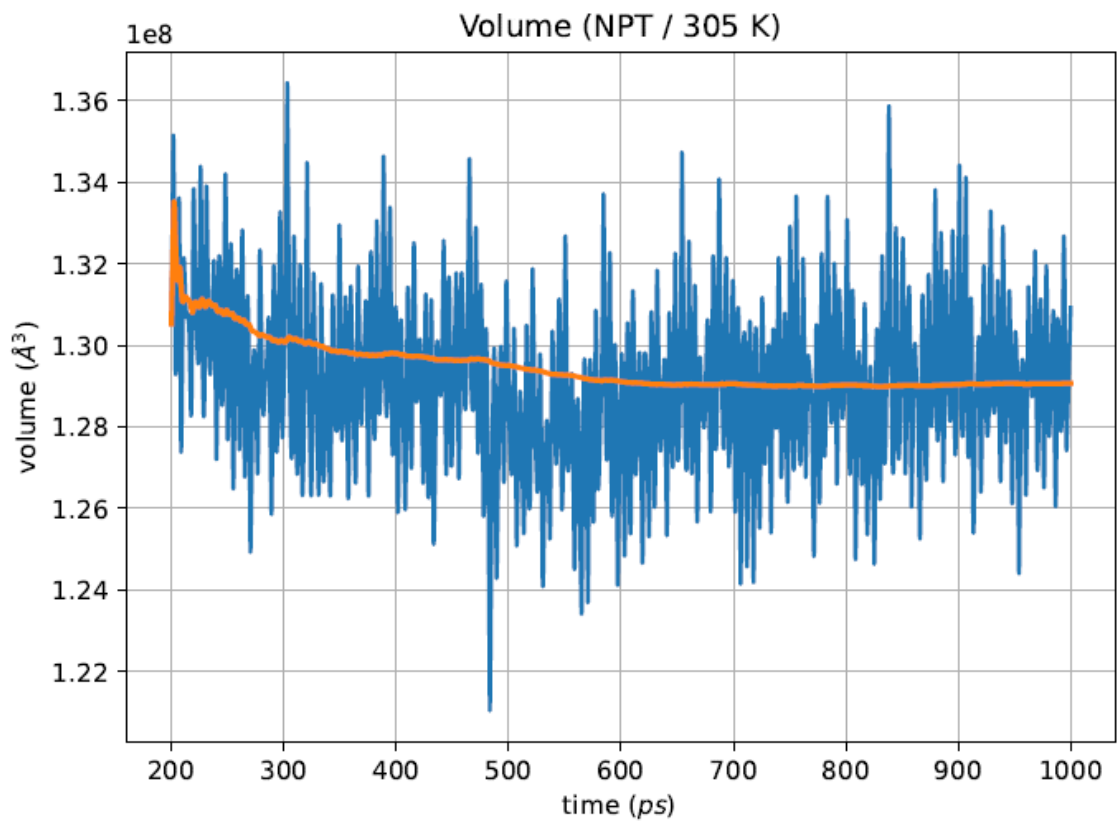


Image A.14:NPT Volume at 305K for CO<sub>2</sub>

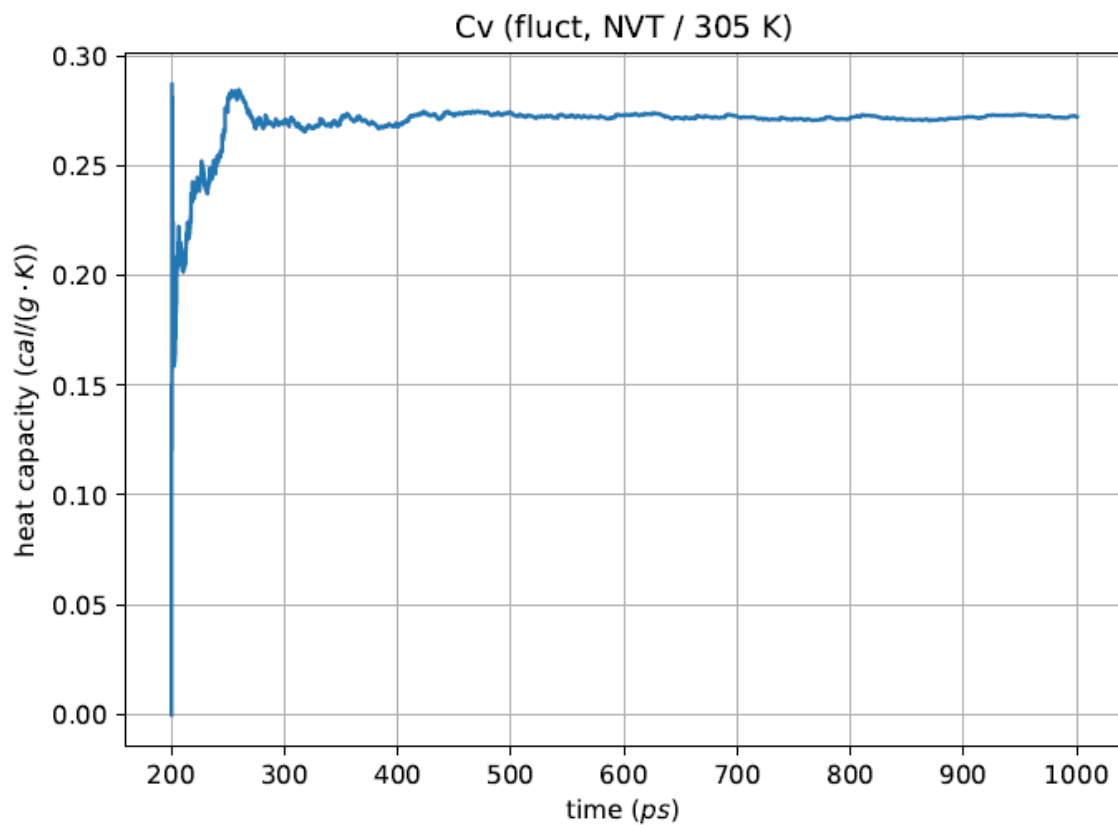


Image A.15:Cv at 305K for CO<sub>2</sub>

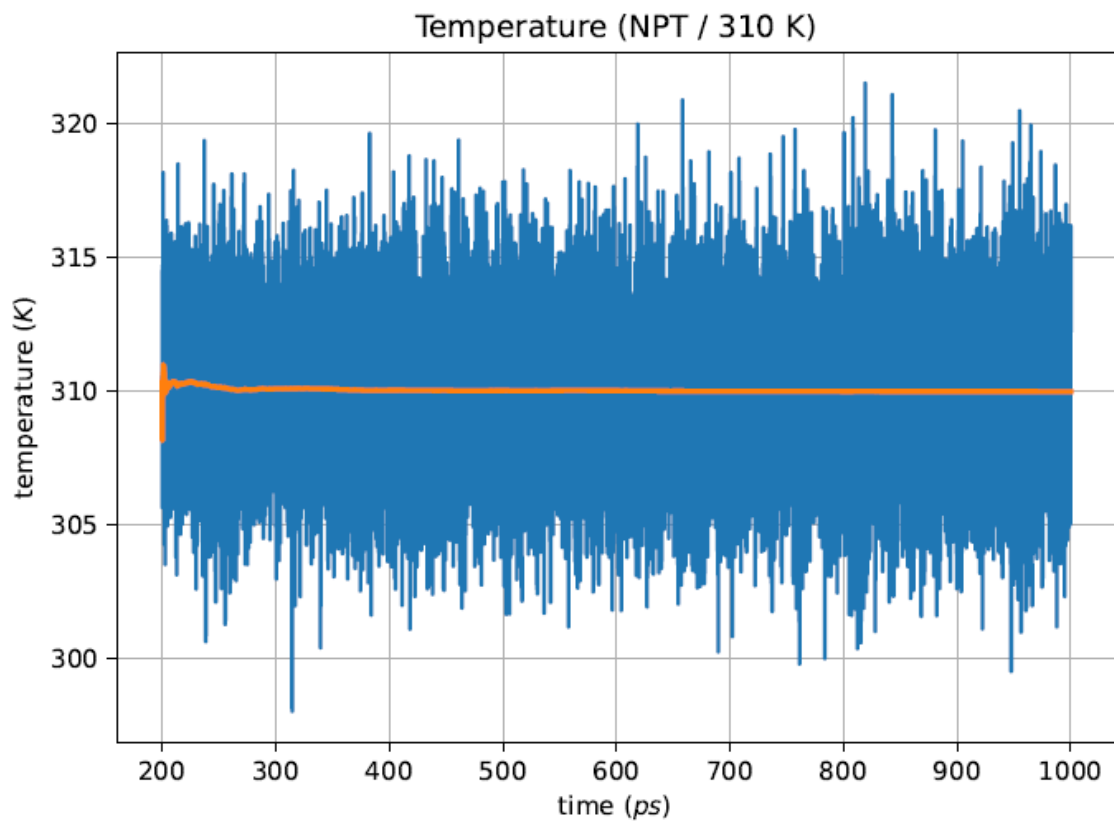


Image A.16:NPT temperature at 310K for CO<sub>2</sub>

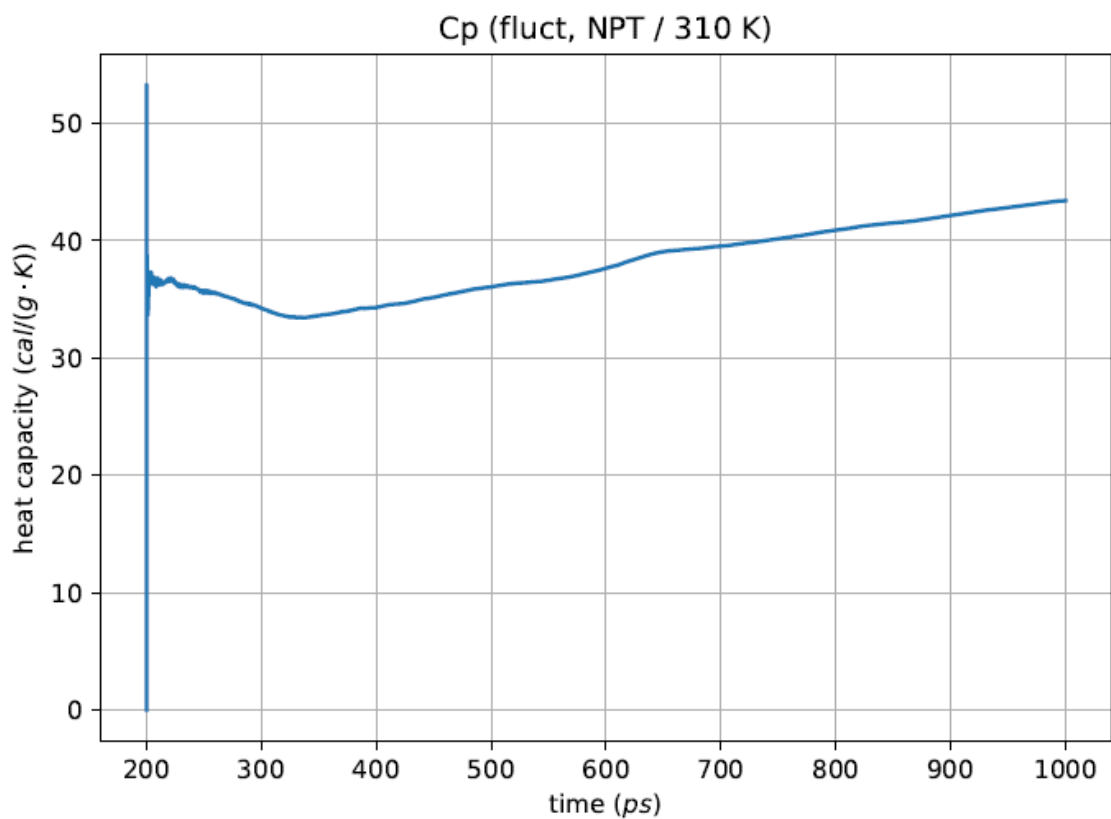


Image A.17: Cp at 310K for CO<sub>2</sub>

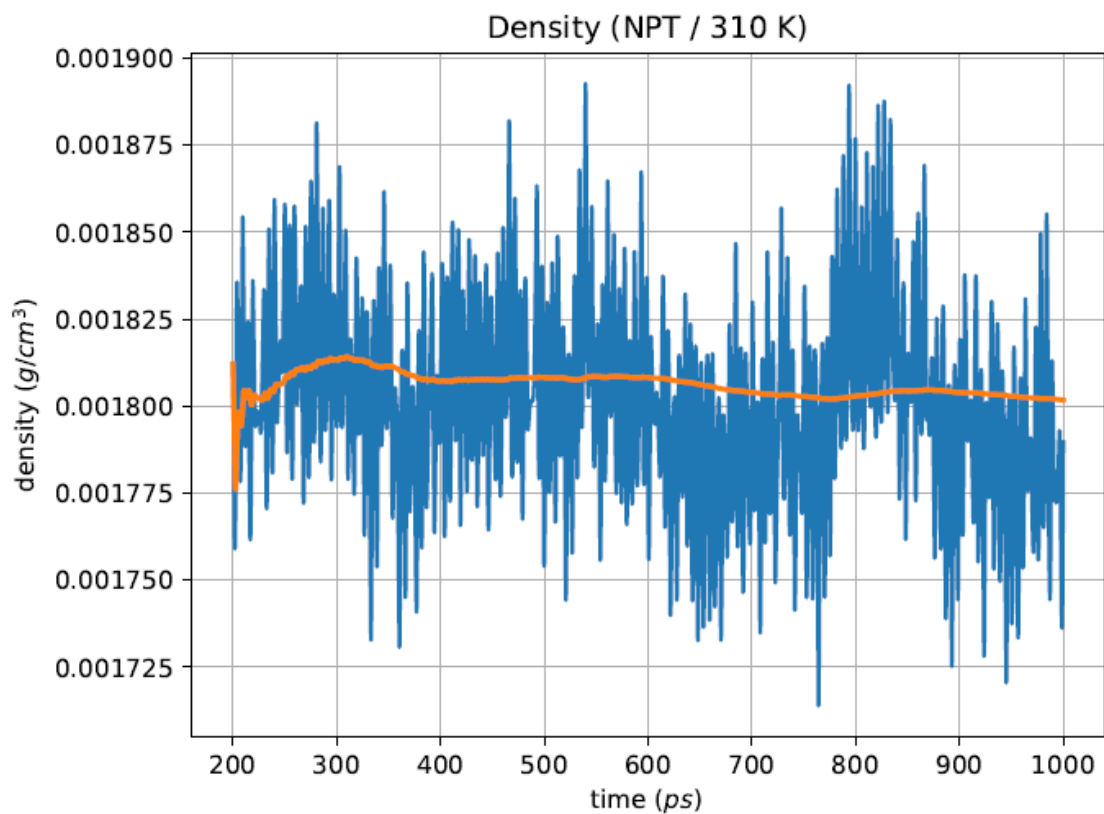


Image A.18:NPT Density at 310K for CO<sub>2</sub>

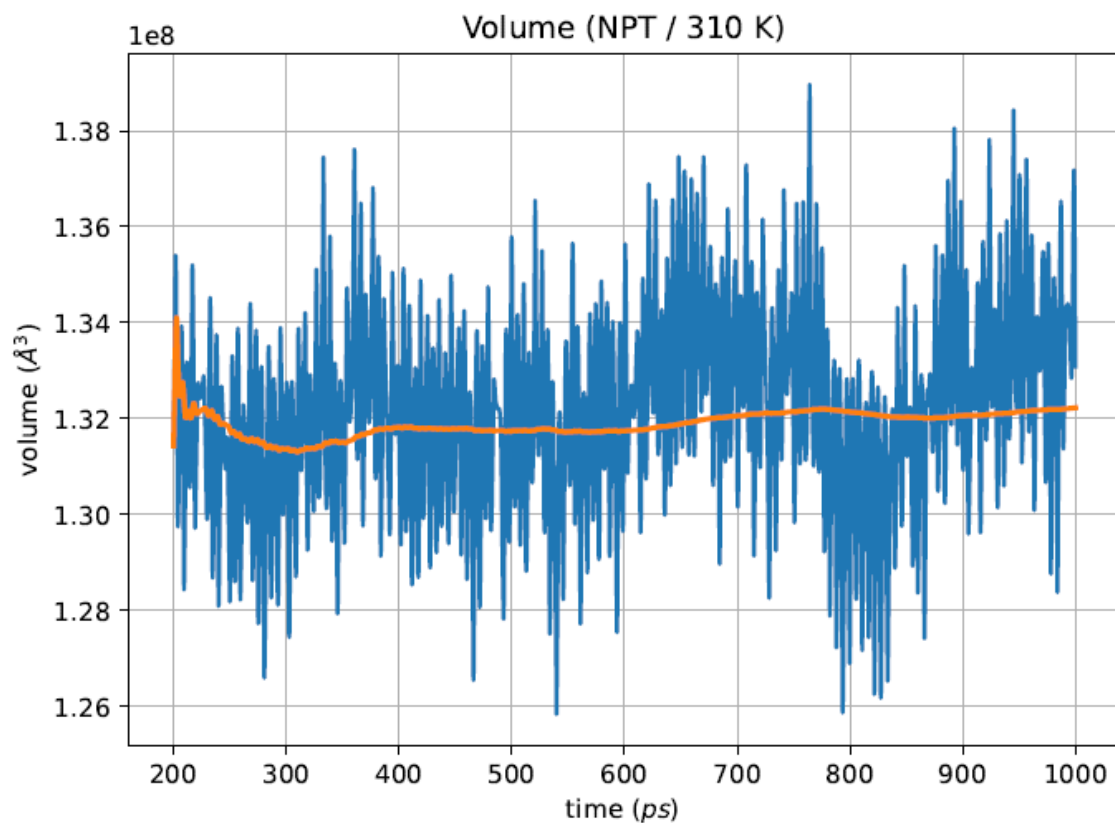


Image A.19:NPT Volume at 310K for CO<sub>2</sub>



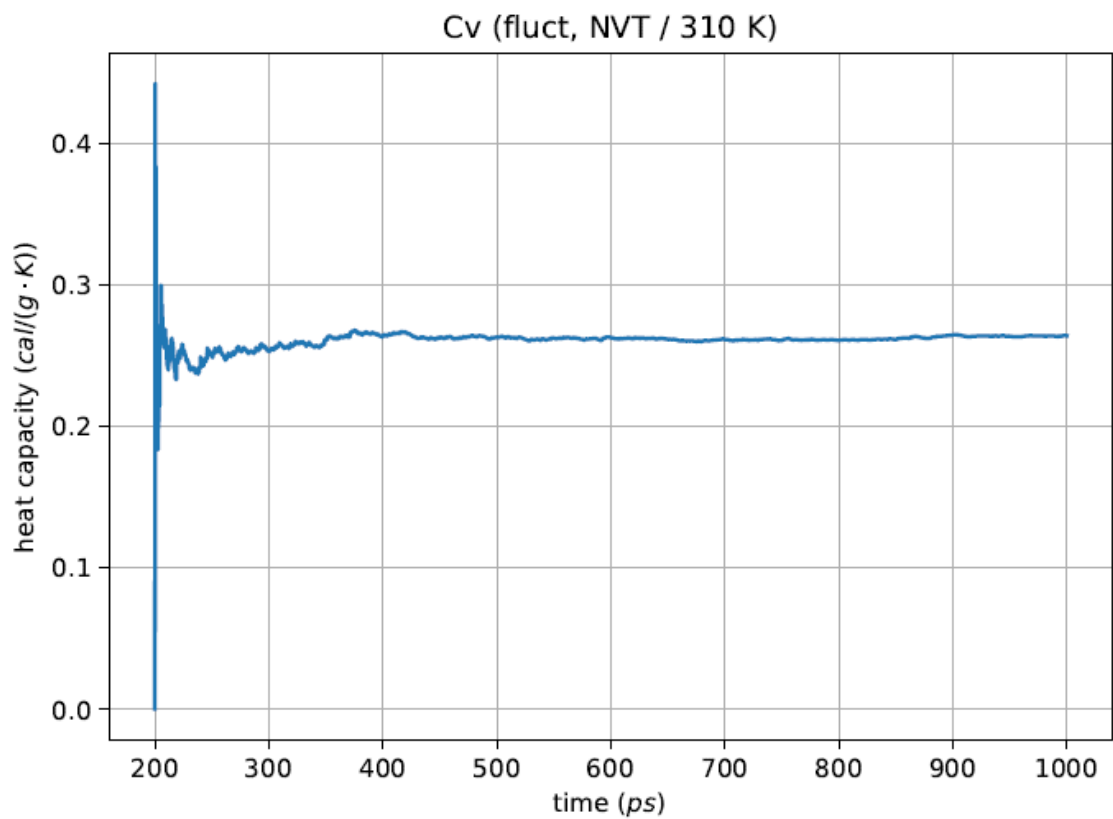


Image A.20:Cv at 310K for CO<sub>2</sub>

## 2.- MeOH

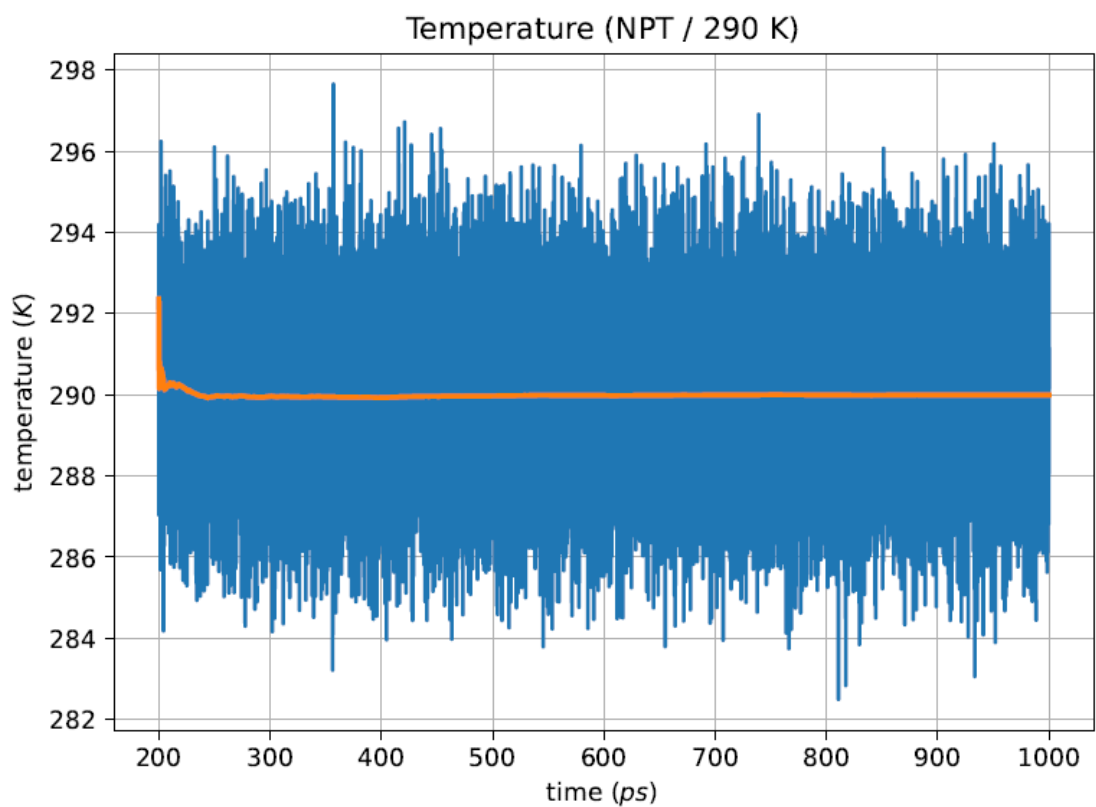


Image A.21:NPT temperature at 290K for MeOH

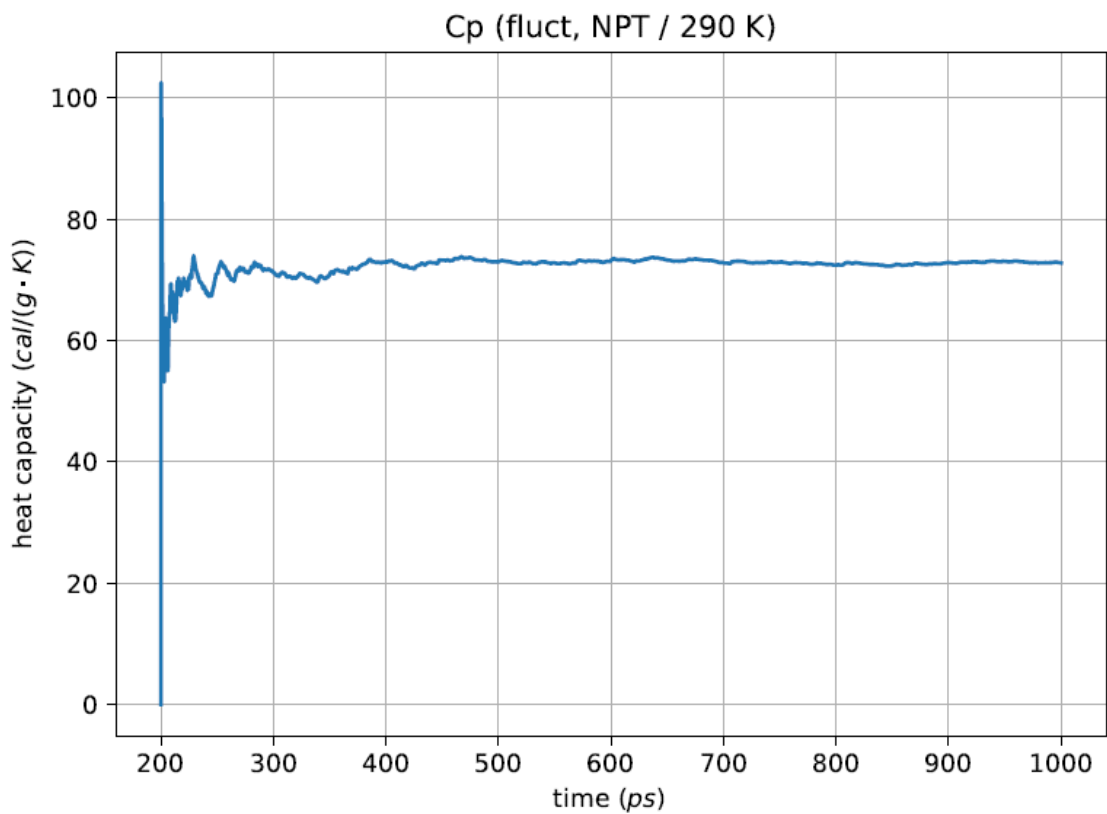


Image A.22:Cp at 290K for MeOH

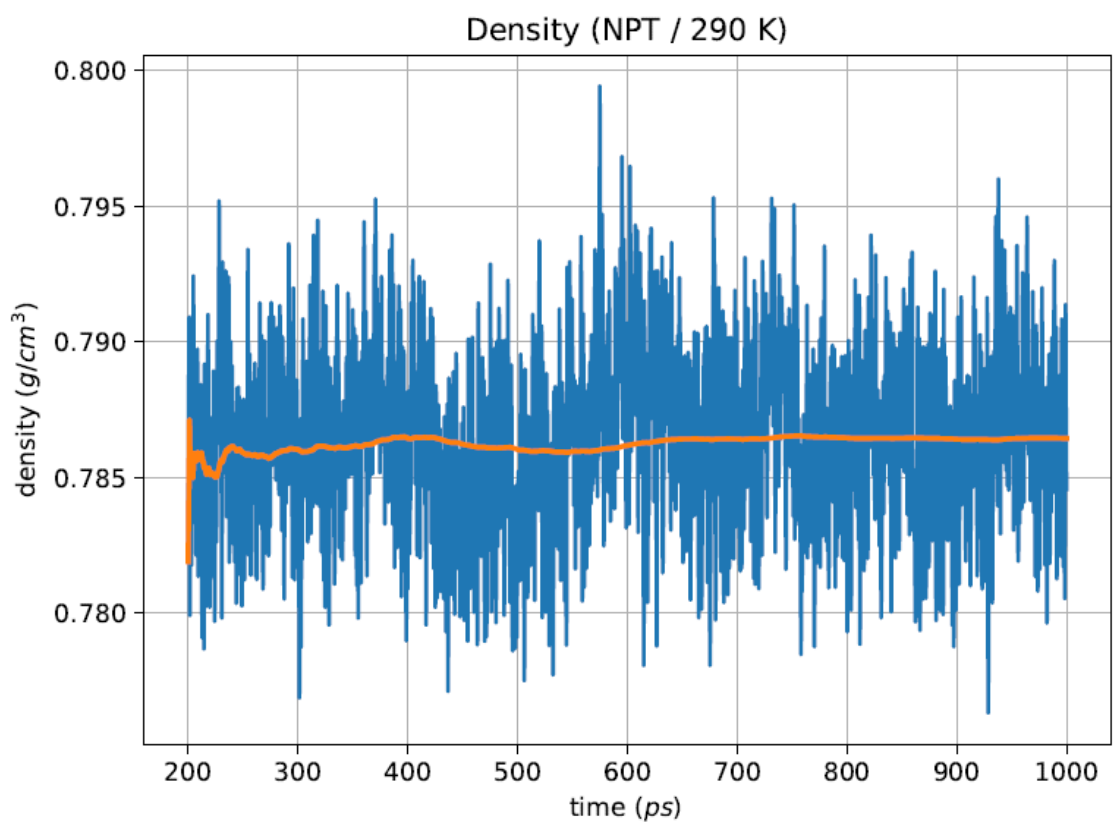


Image A.23:NPT Density at 290K for MeOH

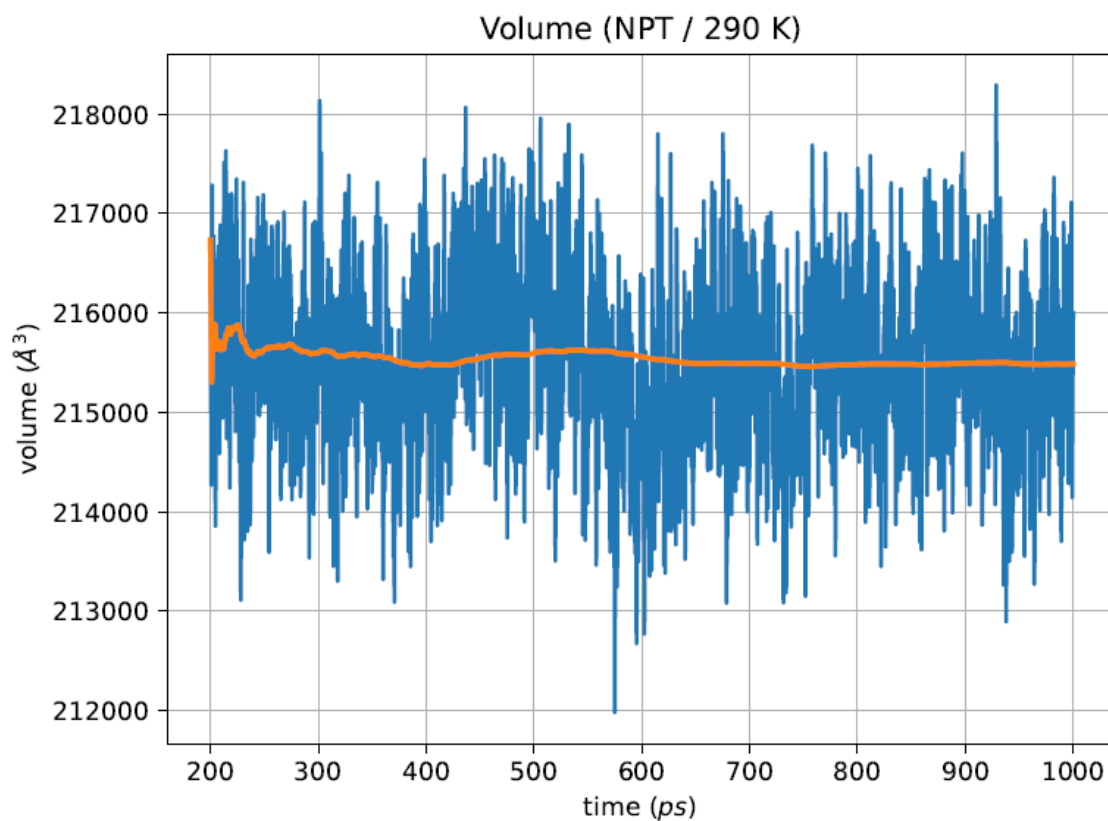


Image A.24:NPT Volume at 290K for MeOH

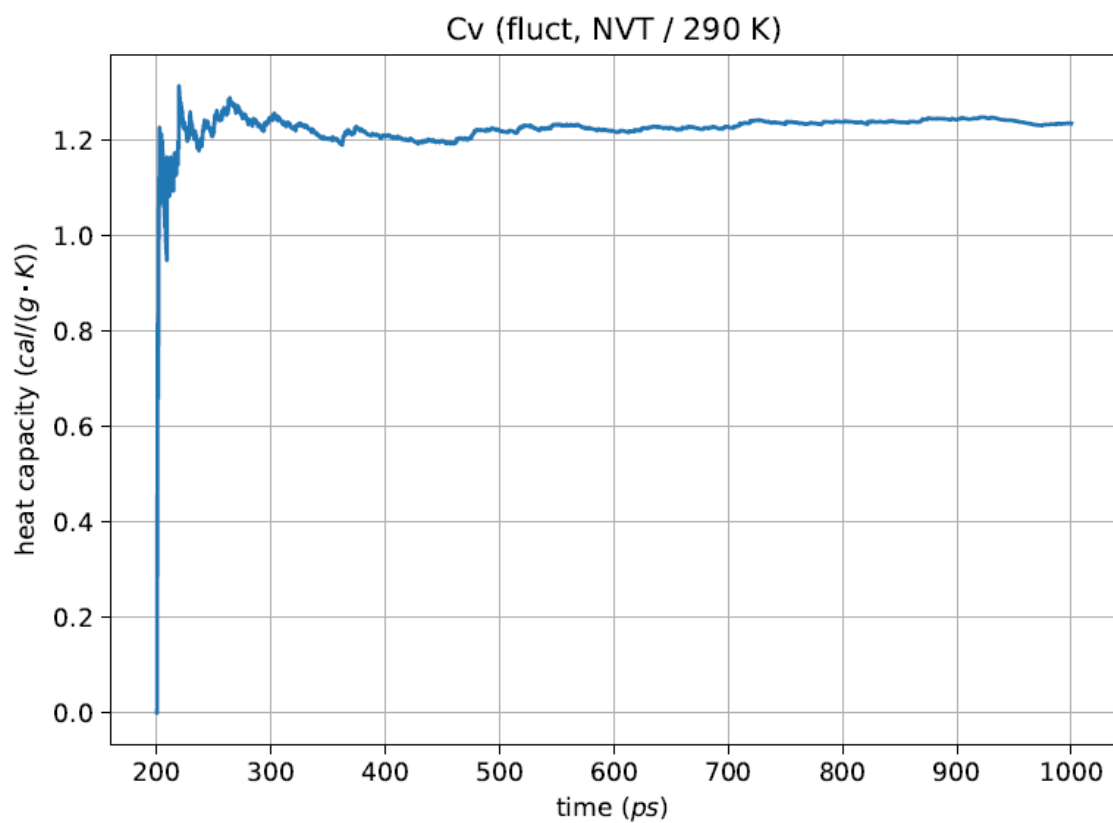


Image A.25:Cv at 290K for MeOH

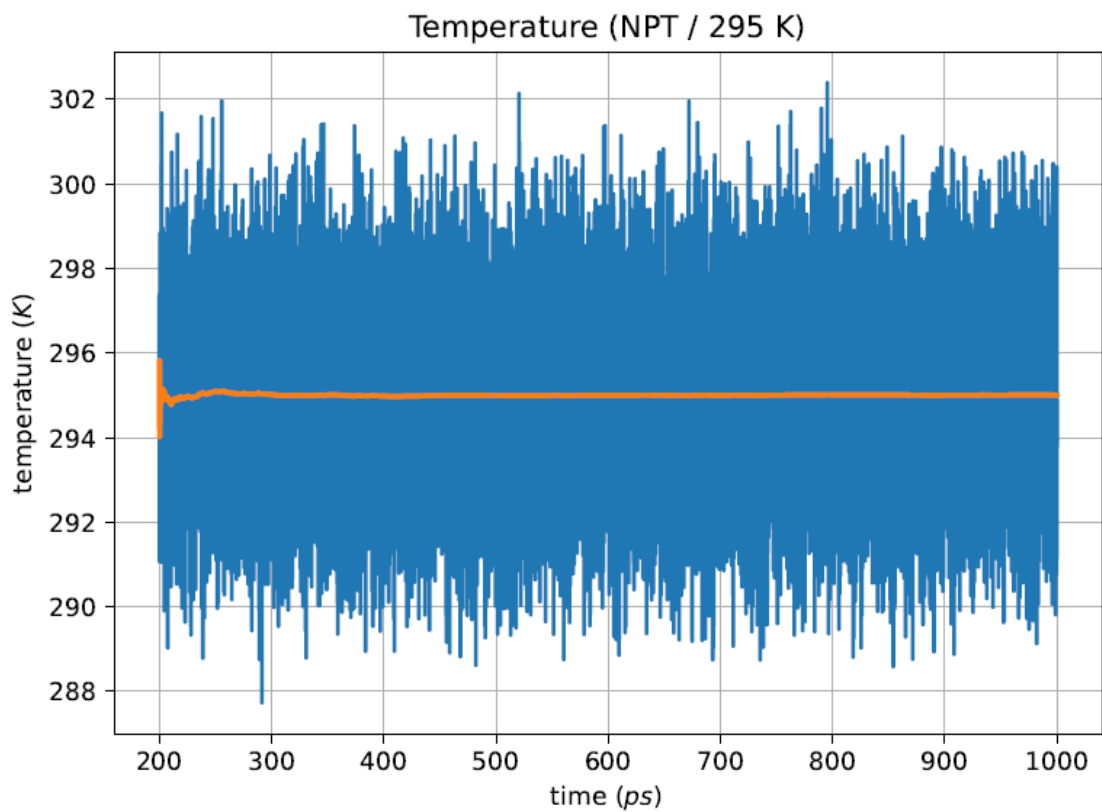


Image A.26:NPT temperature at 295K for MeOH

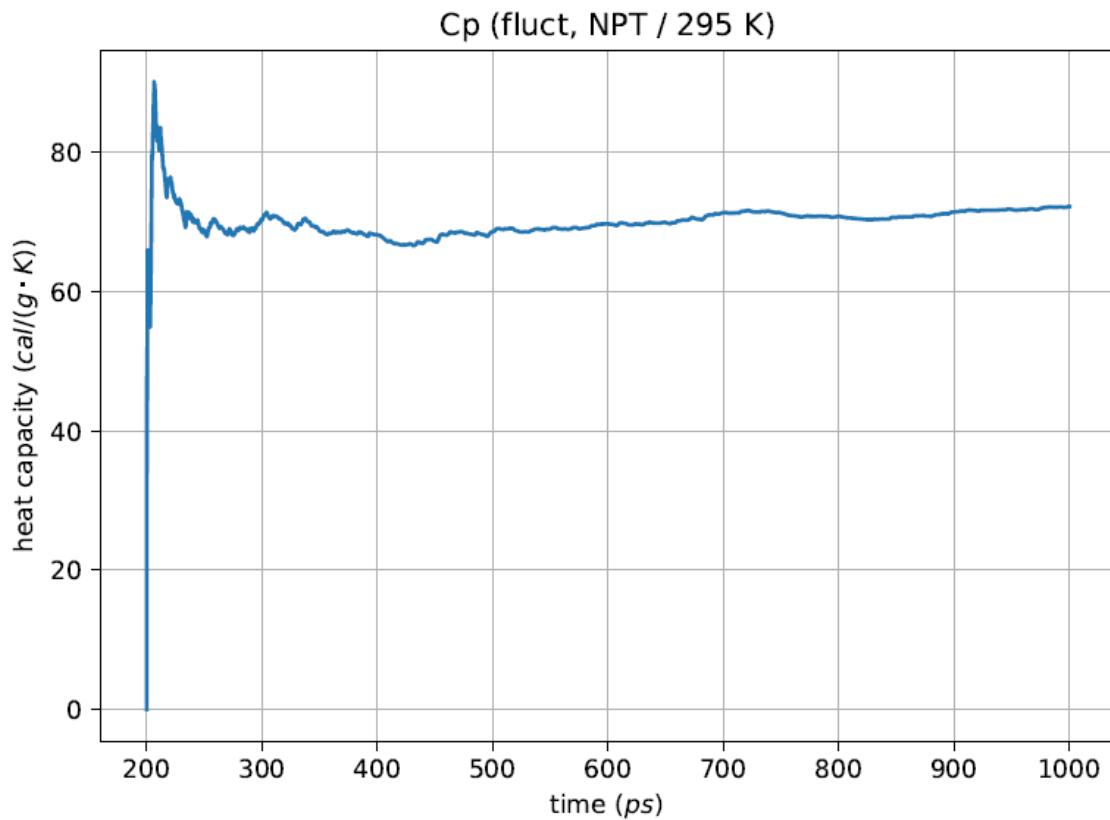


Image A.27:Cp at 295K for MeOH

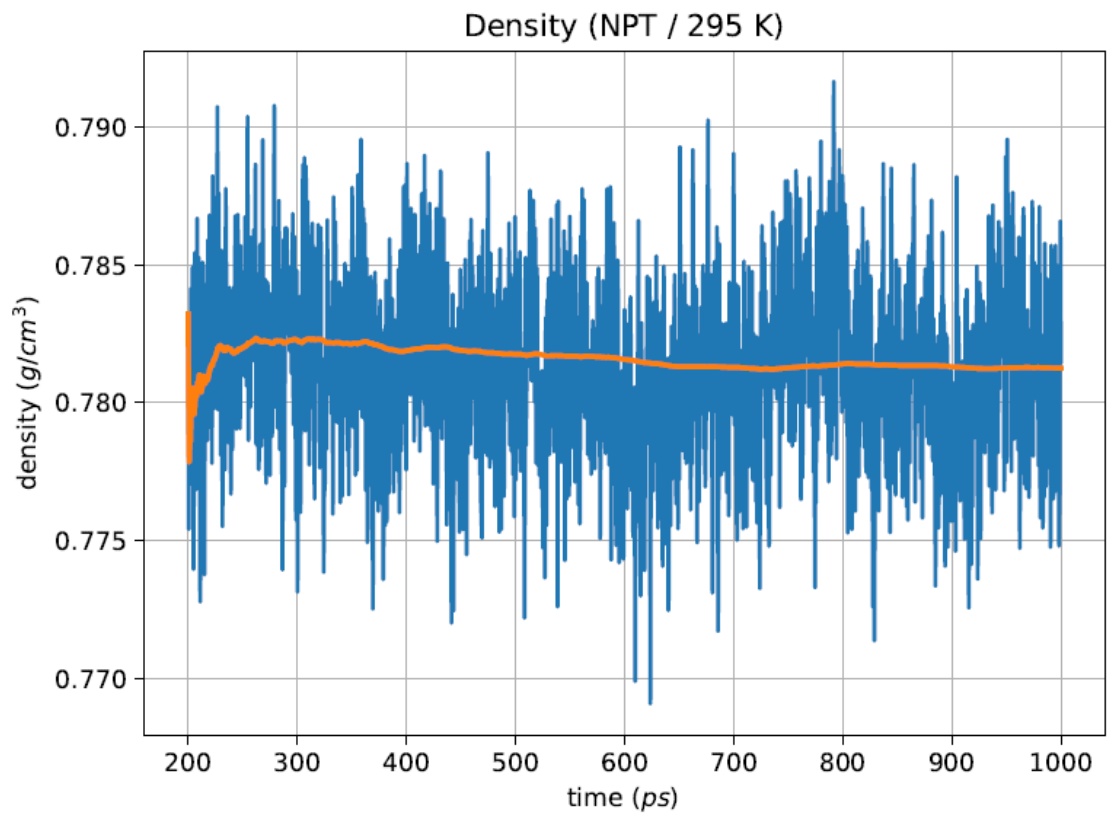


Image A.28:NPT Density at 295K for MeOH

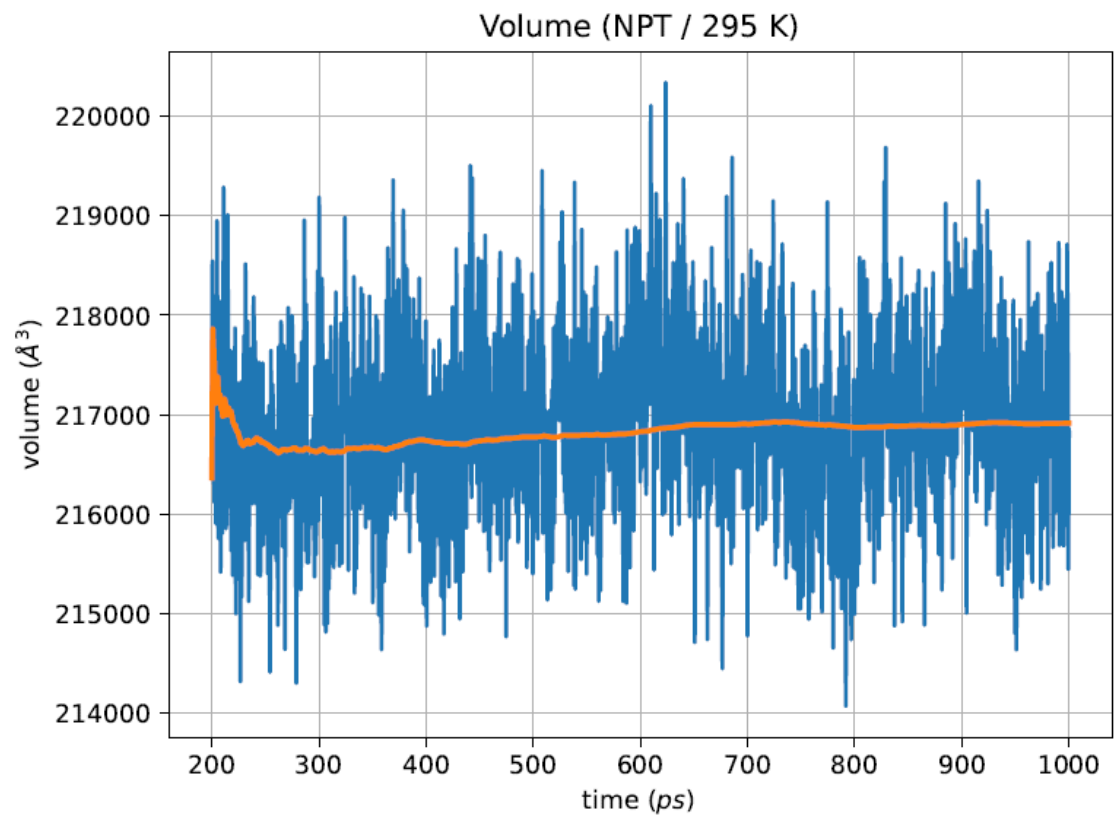


Image A.29:NPT Volume at 295K for MeOH

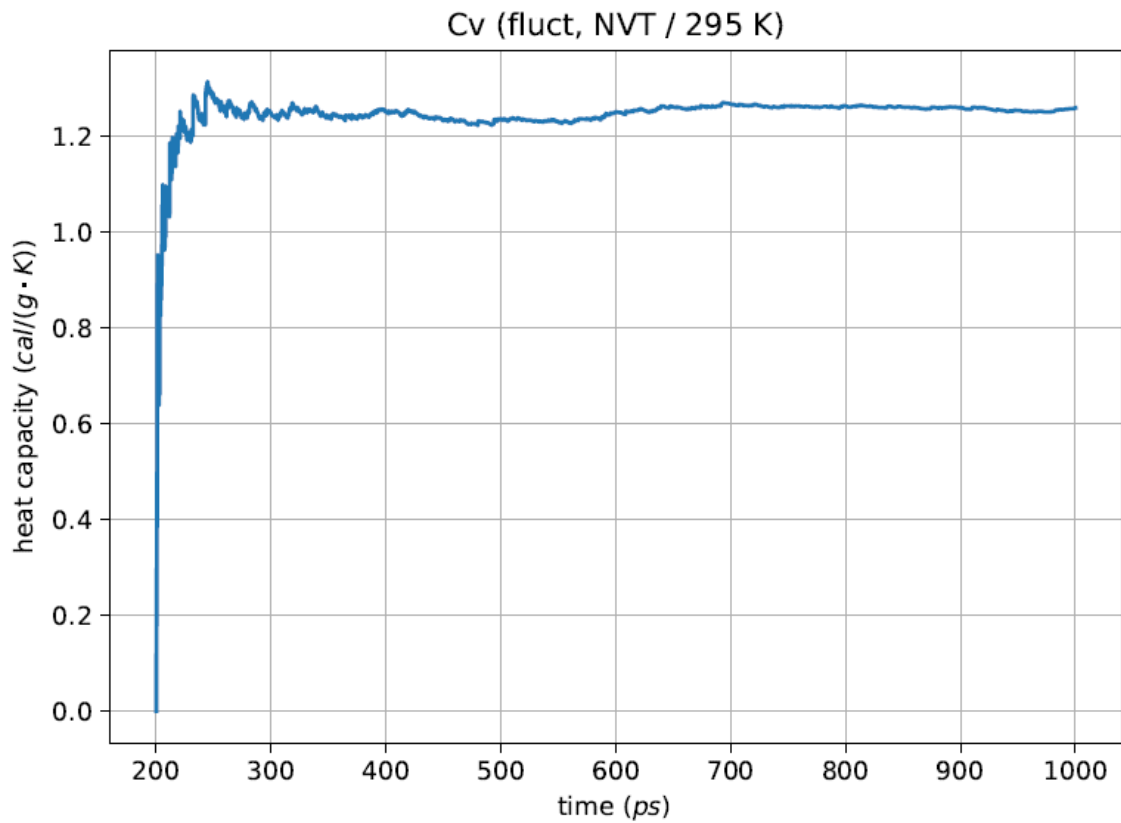


Image A.30: Cv at 295K for MeOH

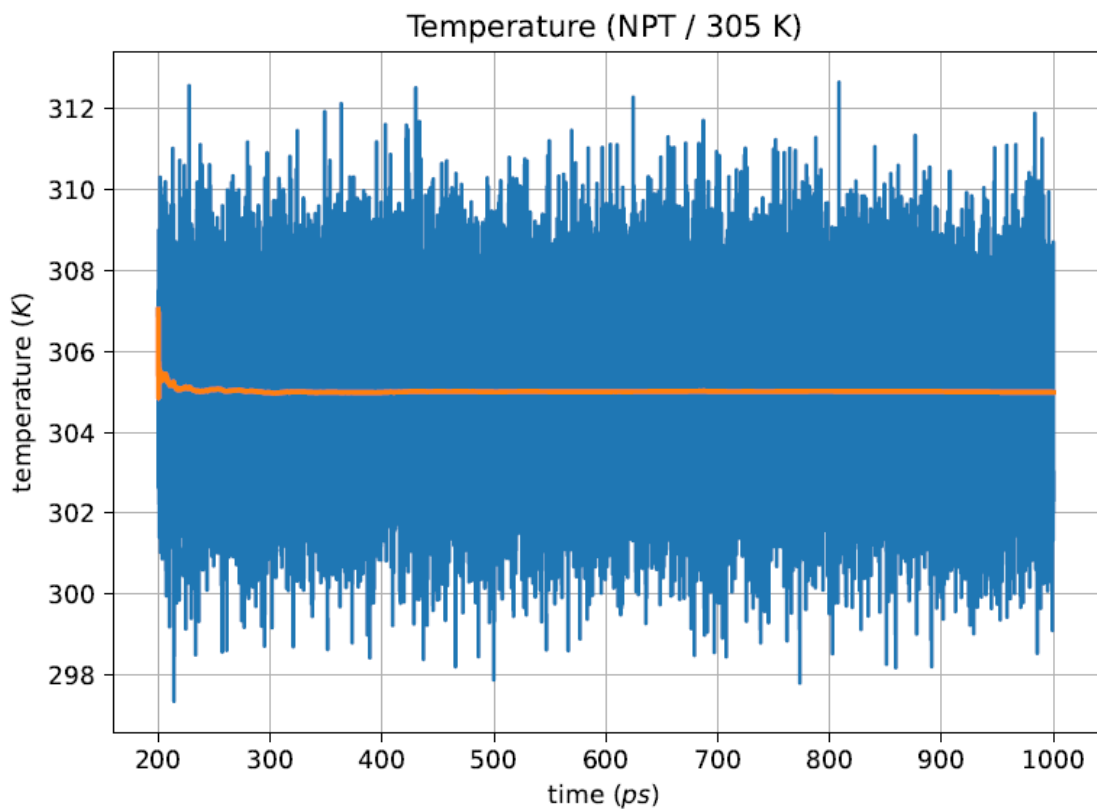


Image A.31:NPT temperature at 305K for MeOH

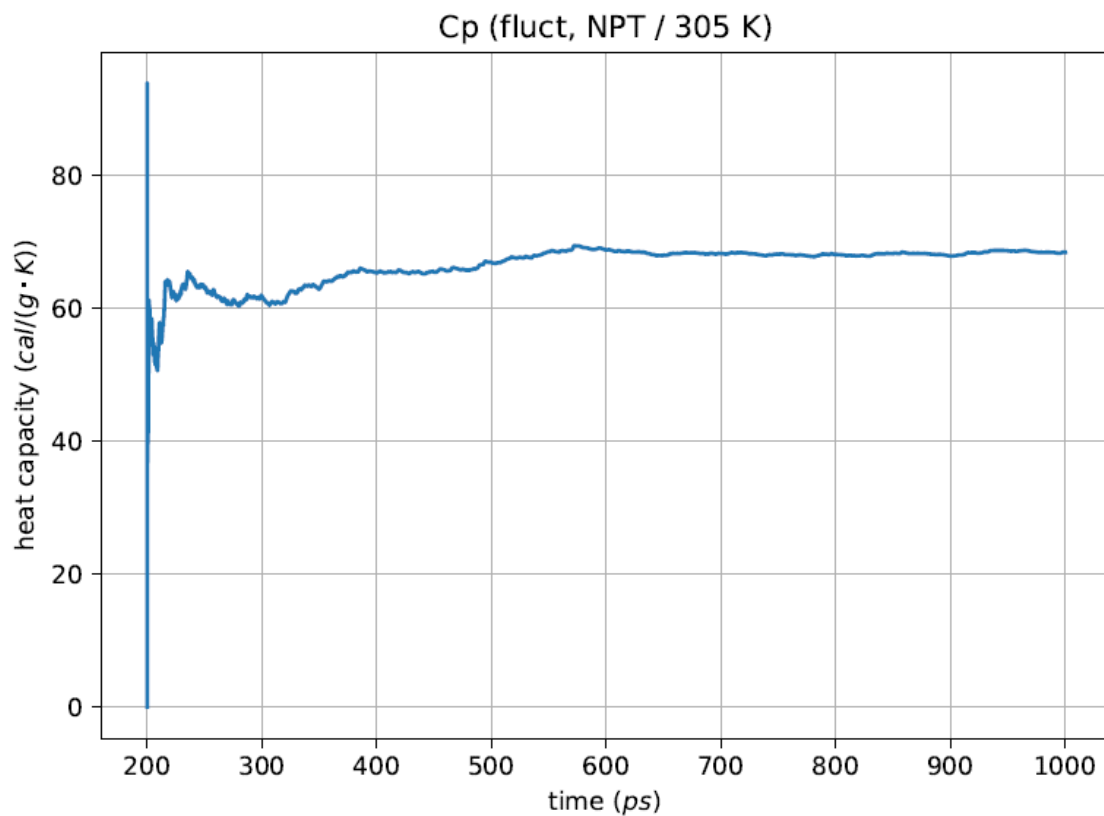


Image A.32:Cp at 305K for MeOH

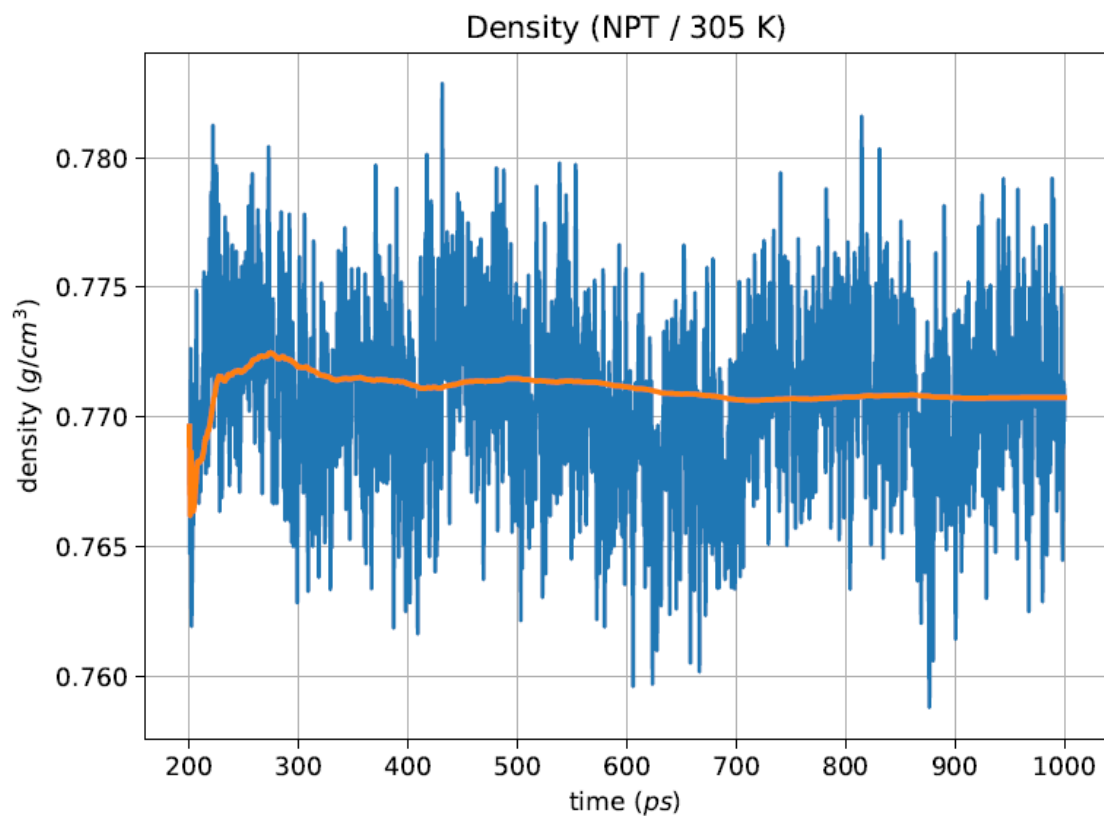


Image A.33:NPT Density at 305K for MeOH

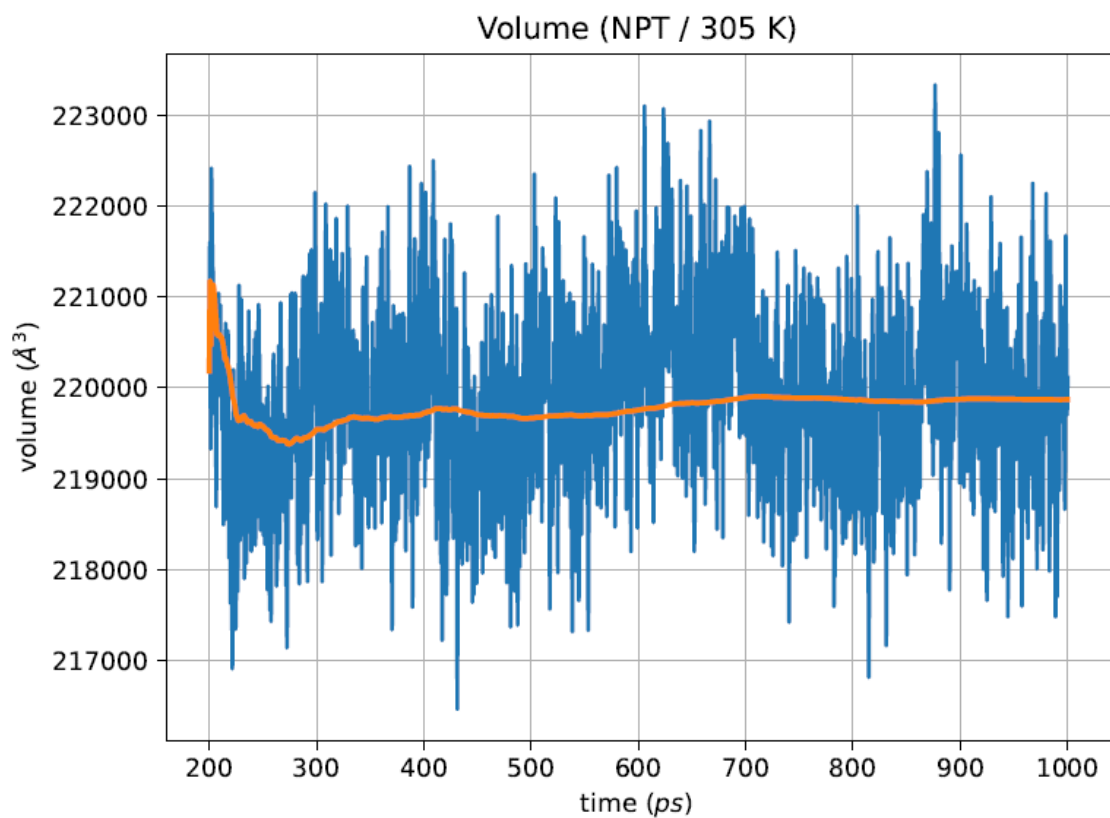


Image A.34:NPT Volume at 305K for MeOH

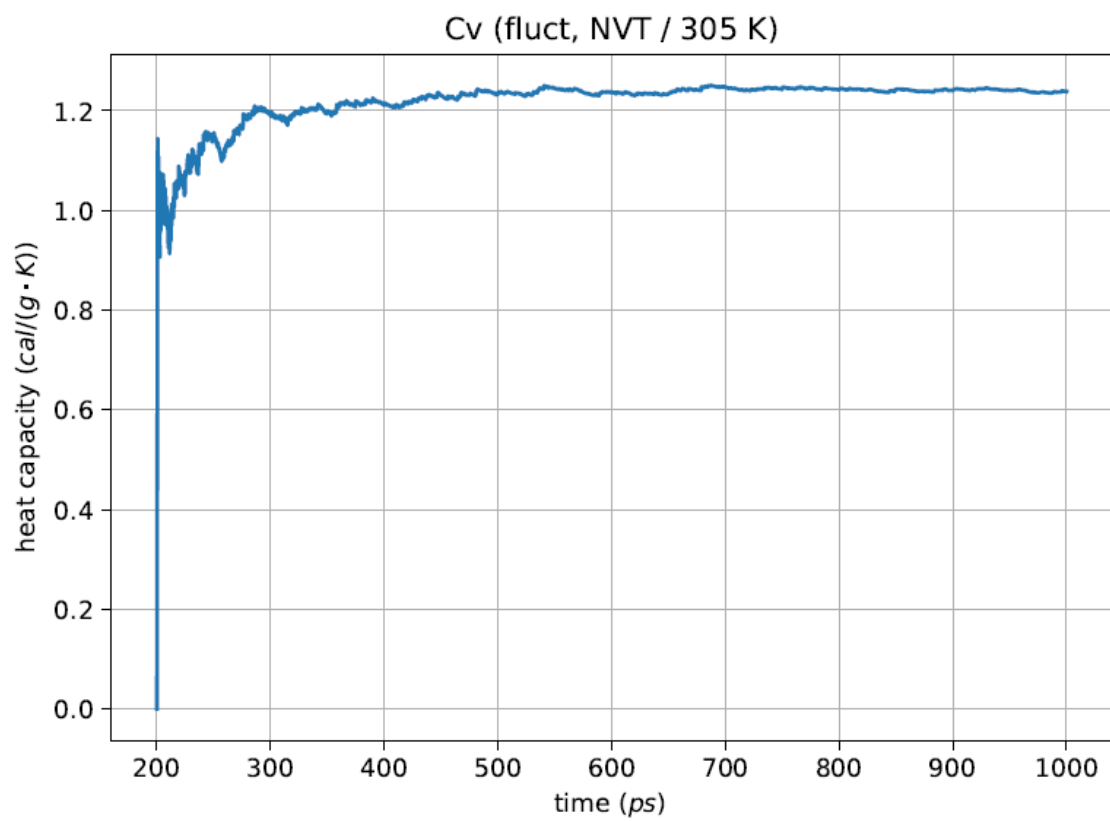


Image A.35:Cv at 305K for MeOH



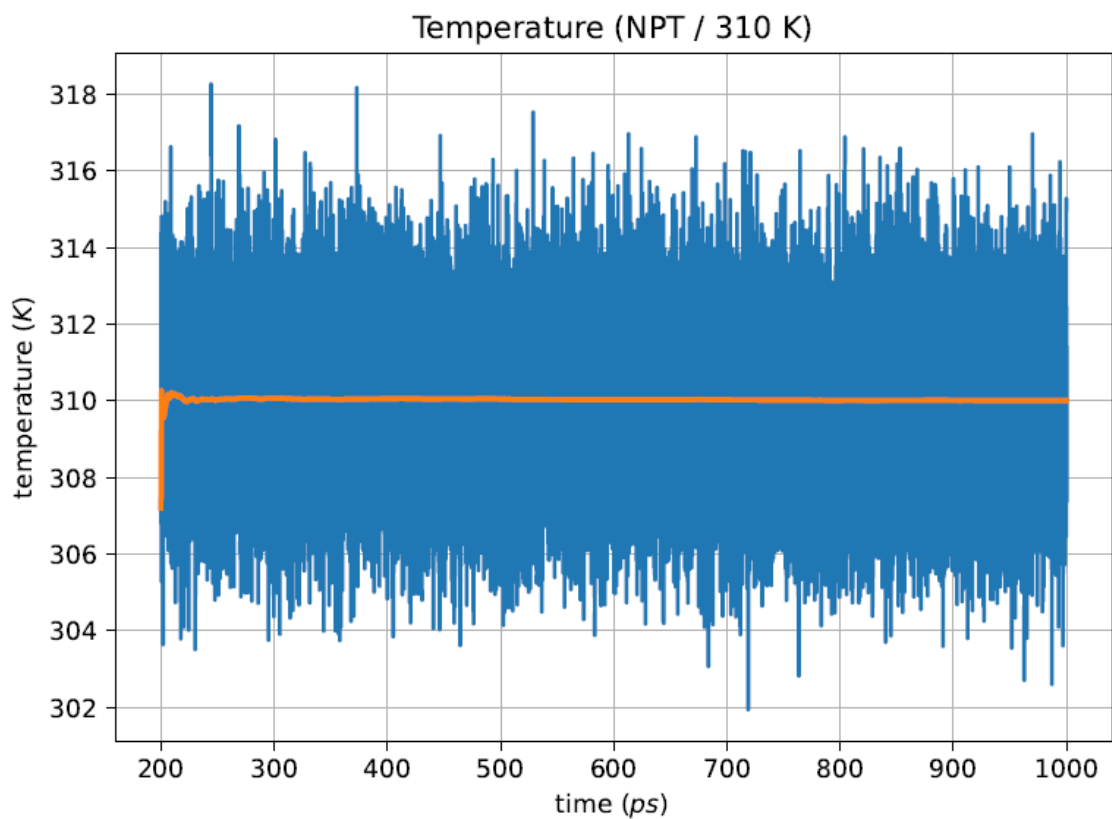


Image A.36:NPT temperature at 310K for MeOH

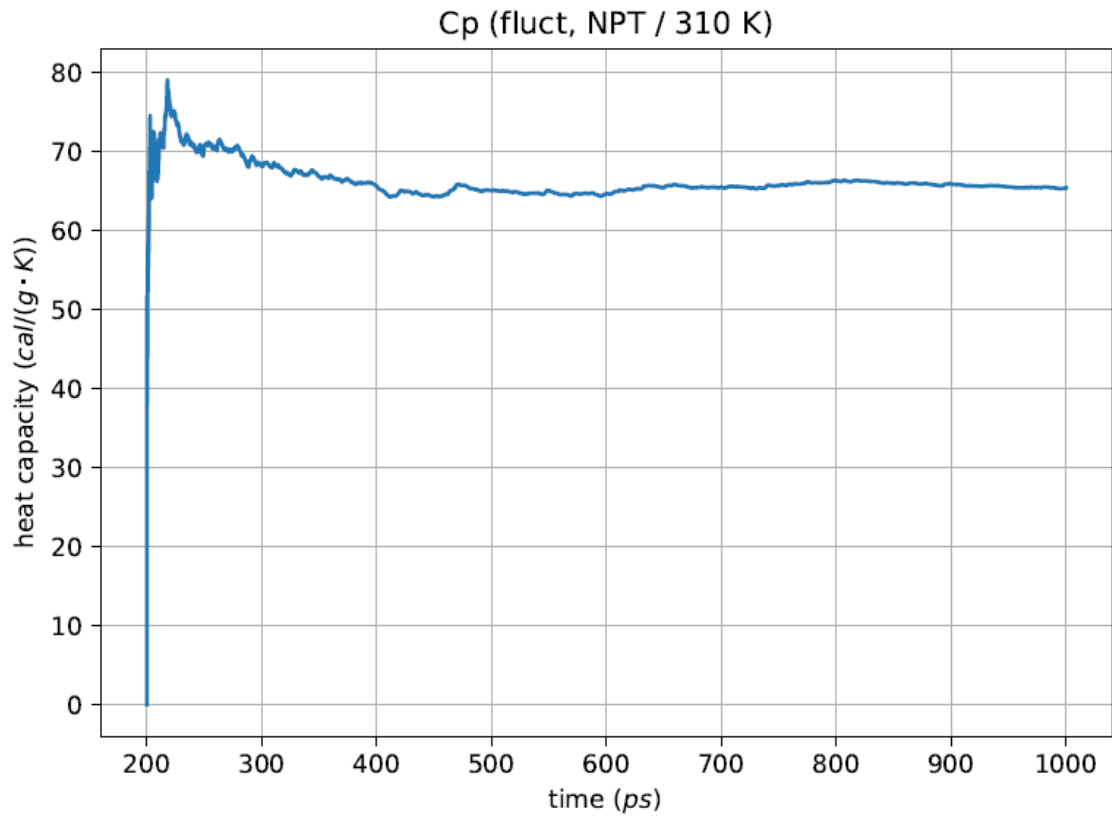


Image A.37:Cp at 310K for MeOH

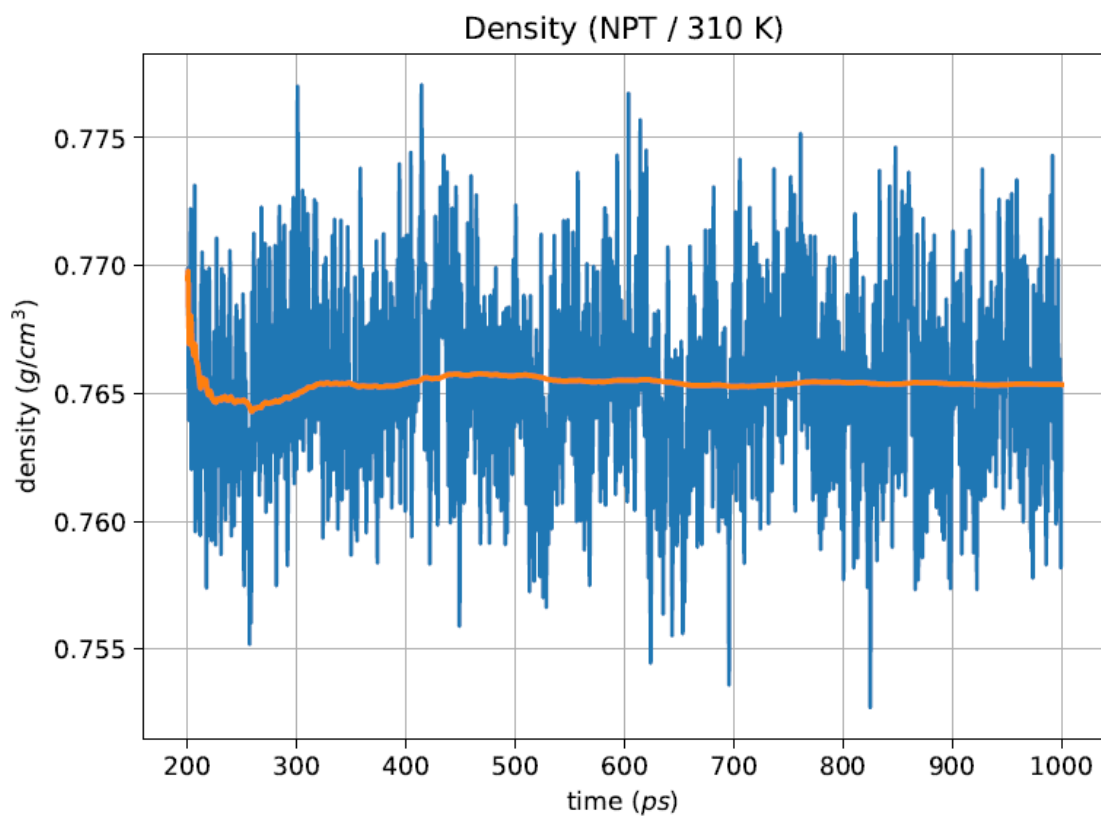


Image A.38:NPT Density at 310K for MeOH

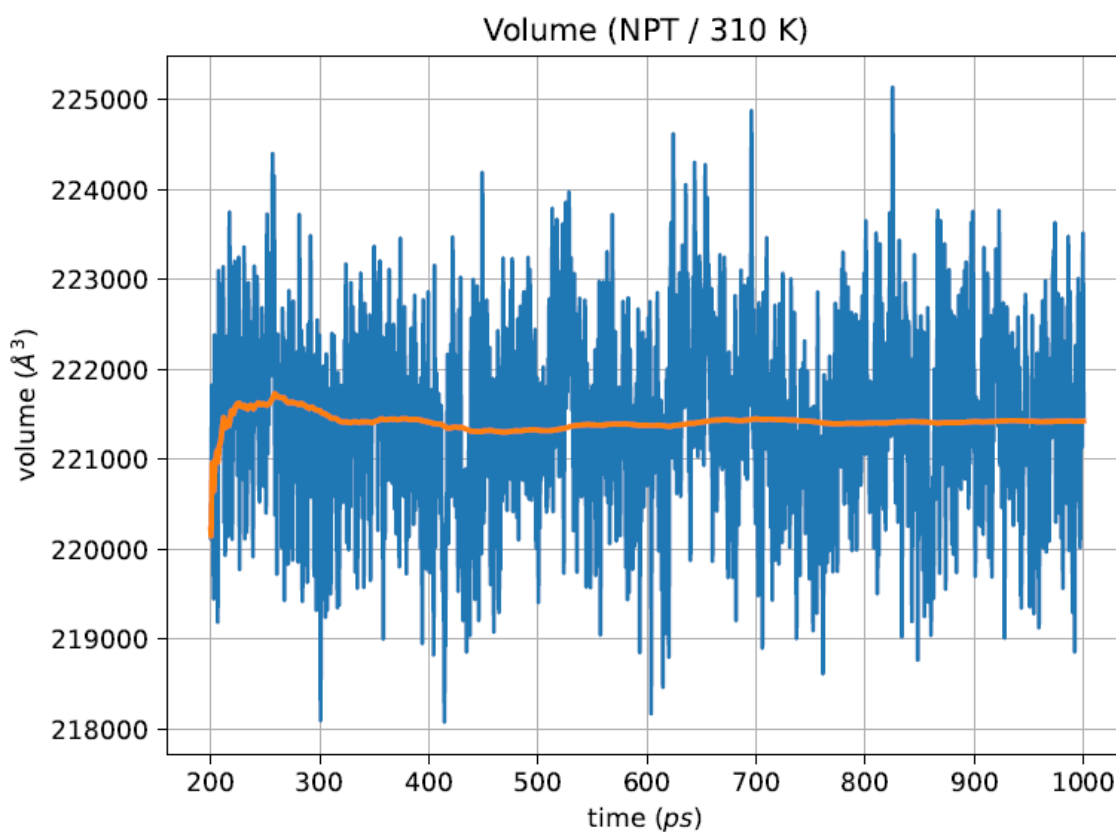


Image A.39:NPT Volume at 310K for MeOH

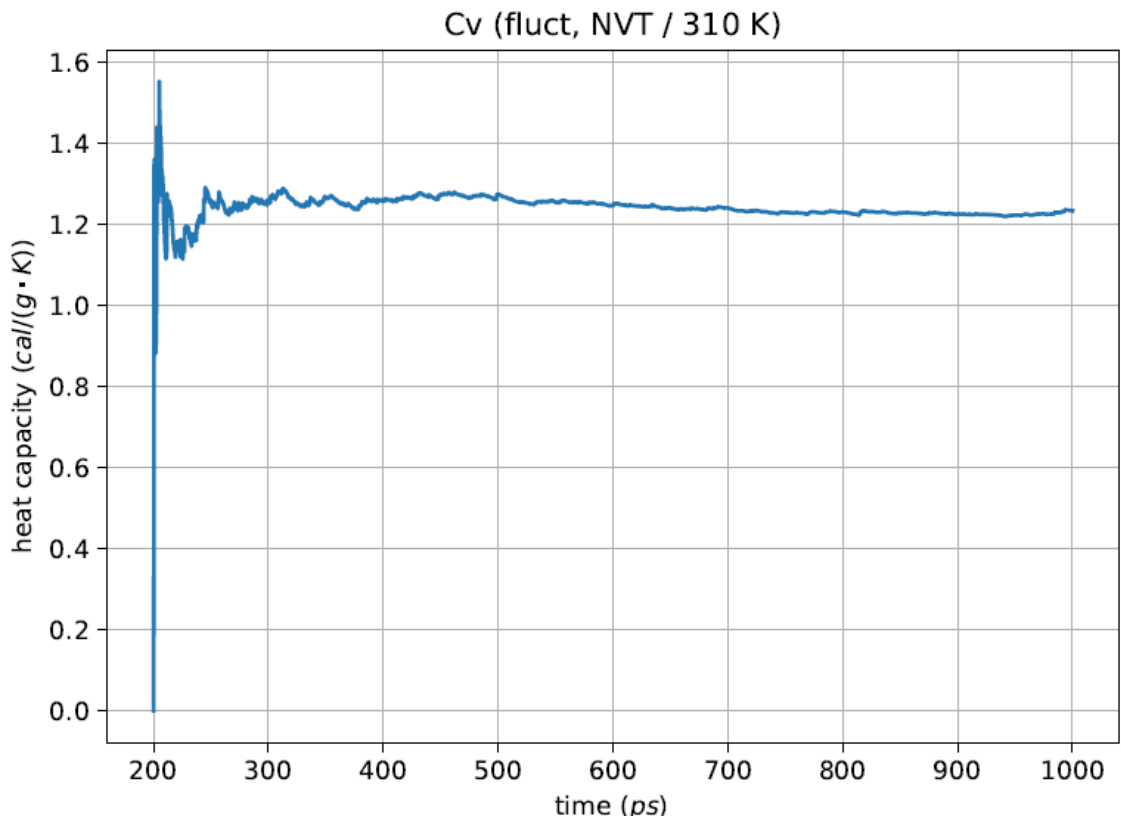


Image A.40: Cv at 310K for MeOH

### 3.-H<sub>2</sub>O (model 1):

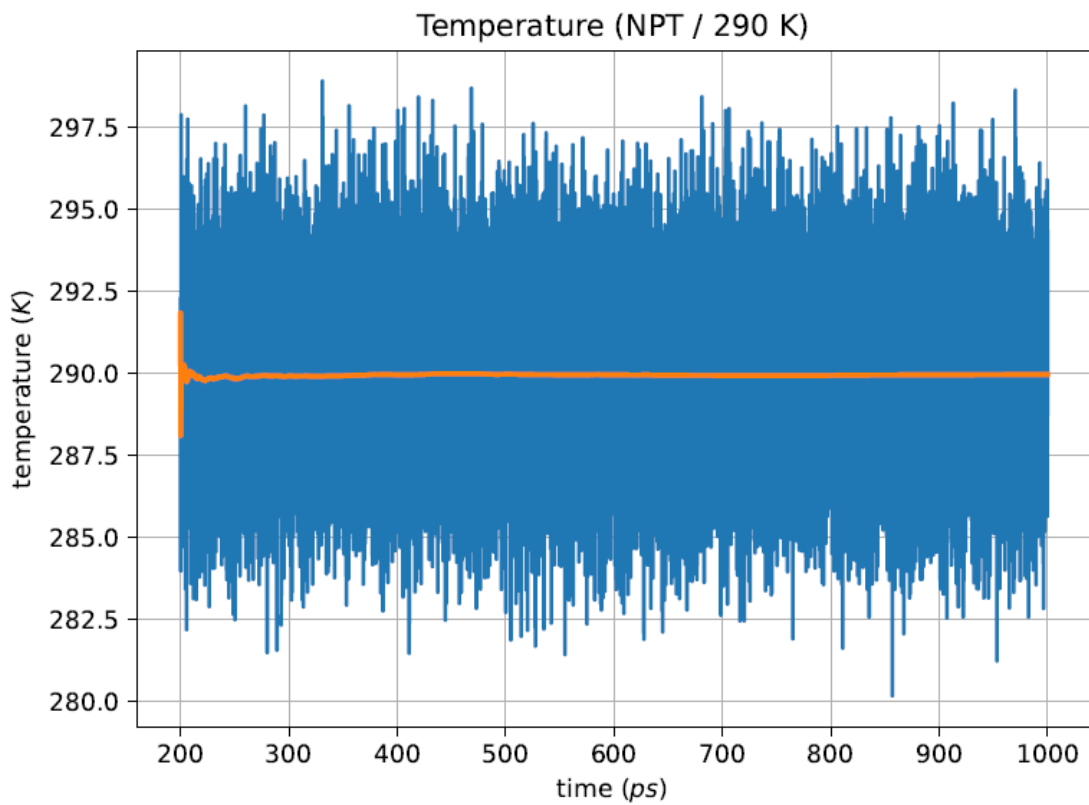


Image A.41:NPT temperature at 290K for H<sub>2</sub>O model1

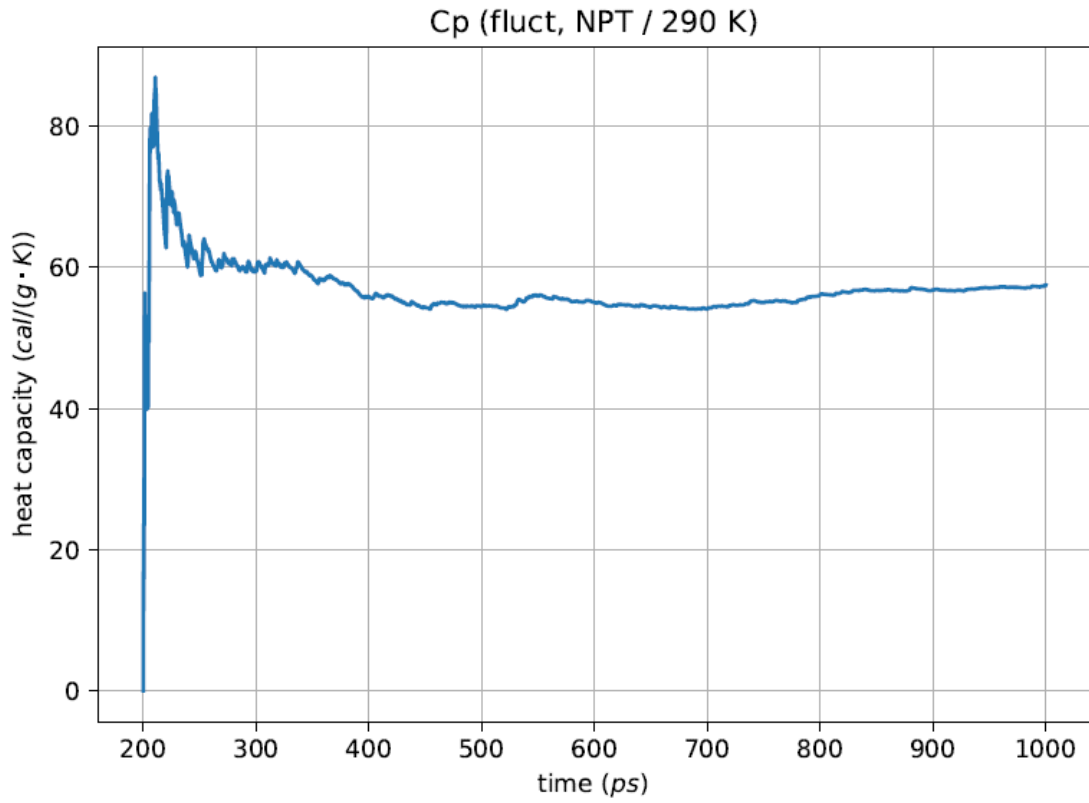


Image A.42:Cp at 290K for H<sub>2</sub>O **model1**

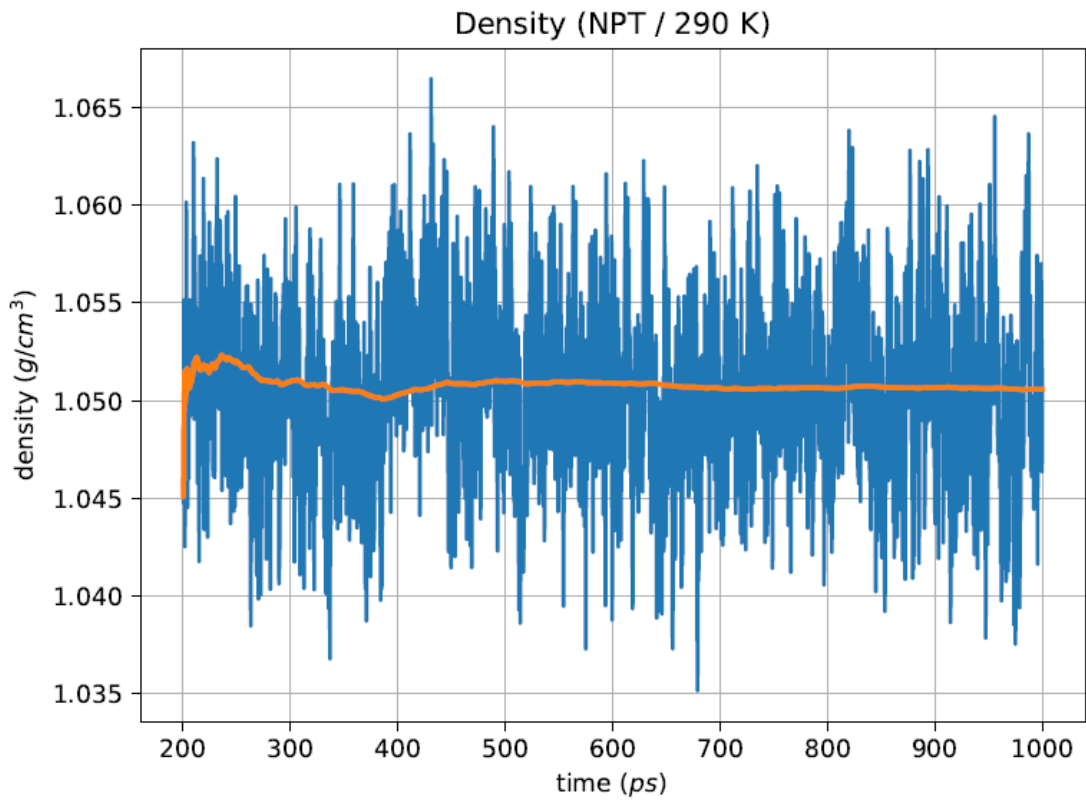


Image A.43:NPT Density at 290K for H<sub>2</sub>O **model1**

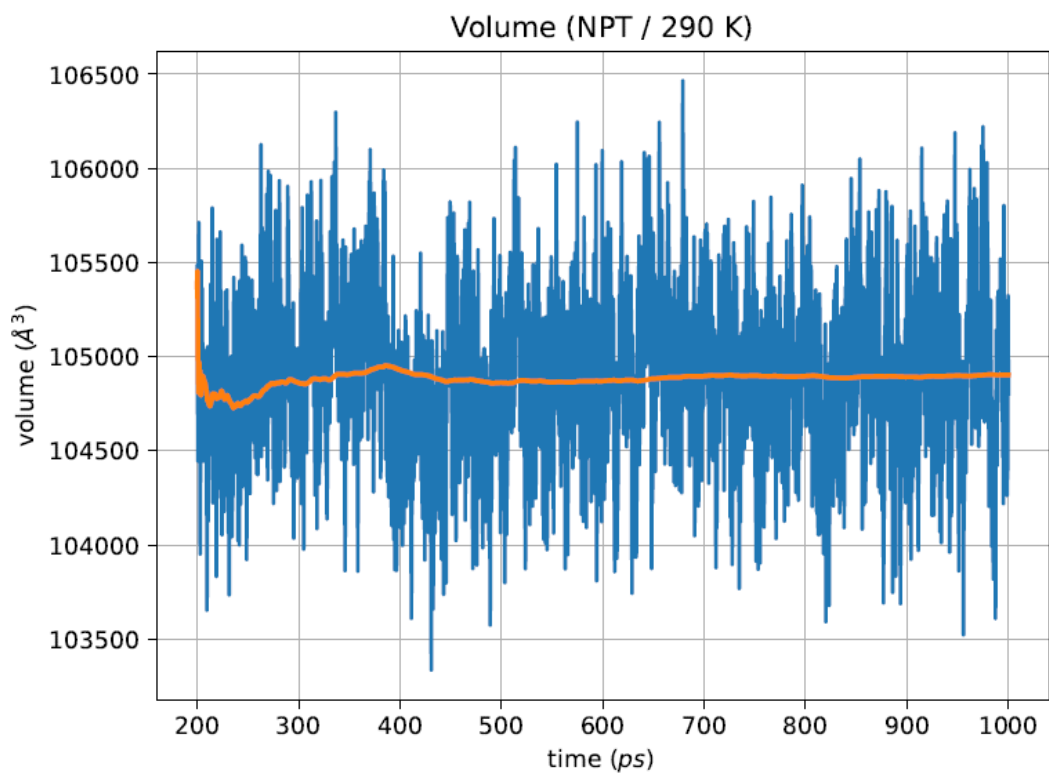


Image A.44:NPT Volume at 290K for H<sub>2</sub>O model1

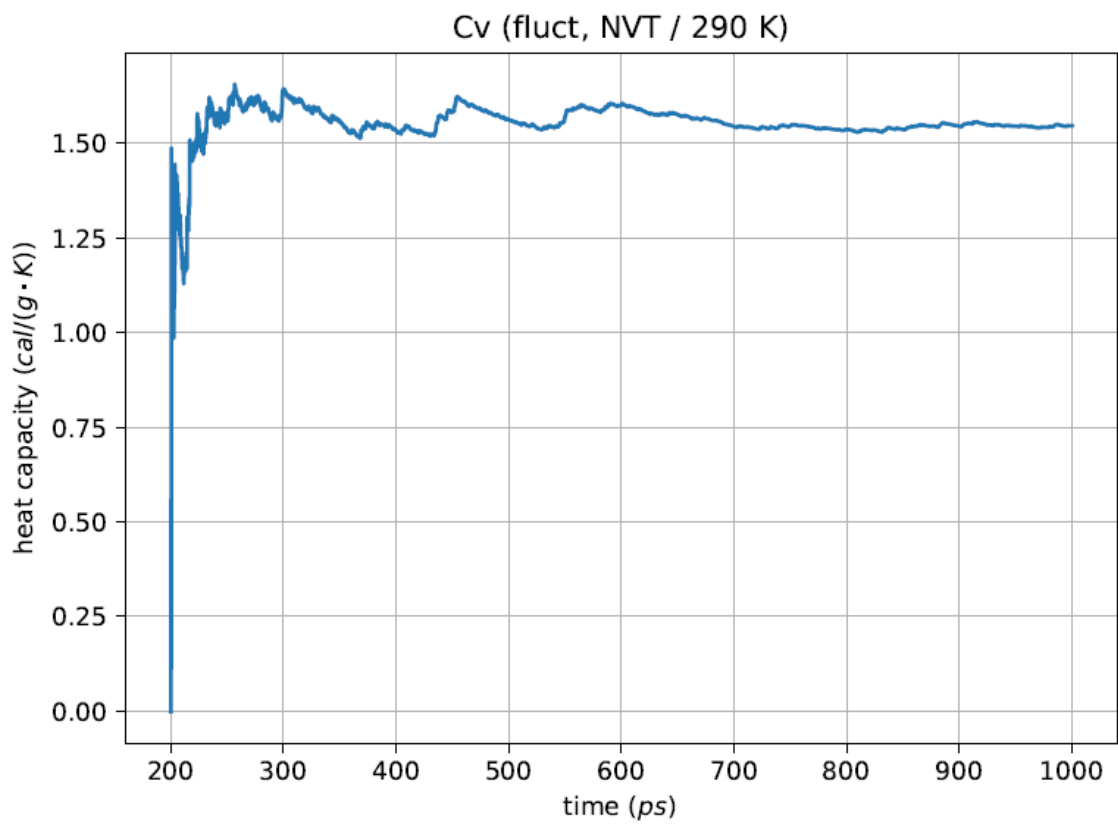


Image A.45: $C_v$  at 290K for H<sub>2</sub>O model1

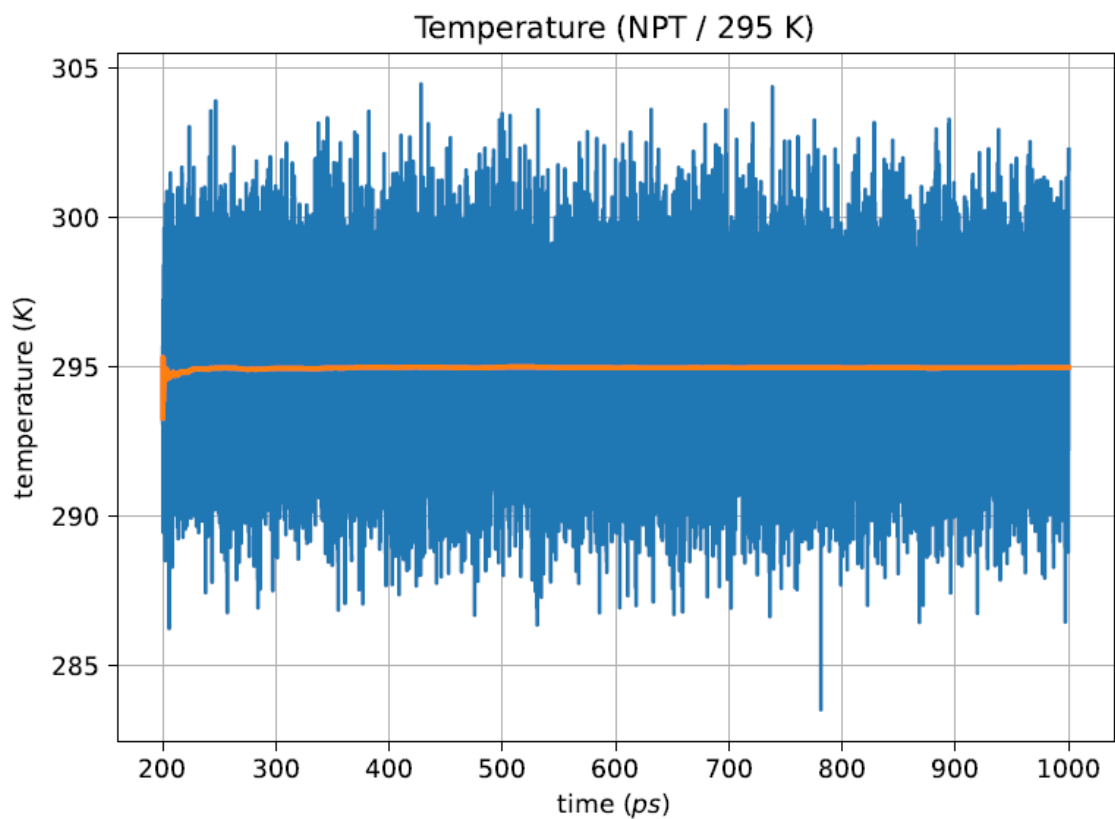


Image A.46:NPT temperature at 295K for H<sub>2</sub>O **model1**

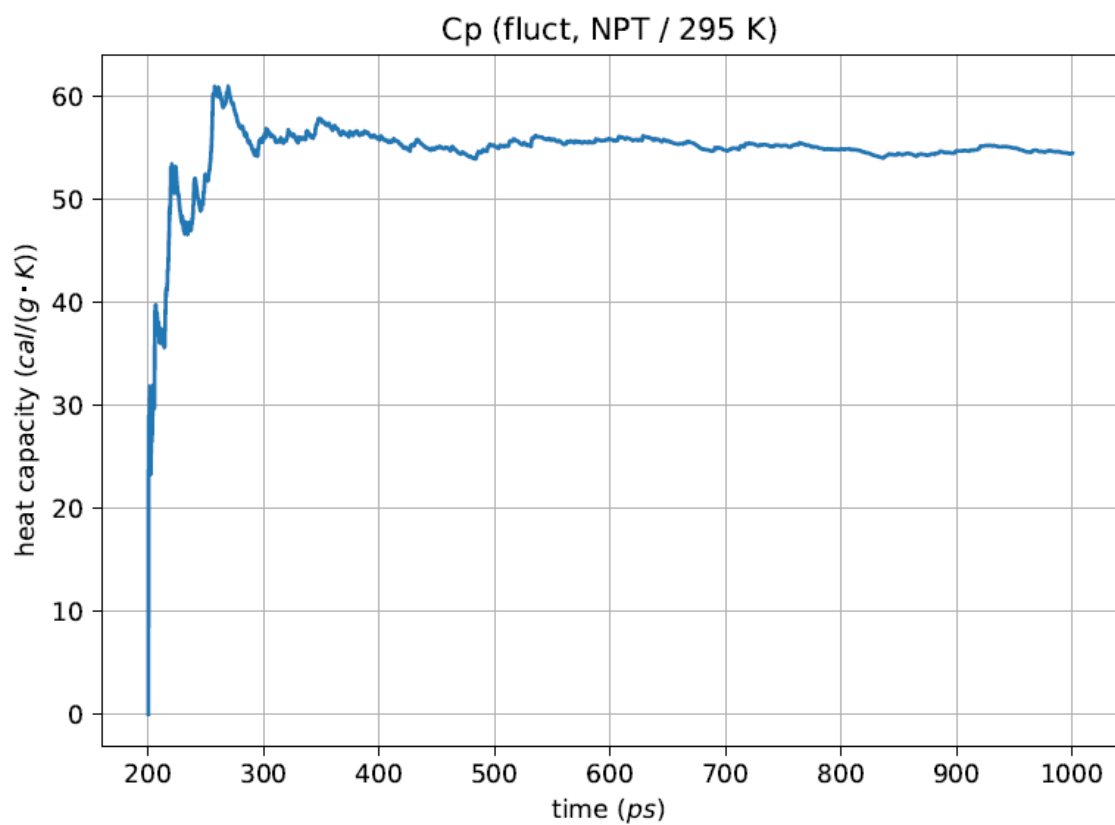


Image A.47:Cp at 295K for H<sub>2</sub>O **model1**

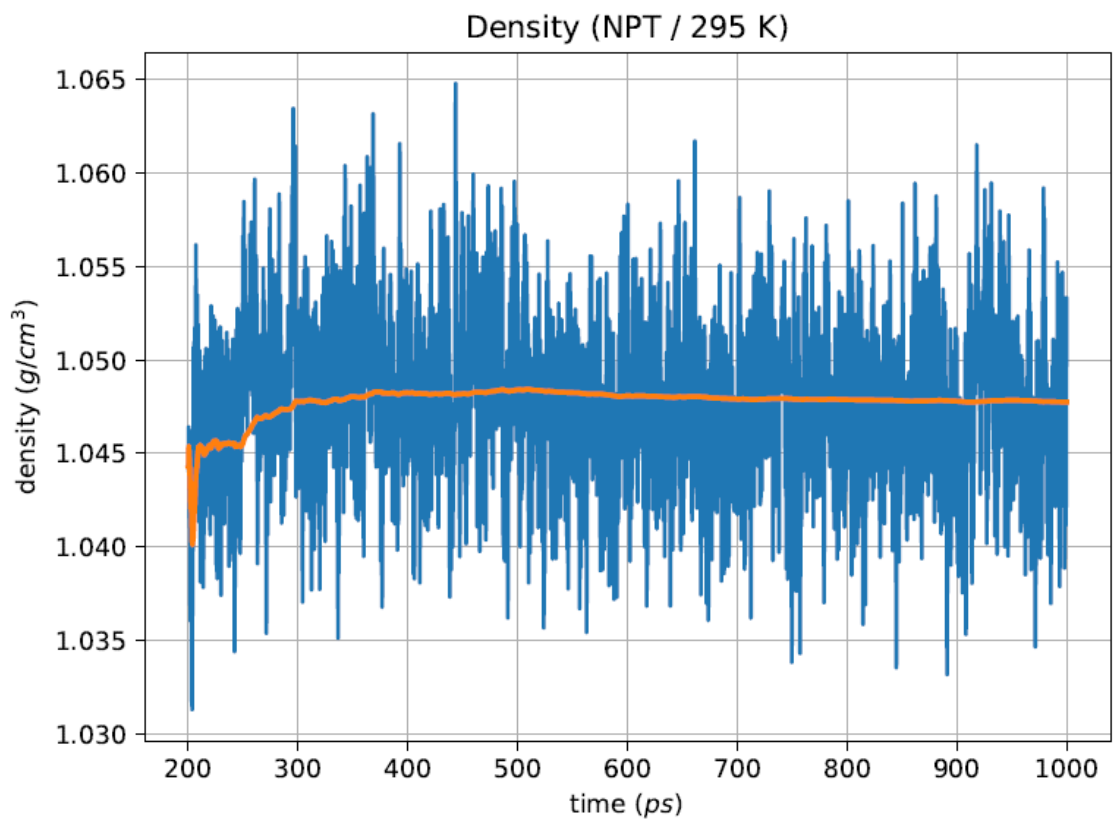


Image A.48:NPT Density at 295K for H<sub>2</sub>O **model1**

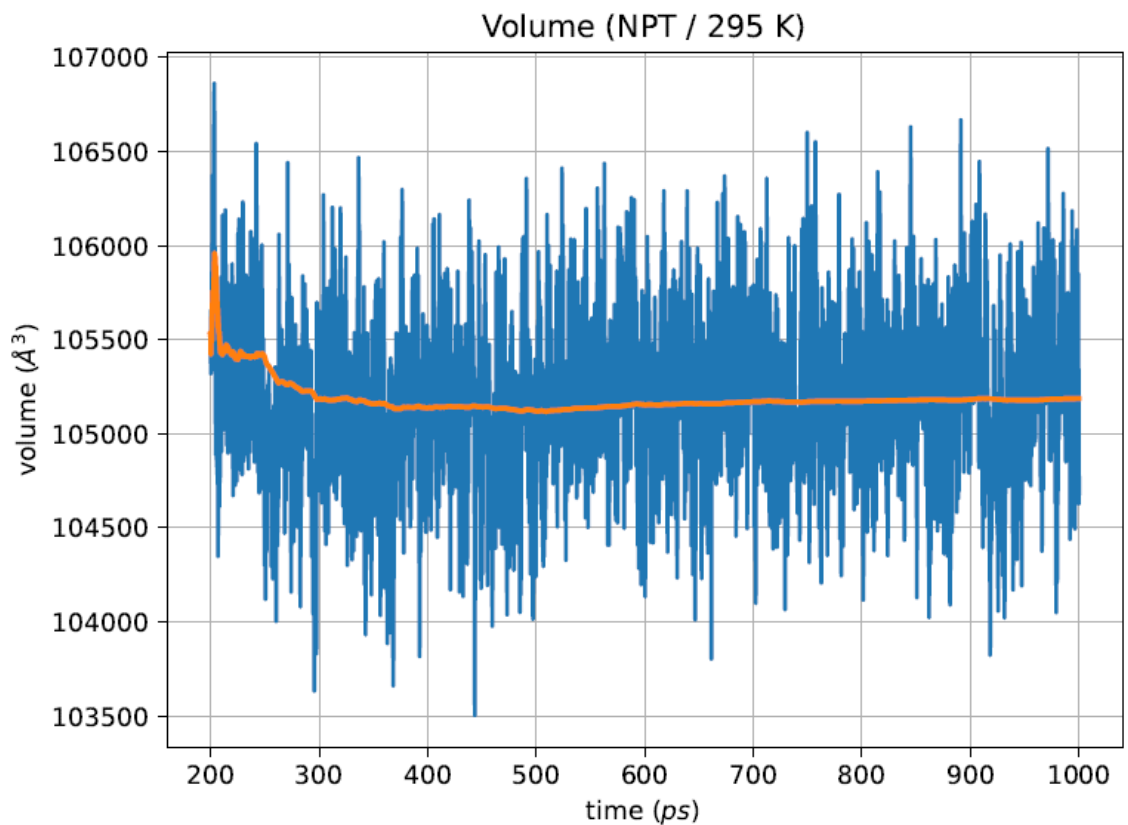


Image A.49:NPT Volume at 295K for H<sub>2</sub>O **model1**

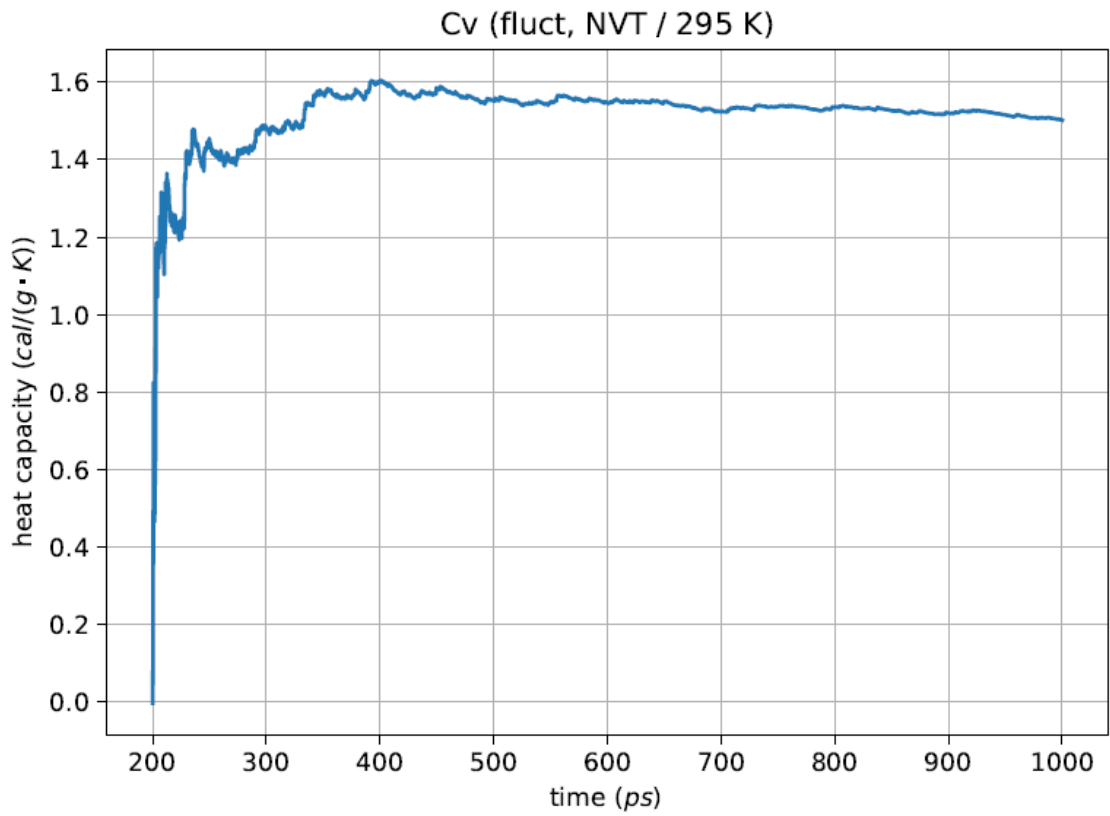


Image A.50:Cv at 295K for H<sub>2</sub>O **model1**

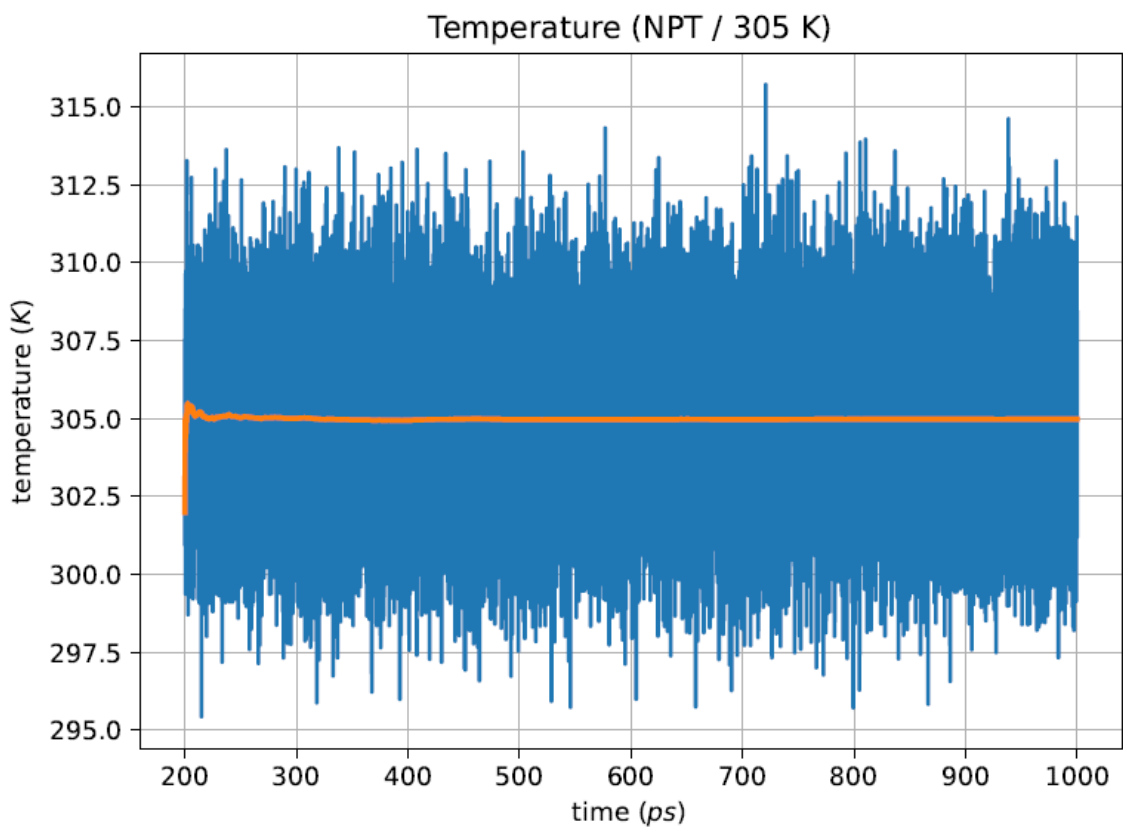


Image A.51:NPT temperature at 305K for H<sub>2</sub>O **model1**



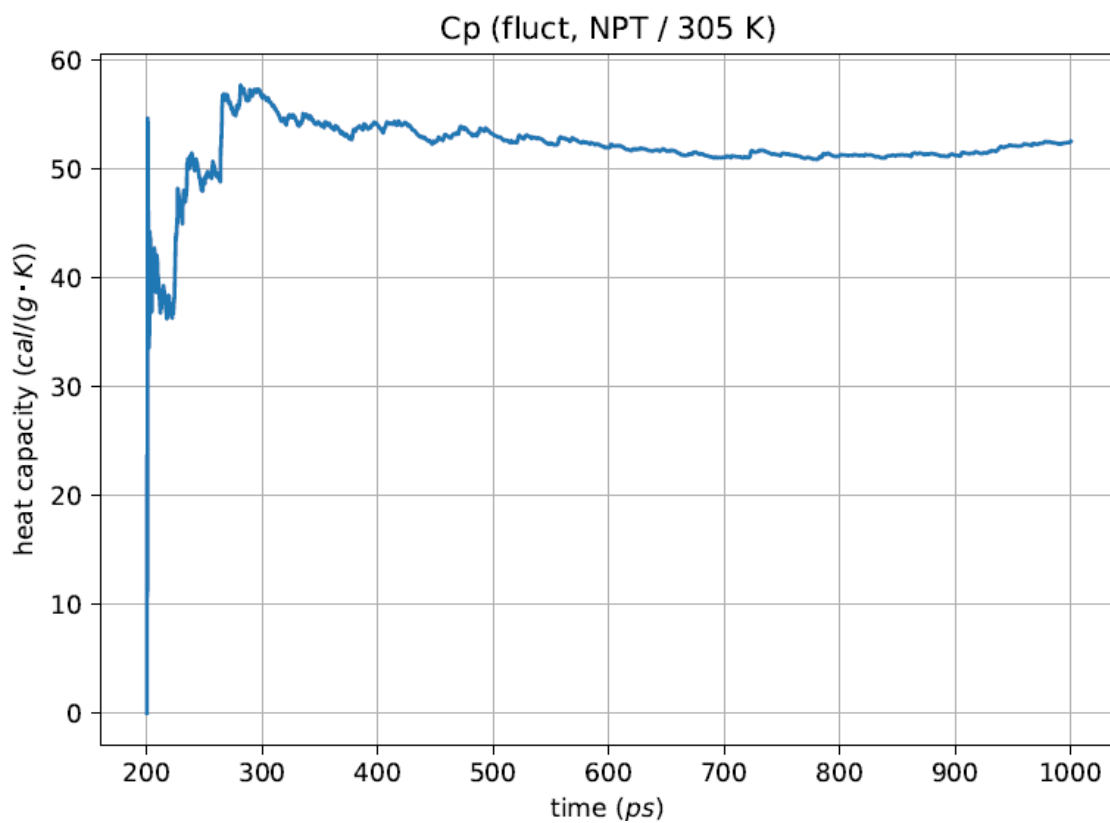


Image A.52: Cp at 305K for H<sub>2</sub>O **model1**

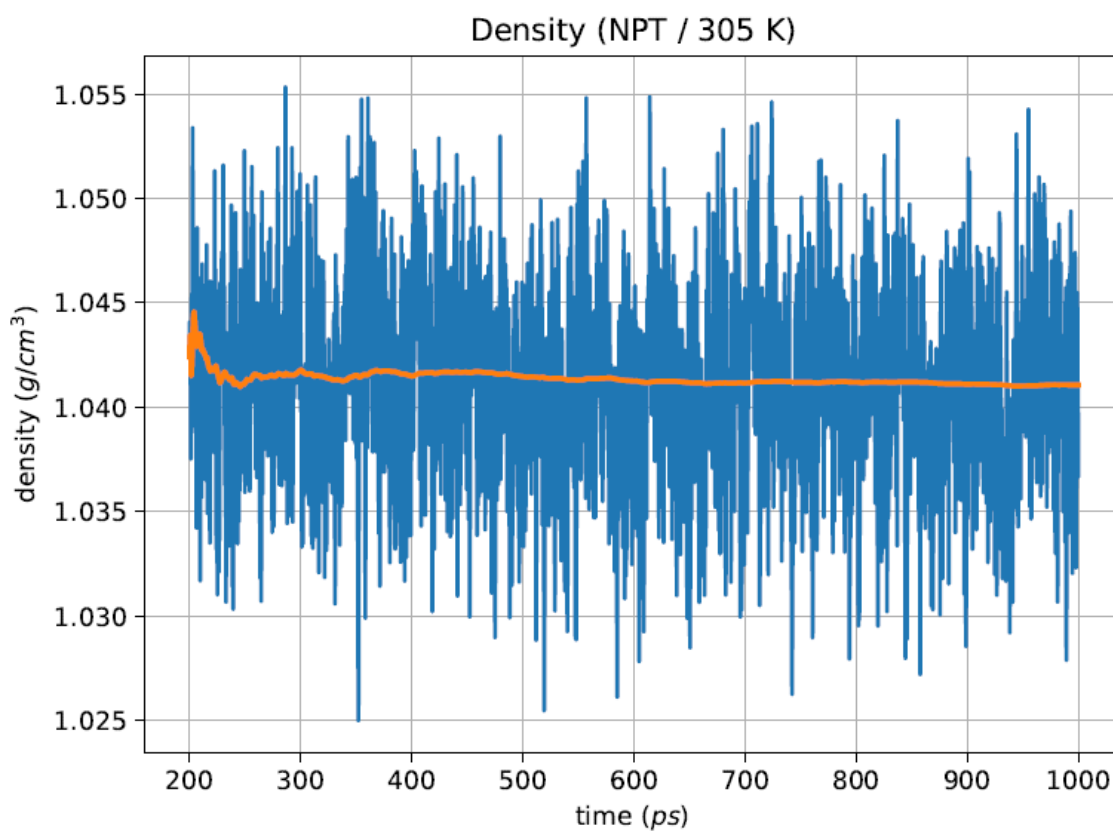


Image A.53: NPT Density at 305K for H<sub>2</sub>O **model1**

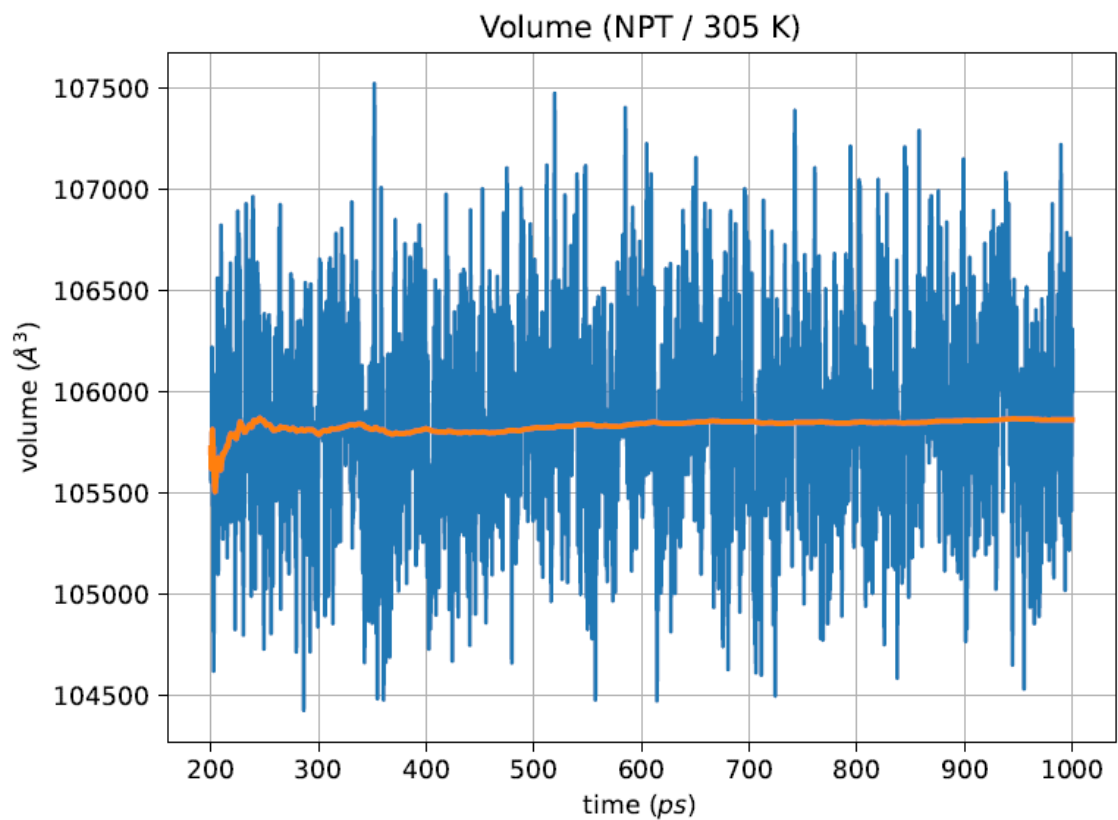


Image A.54:NPT Volume at 305K for H<sub>2</sub>O **model1**

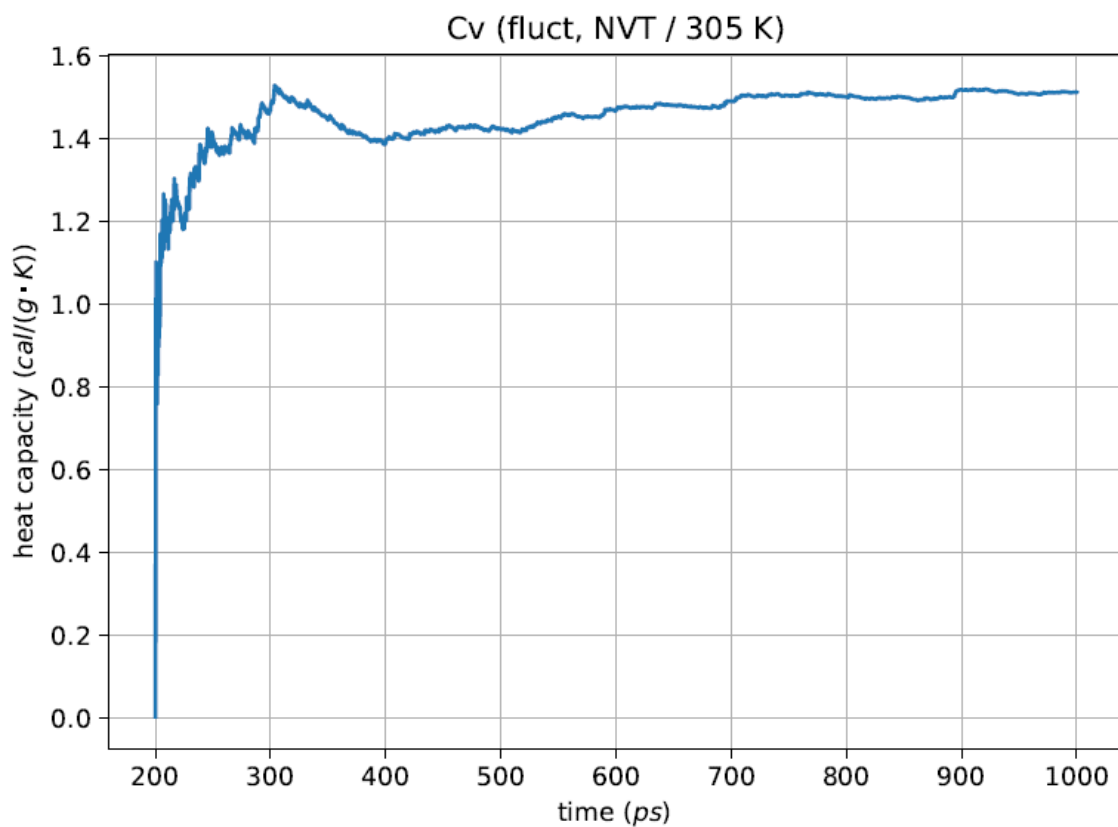


Image A.55: $C_v$  at 305K for H<sub>2</sub>O **model1**

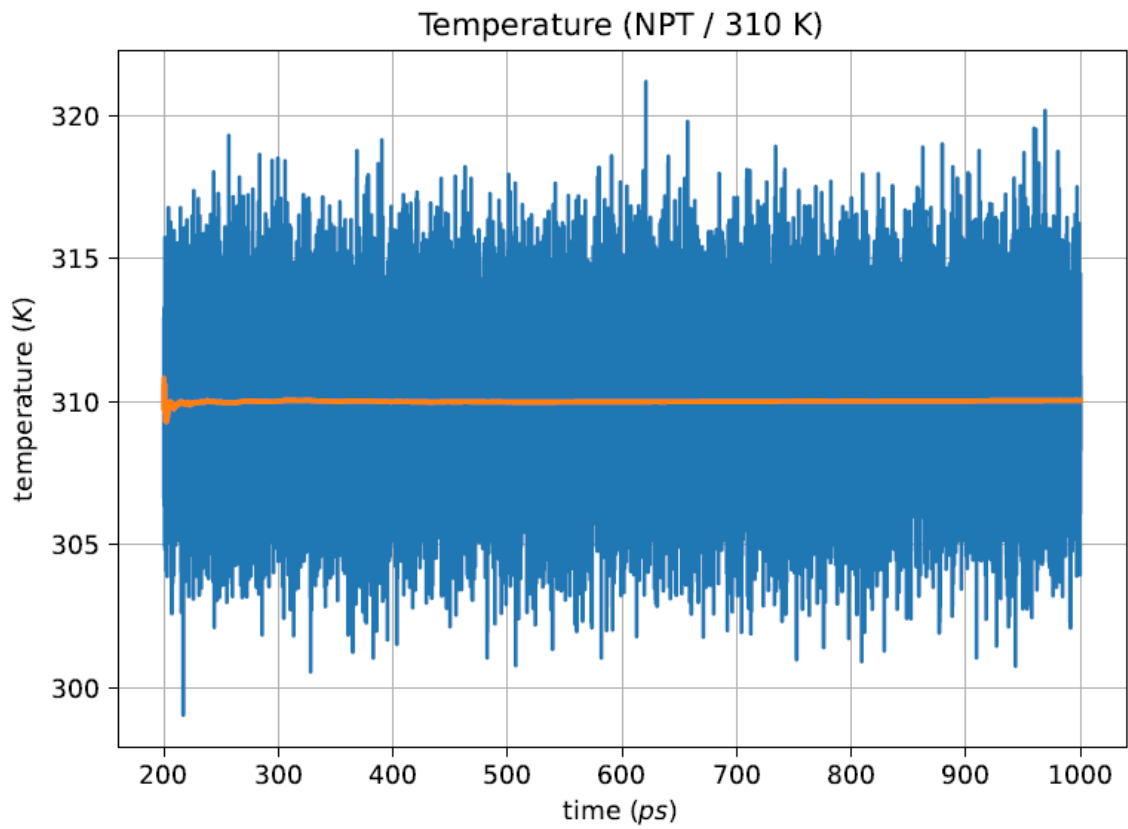


Image A.56:NPT temperature at 310K for H<sub>2</sub>O model1

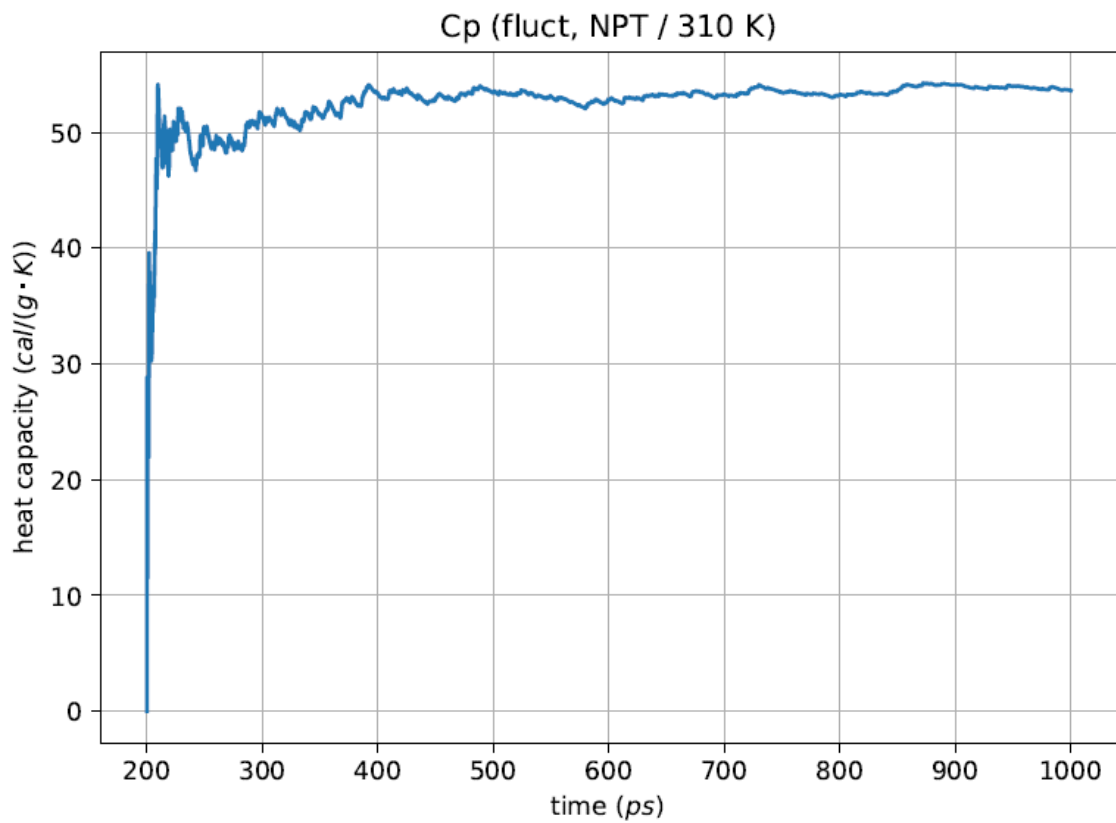


Image A.57:Cp at 310K for H<sub>2</sub>O model1

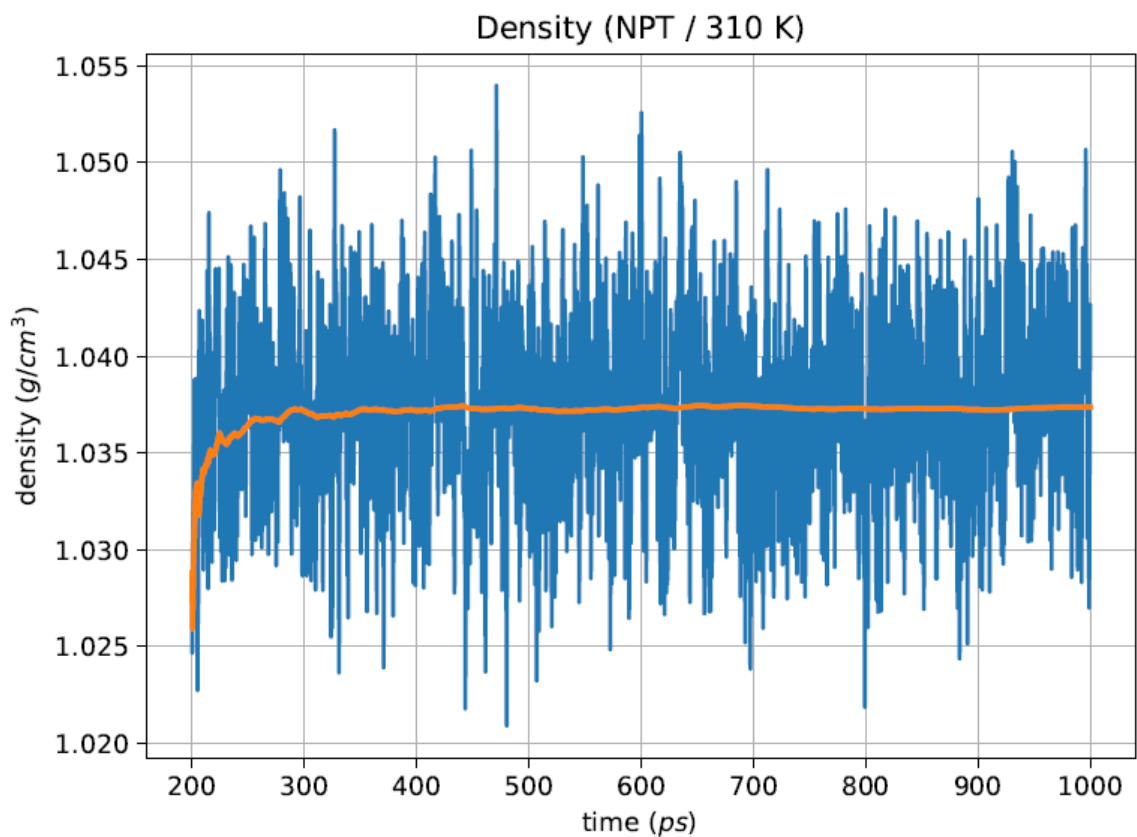


Image A.58:NPT Density at 310K for H<sub>2</sub>O **model1**

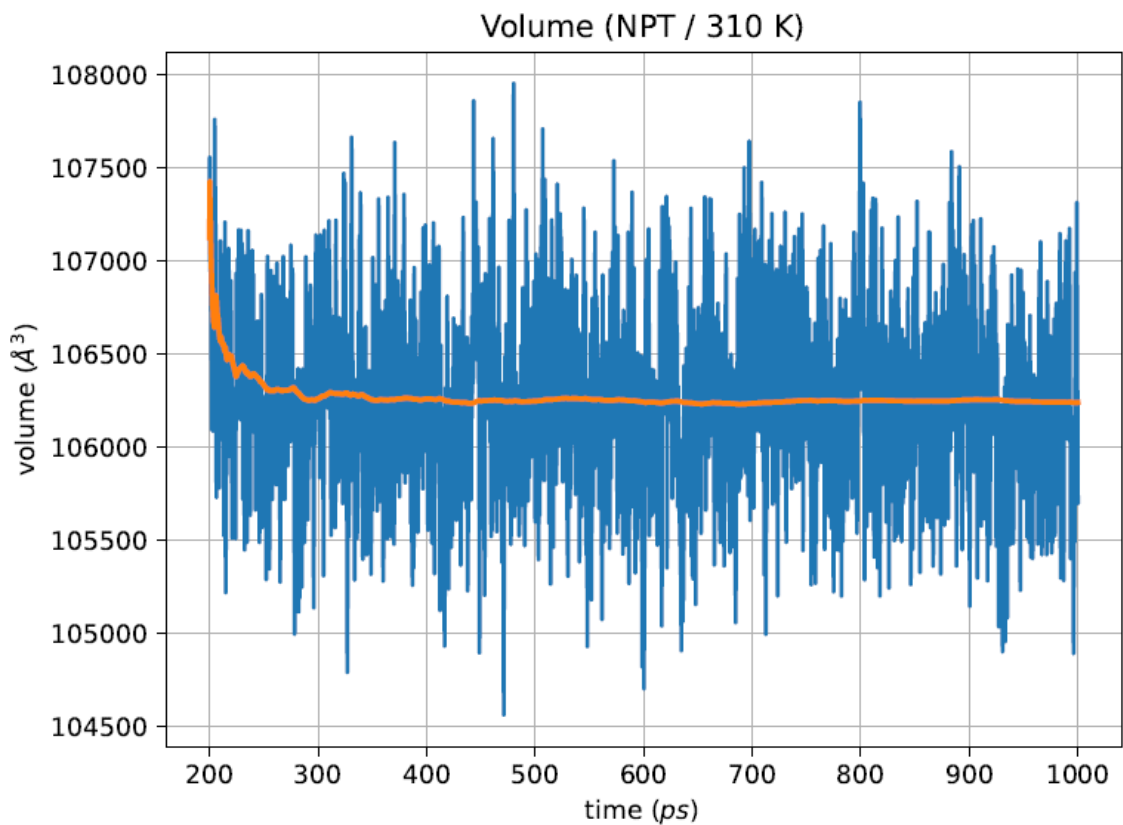


Image A.59:NPT Volume at 310K for H<sub>2</sub>O **model1**

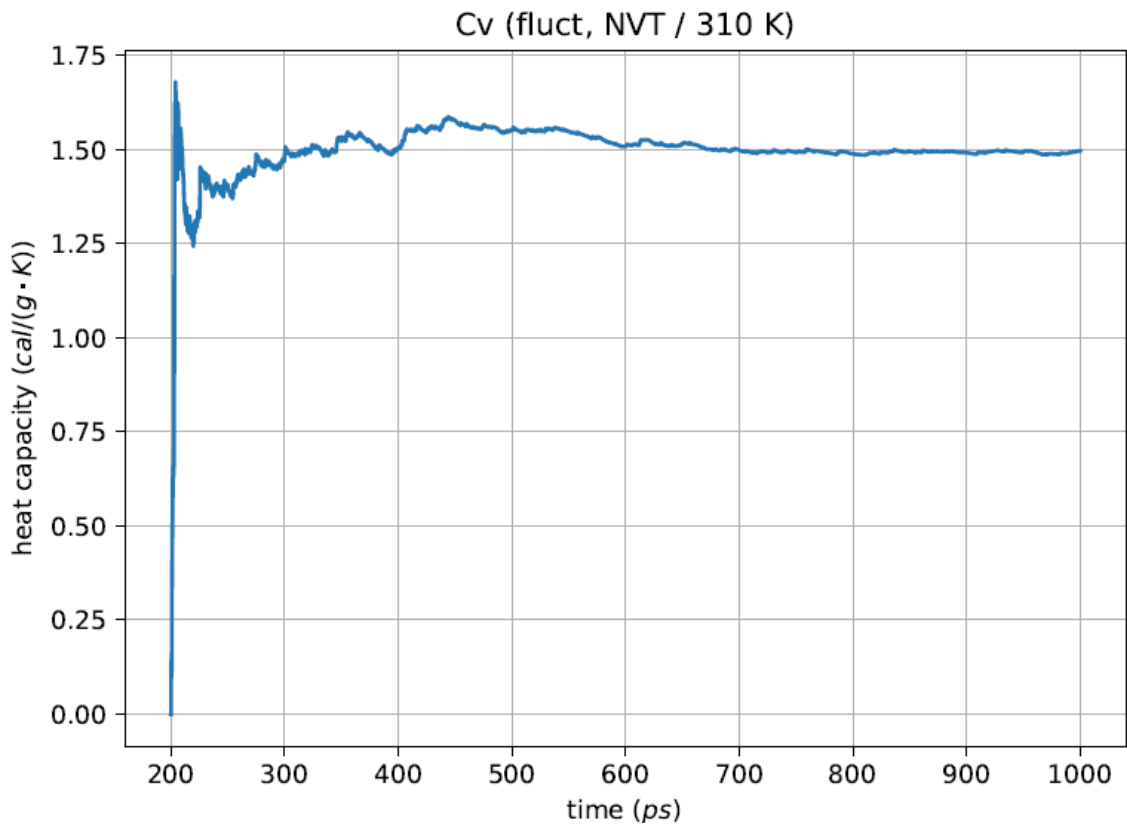


Image A.60:  $C_v$  at 310K for H<sub>2</sub>O **model1**

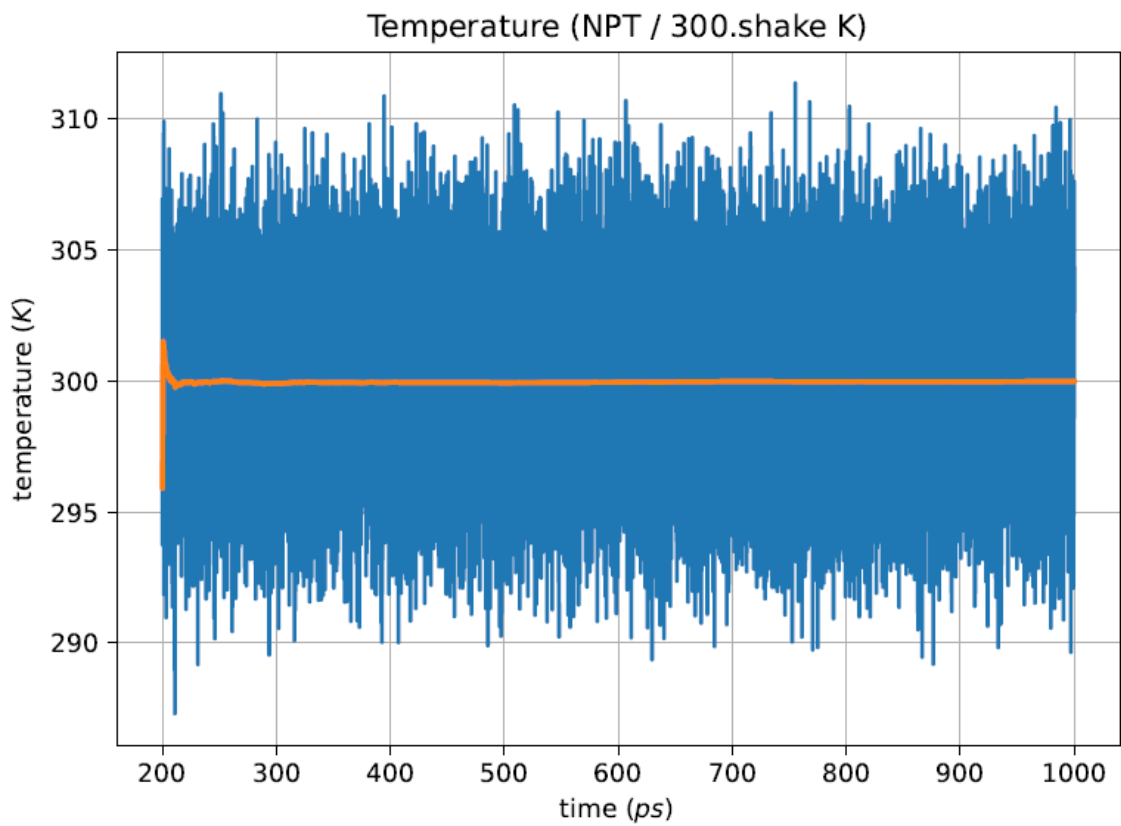


Image A.61: NPT temperature at 300K for H<sub>2</sub>O rigid **model1**

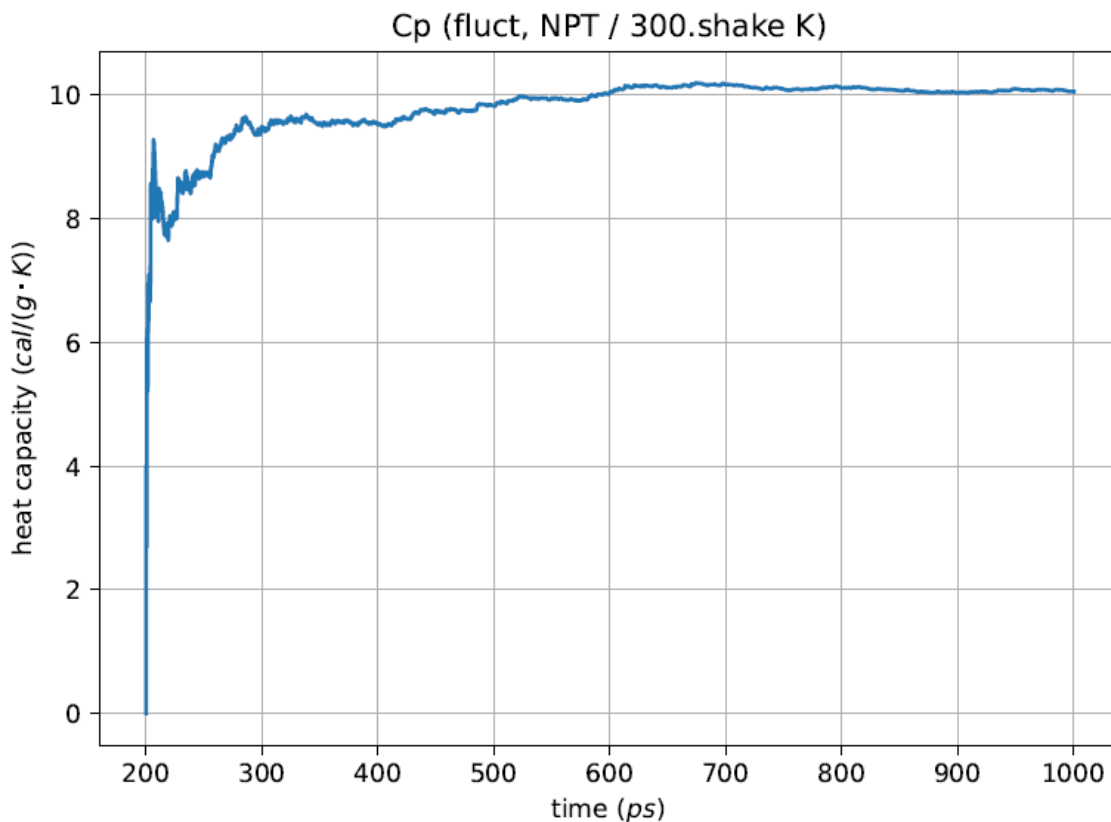


Image A.62:Cp at 300K for H<sub>2</sub>O rigid **model1**

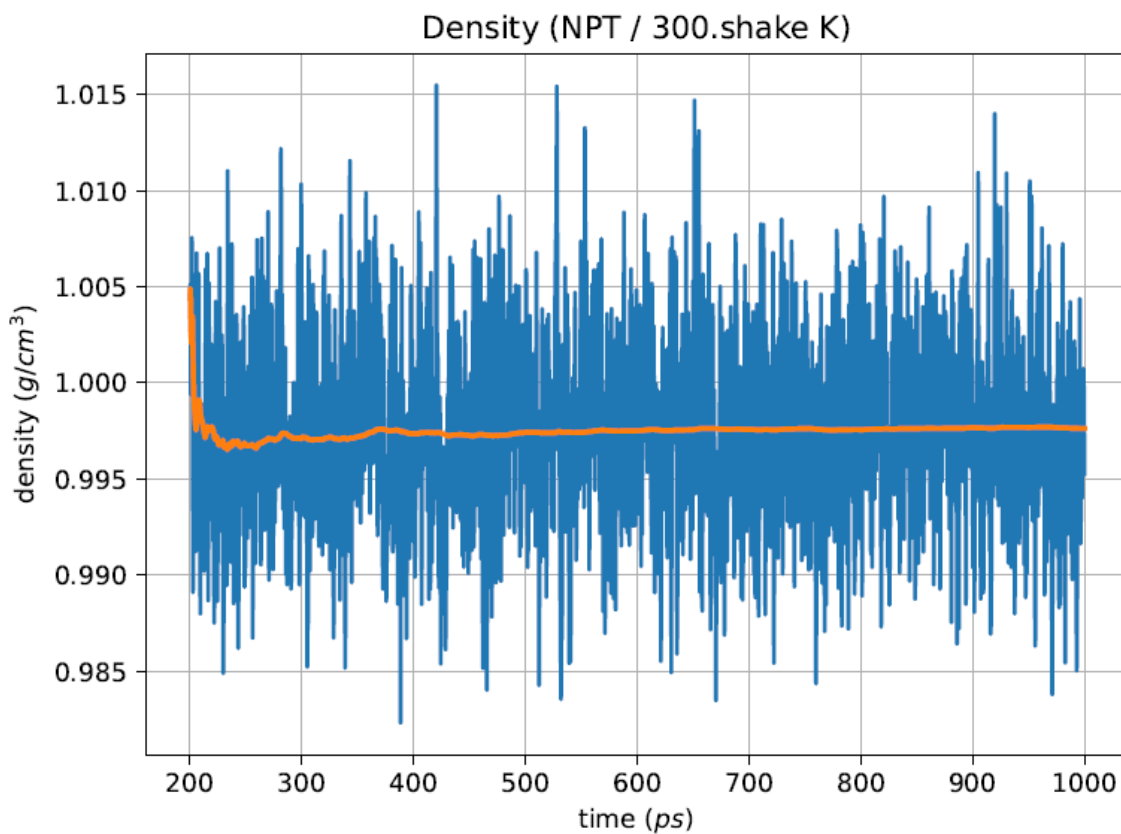


Image A.63:NPT Density at 300K for H<sub>2</sub>O rigid **model1**

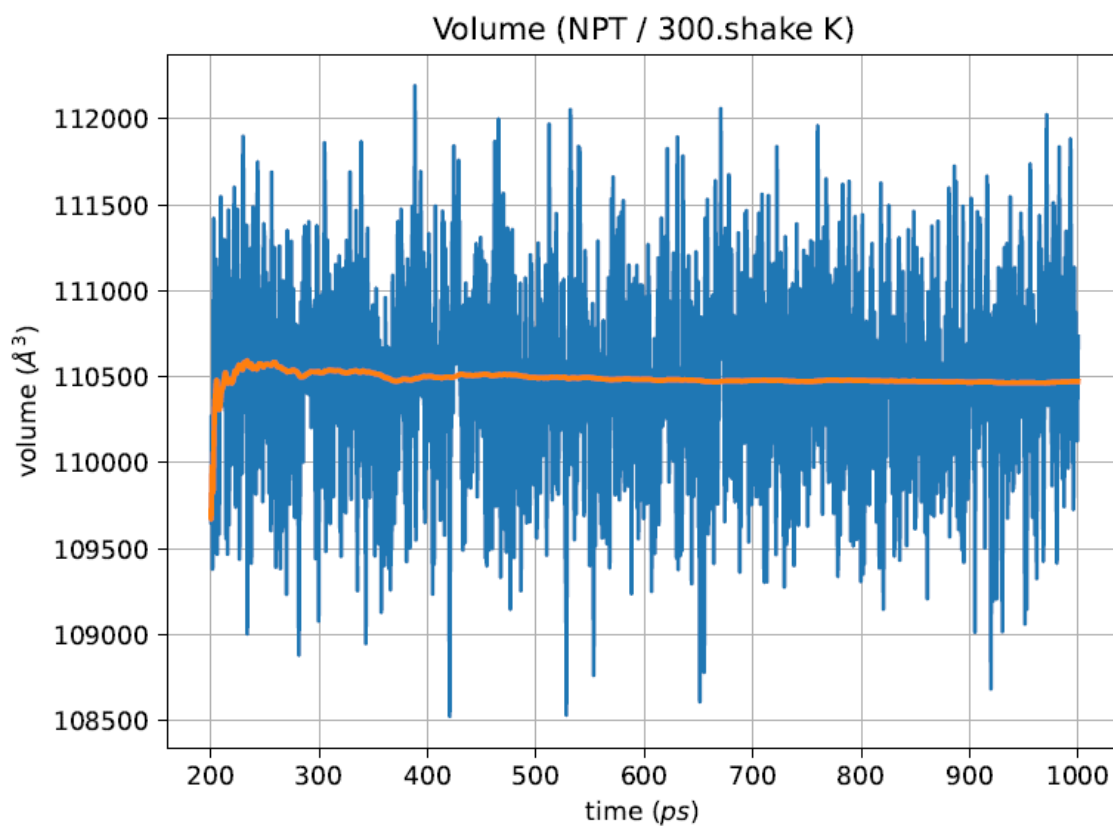


Image A.64:NPT Volume at 300K for H<sub>2</sub>O rigid **model1**

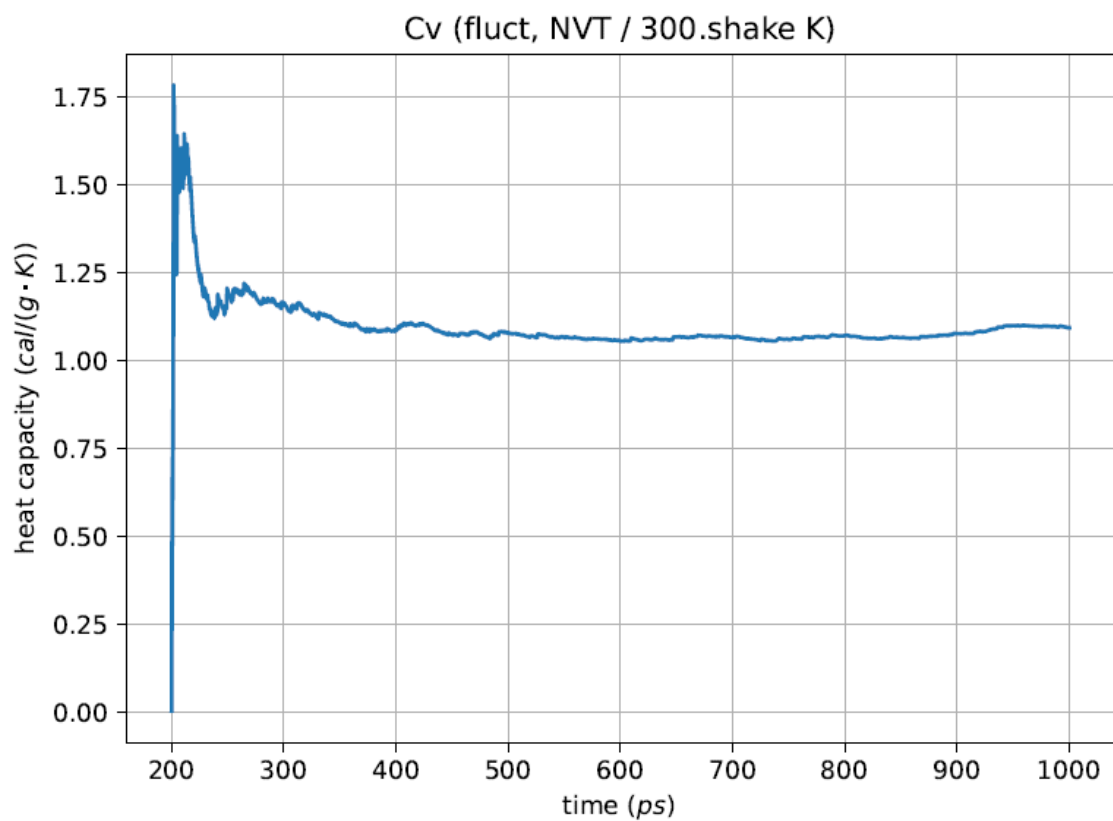


Image A.65:Cv at 300K for H<sub>2</sub>O rigid **model1**

### 3.-H<sub>2</sub>O (model 2):

#### Parameters

O 8 0.1521 3.1507

H 1 0.000 0.000

O 0.000000 0.000000 0.000000 -0.834

H 0.900000 0.000000 0.000000 0.417

H -0.225340 0.871330 0.000000 0.417

H O 450.0 0.9572

H O H 55.0 104.52

Temperature (NPT / 290 K)

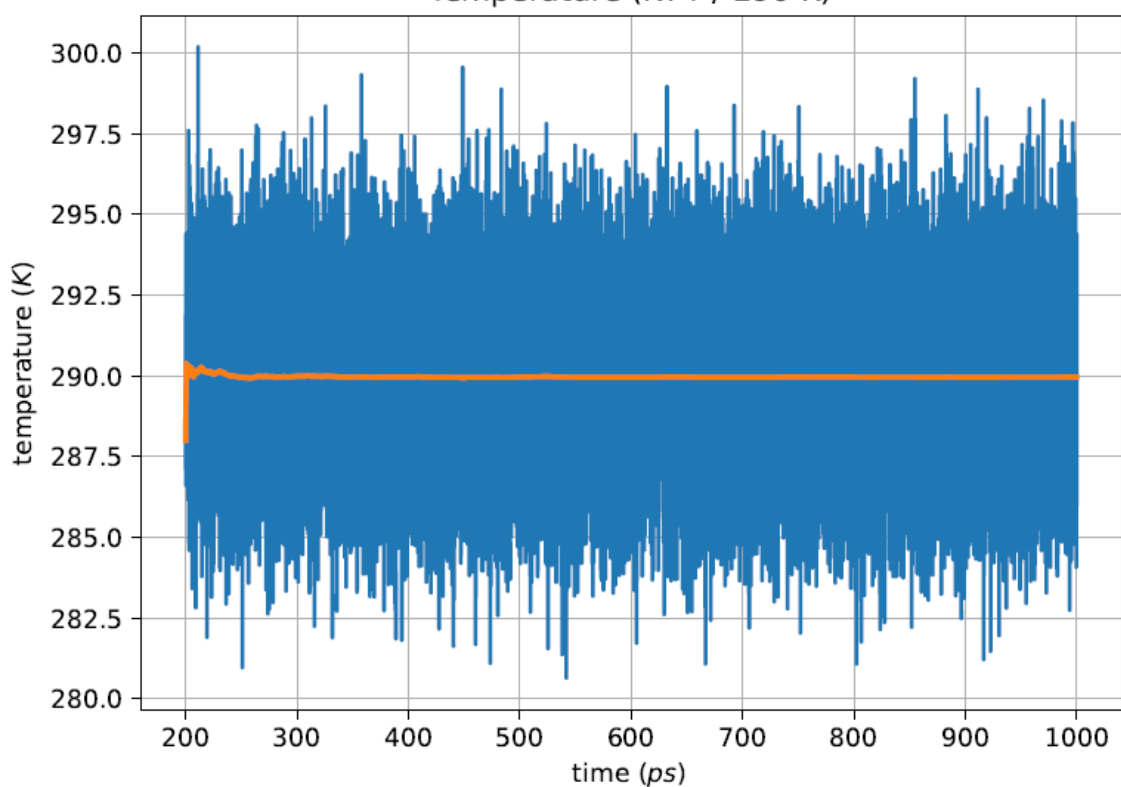


Image A.66:NPT temperature at 290K for H<sub>2</sub>O **model2**



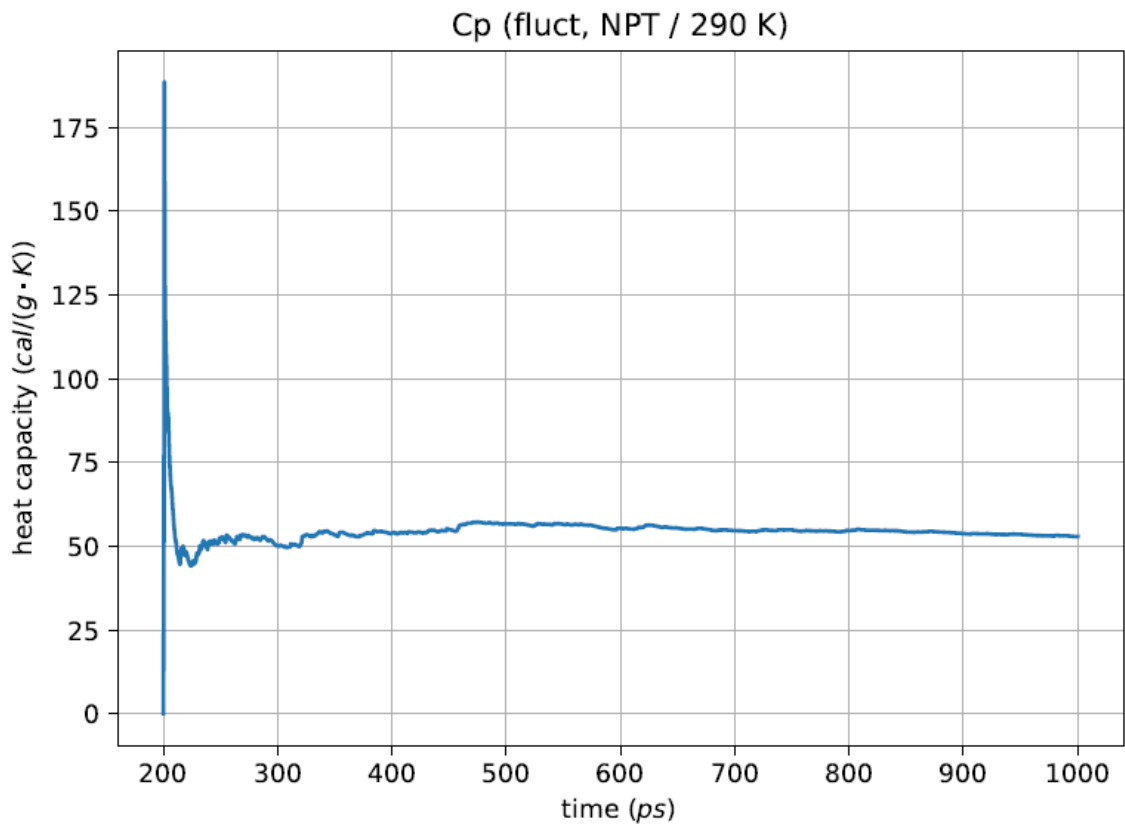


Image A.67:Cp at 290K for H<sub>2</sub>O **model2**

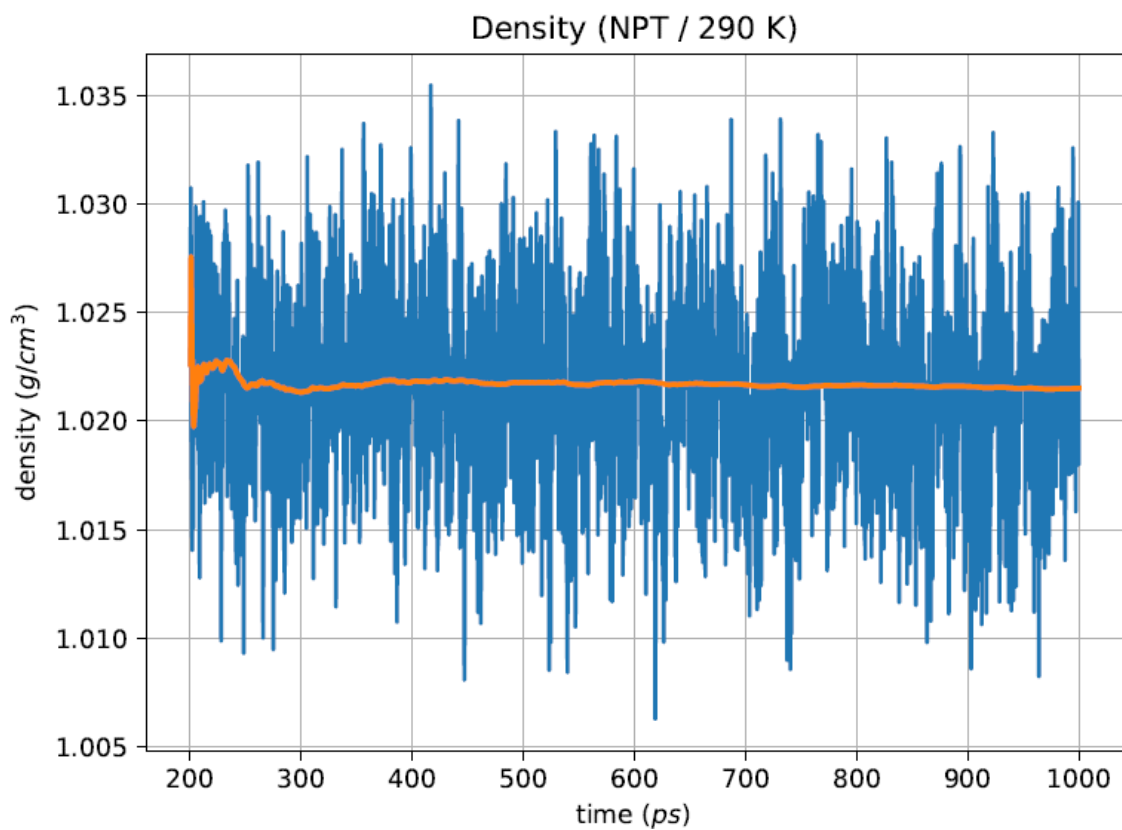


Image A.68:NPT Density at 290K for H<sub>2</sub>O **model2**

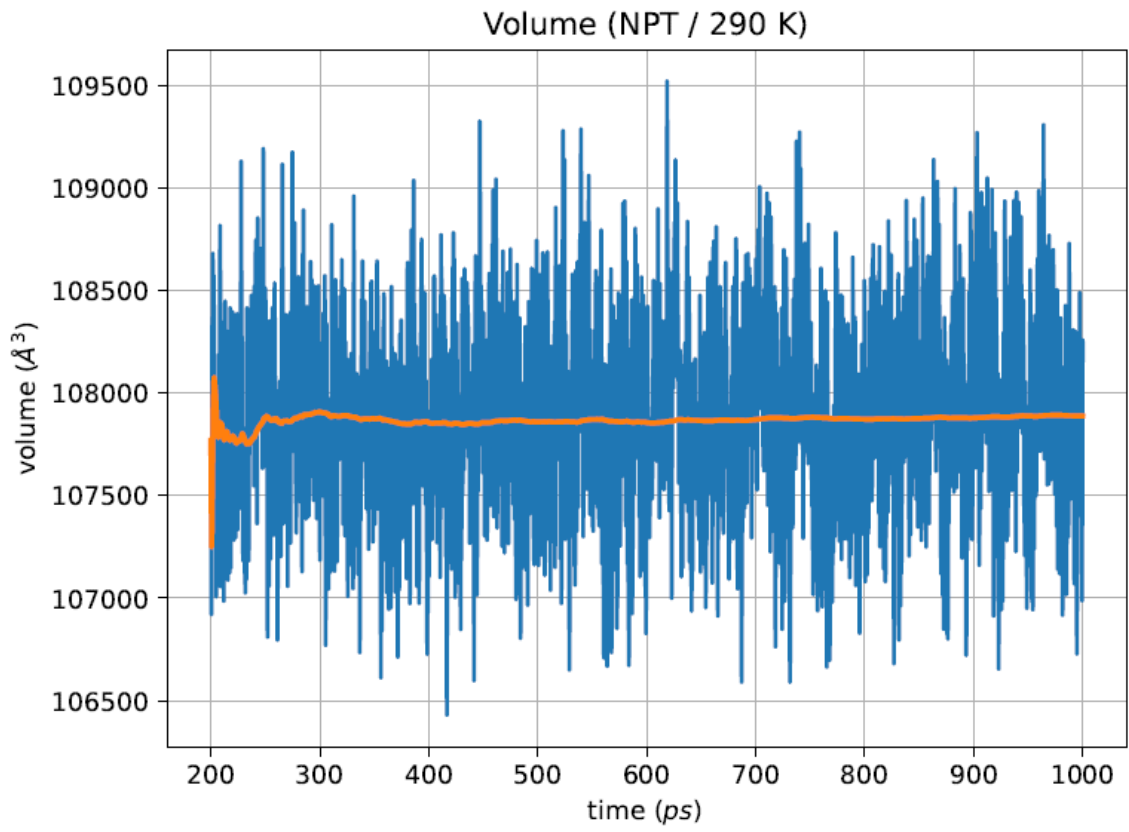


Image A.69:NPT Volume at 290K for H<sub>2</sub>O model2

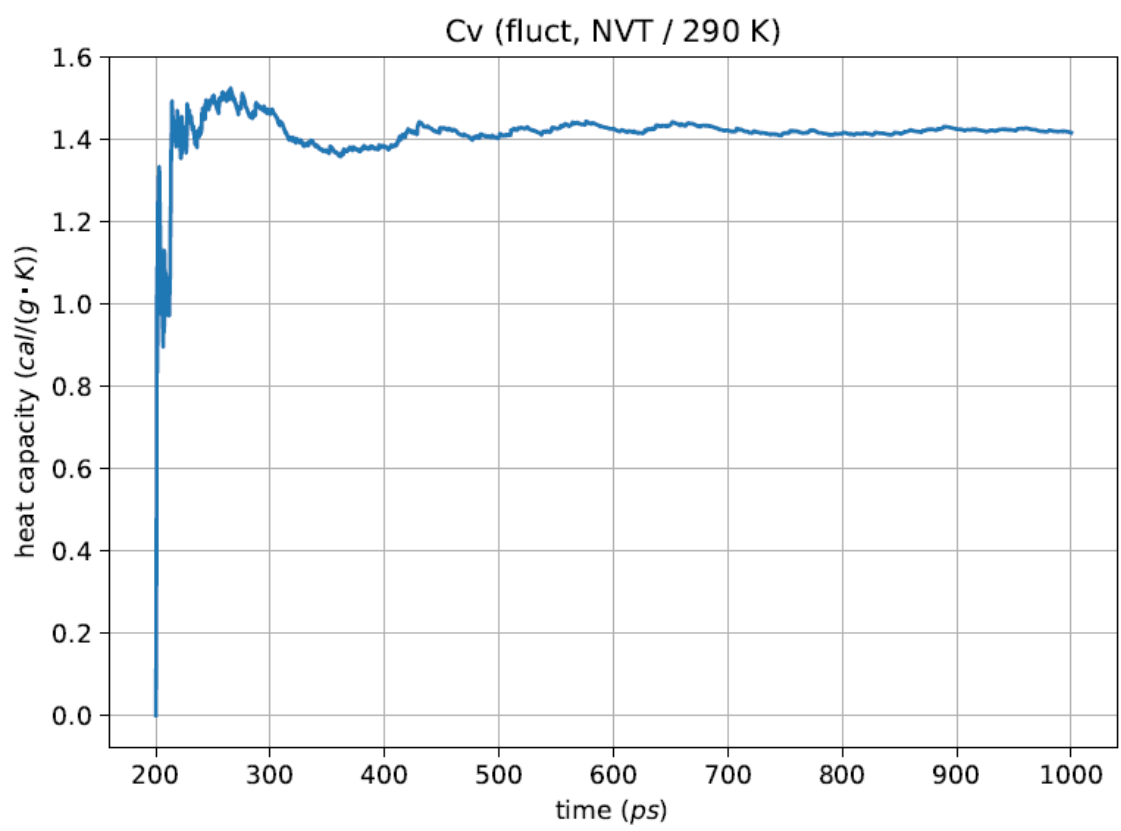


Image A.70:Cv at 290K for H<sub>2</sub>O model2

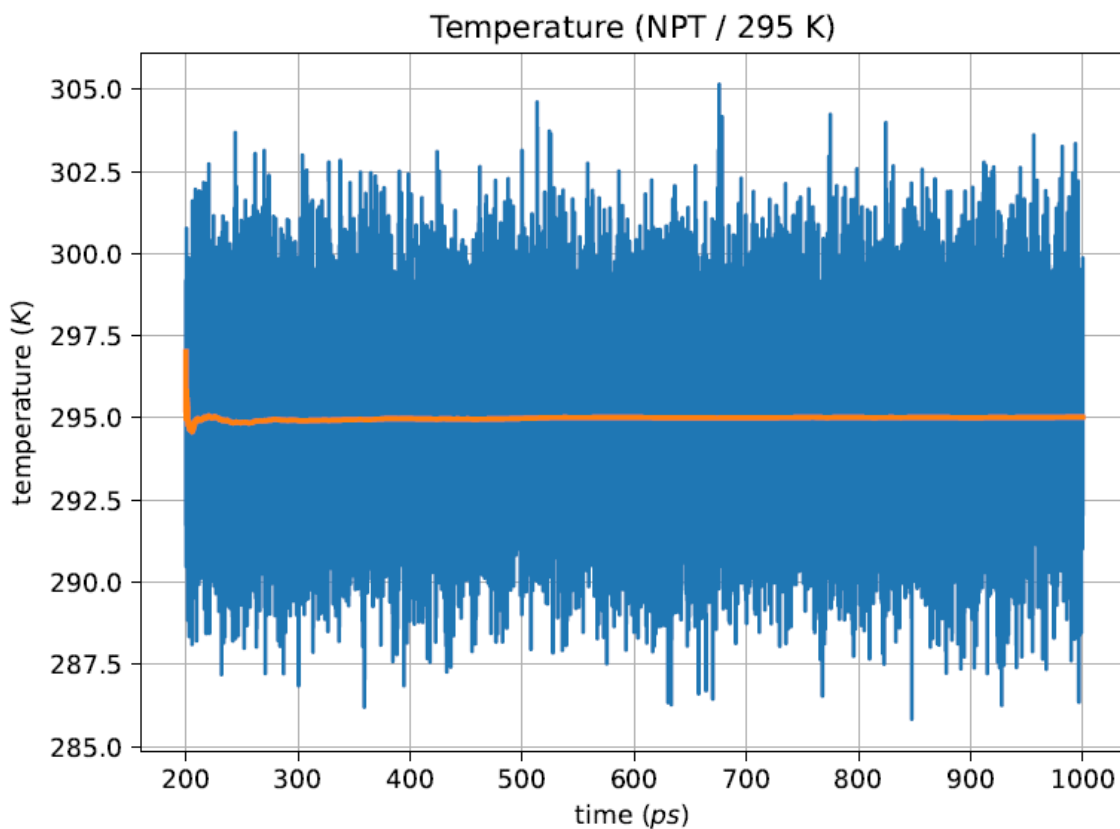


Image A.71:NPT temperature at 295K for H<sub>2</sub>O **model2**

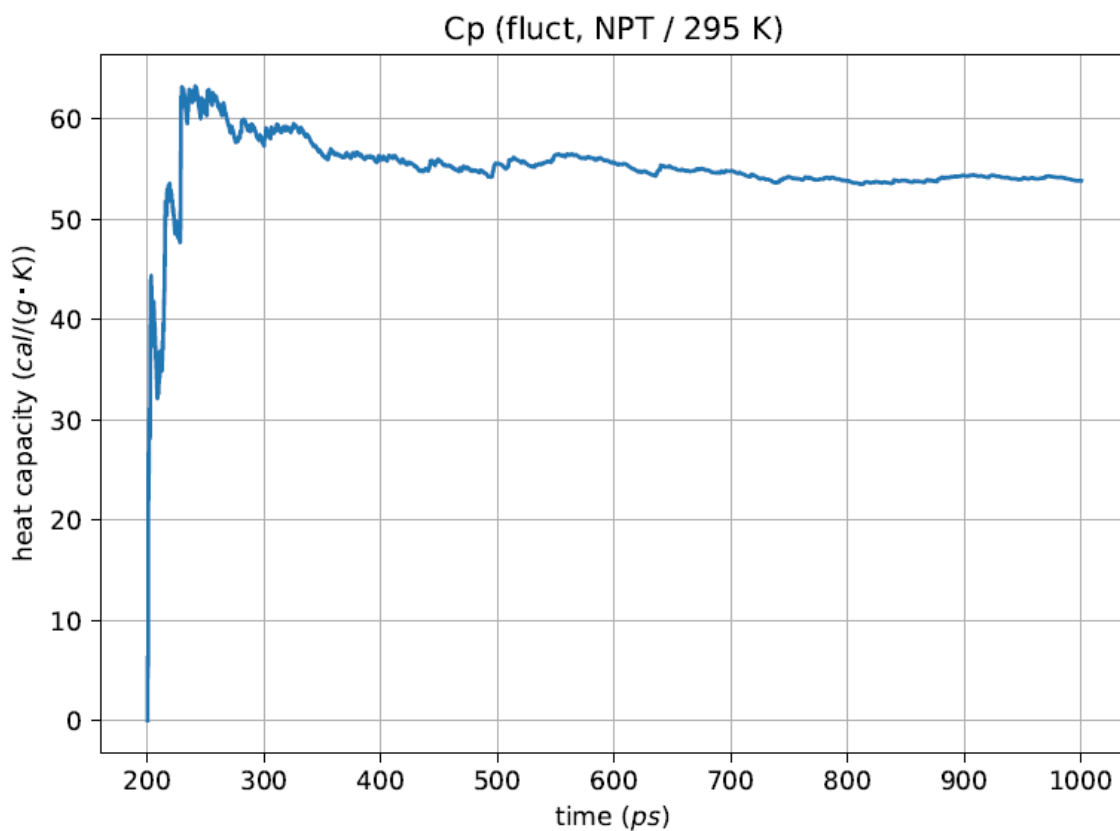


Image A.72:Cp at 295K for H<sub>2</sub>O **model2**

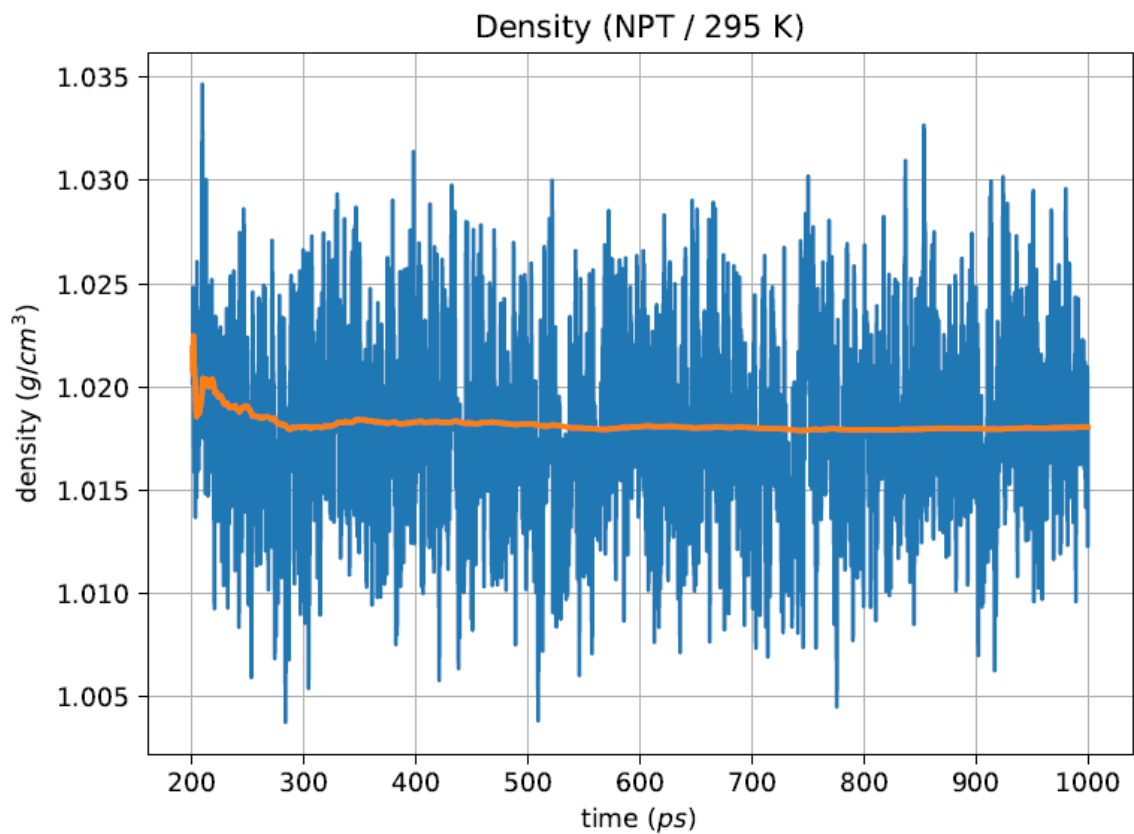


Image A.73:NPT Density at 295K for H<sub>2</sub>O **model2**

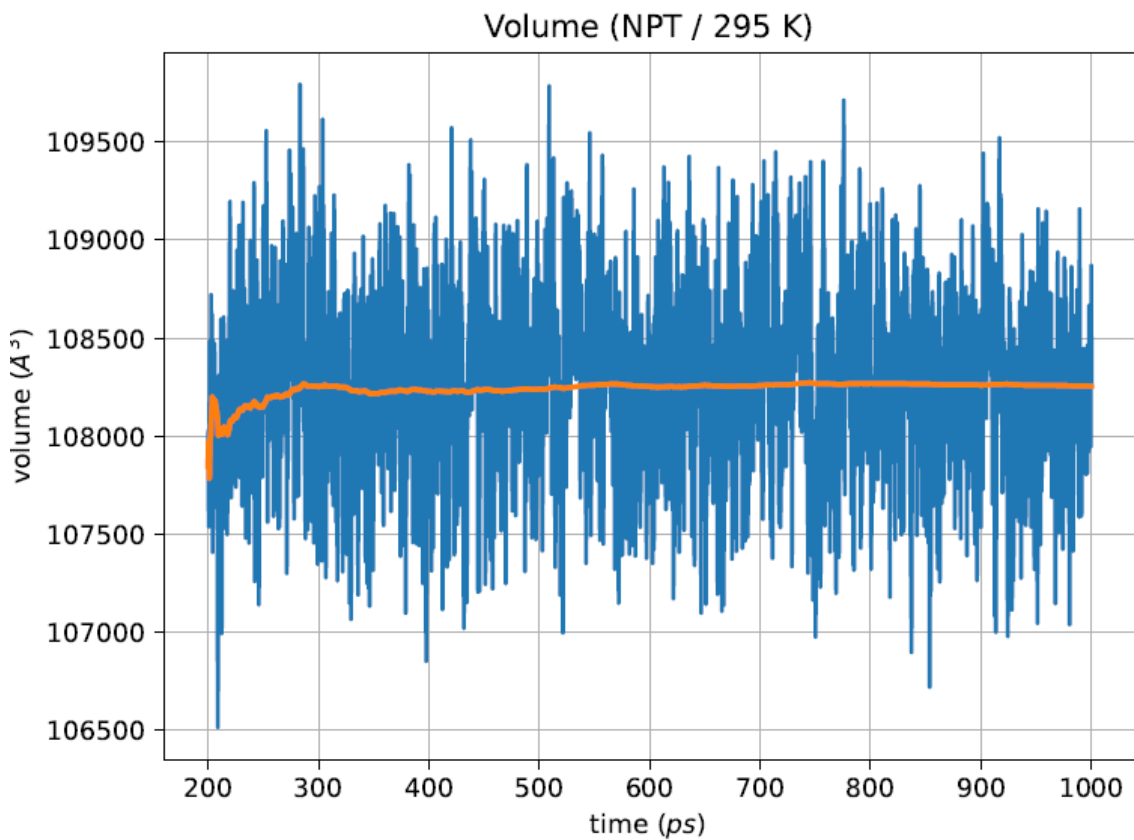


Image A.74:NPT Volume at 295K for H<sub>2</sub>O **model2**

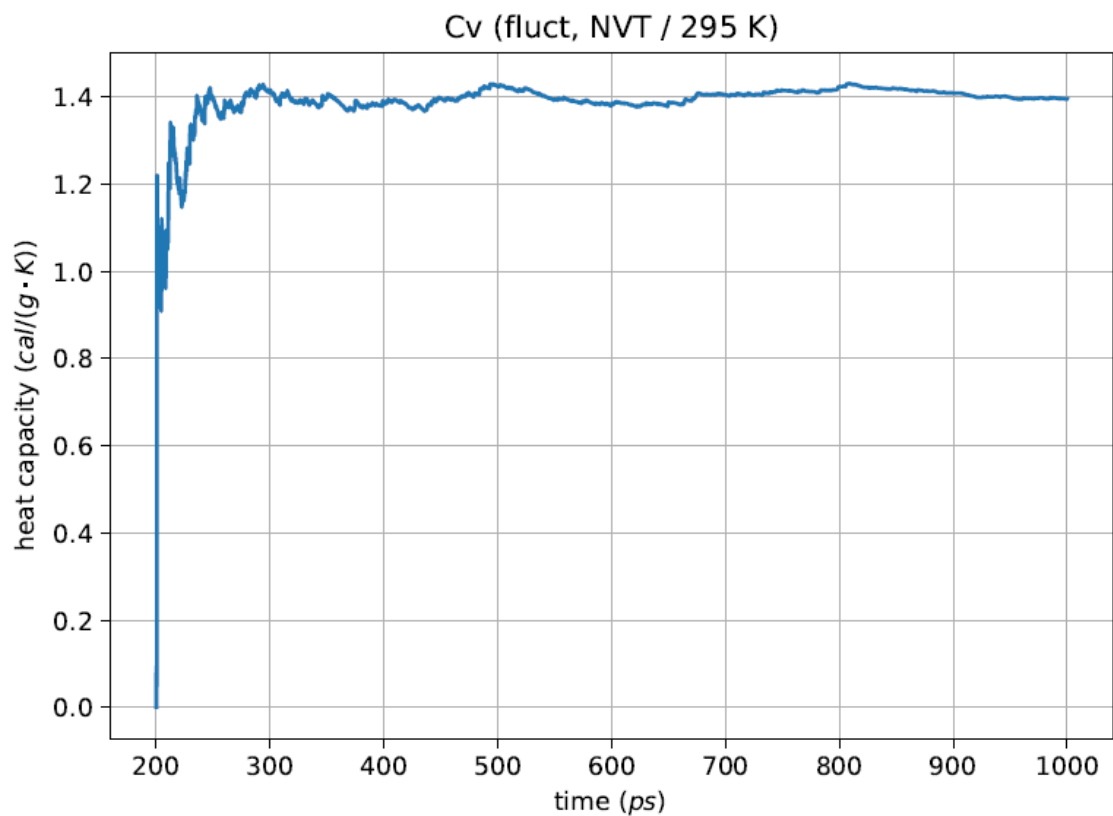


Image A.75:Cv at 295K for H<sub>2</sub>O **model2**

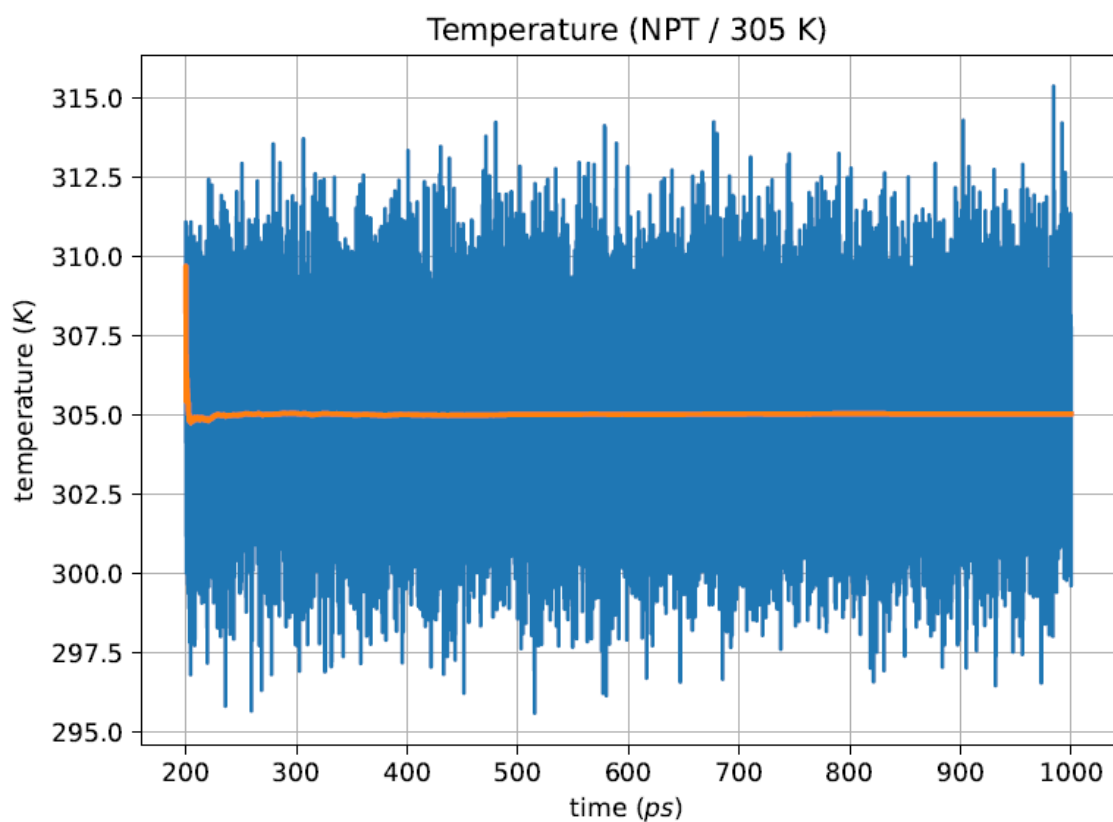


Image A.76:NPT temperature at 305K for H<sub>2</sub>O **model2**

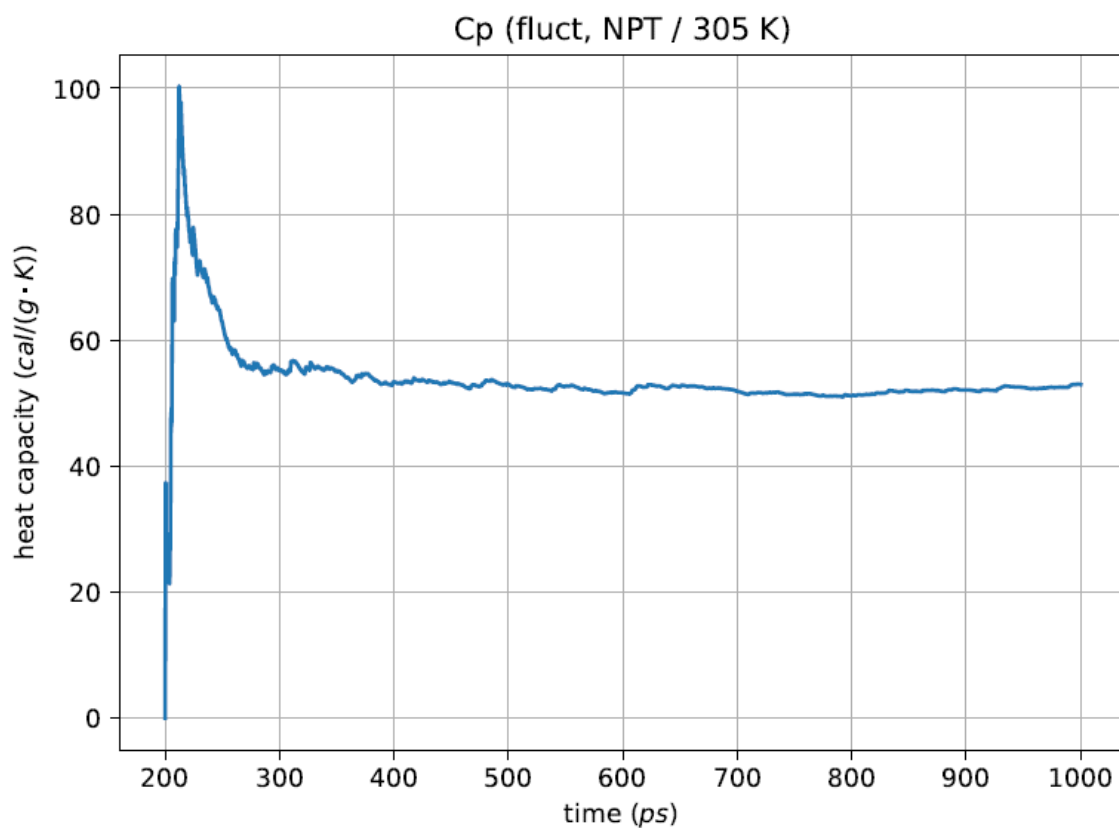


Image A.77:Cp at 305K for H<sub>2</sub>O **model2**

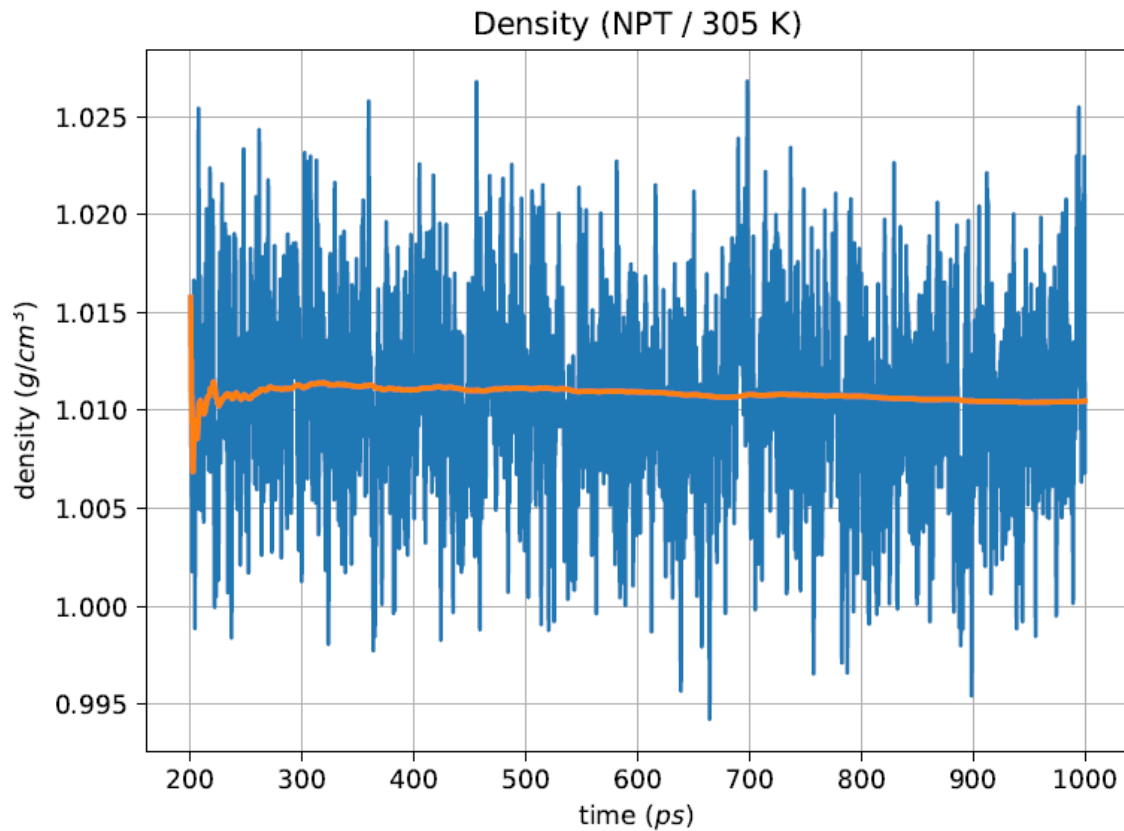


Image A.78:NPT Density at 305K for H<sub>2</sub>O **model2**

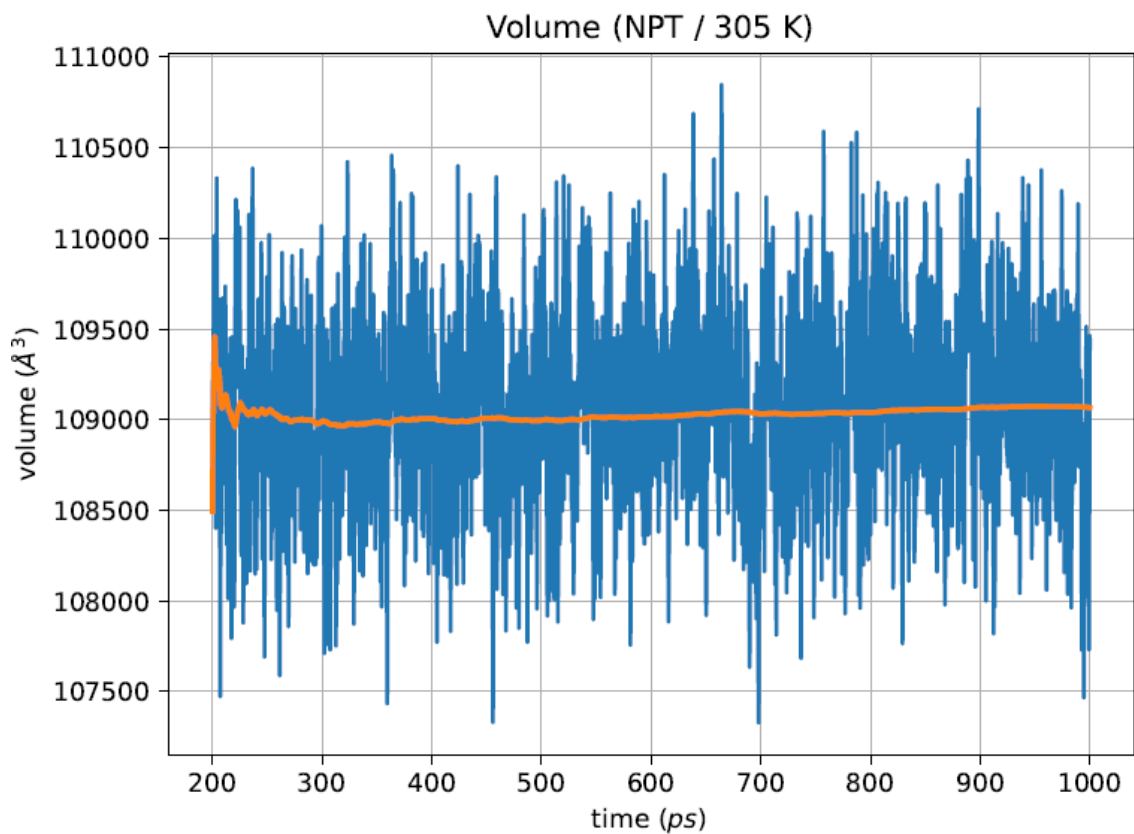


Image A.79:NPT Volume at 305K for H<sub>2</sub>O **model2**

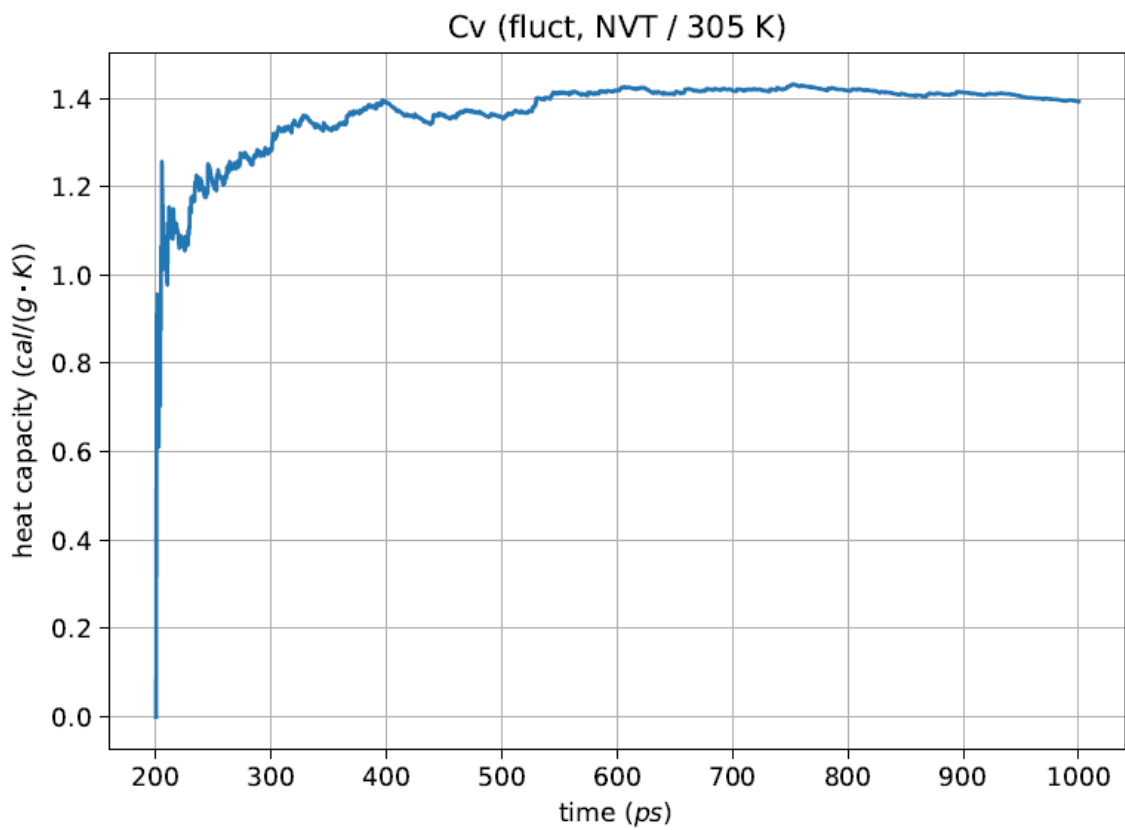


Image A.80Cv at 305K for H<sub>2</sub>O **model2**

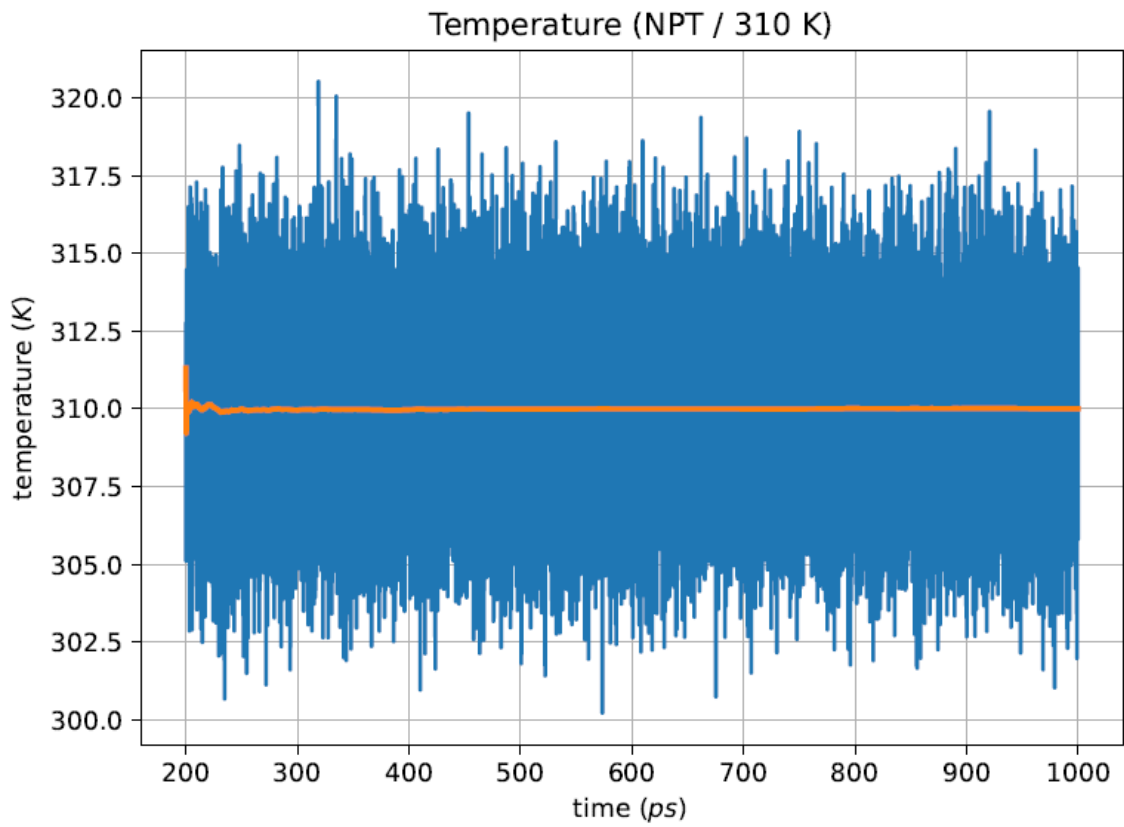


Image A.81:NPT temperature at 310K for H<sub>2</sub>O model2

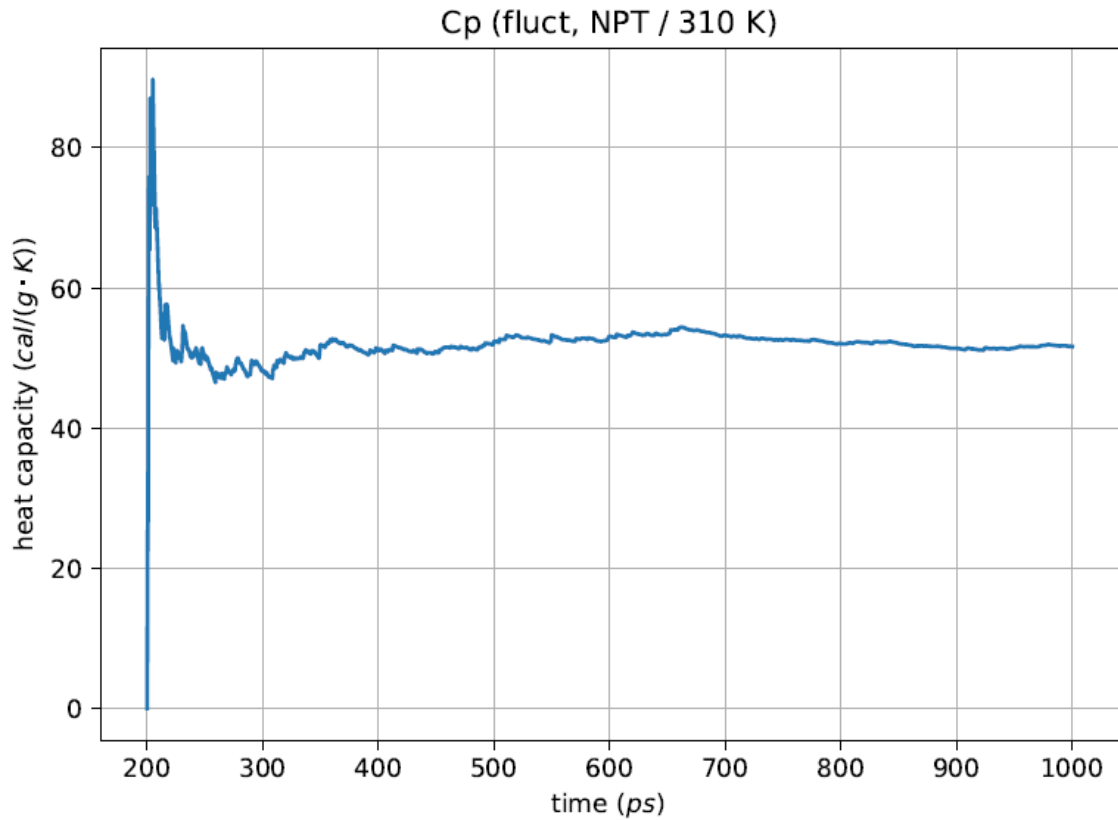


Image A.82:Cp at 310K for H<sub>2</sub>O model2



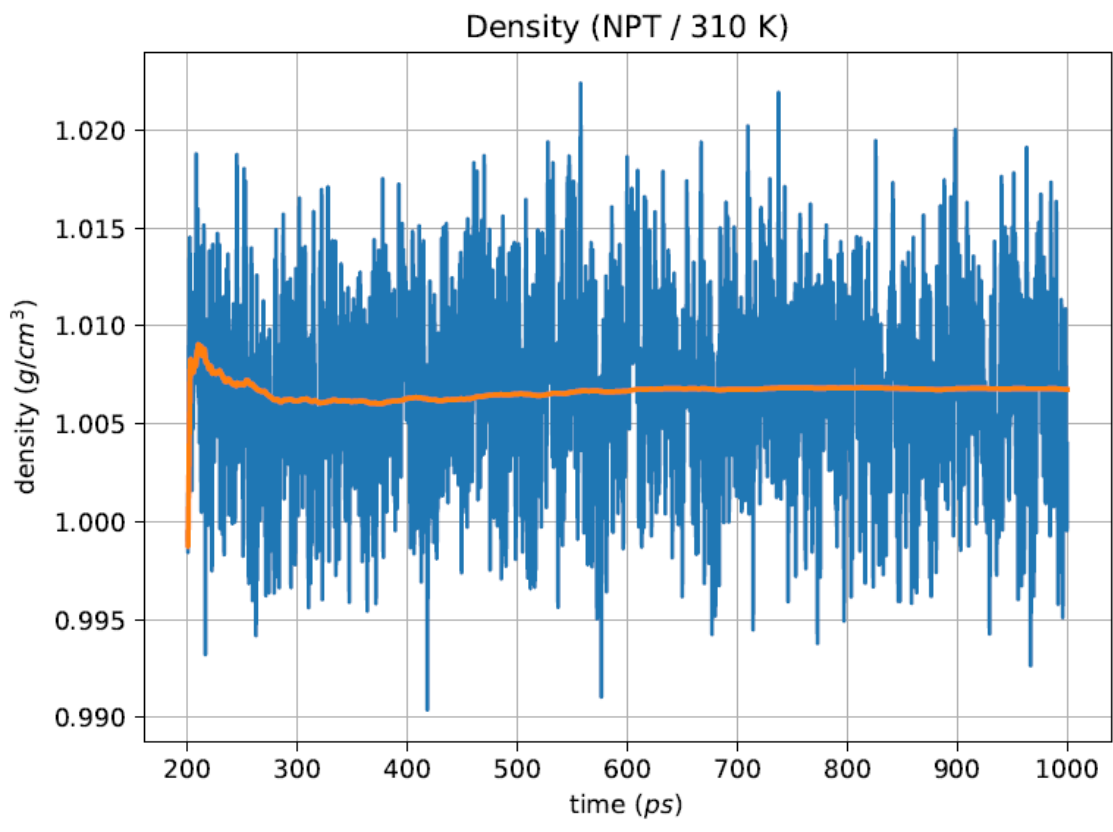


Image A.83:NPT Density at 310K for H<sub>2</sub>O model2

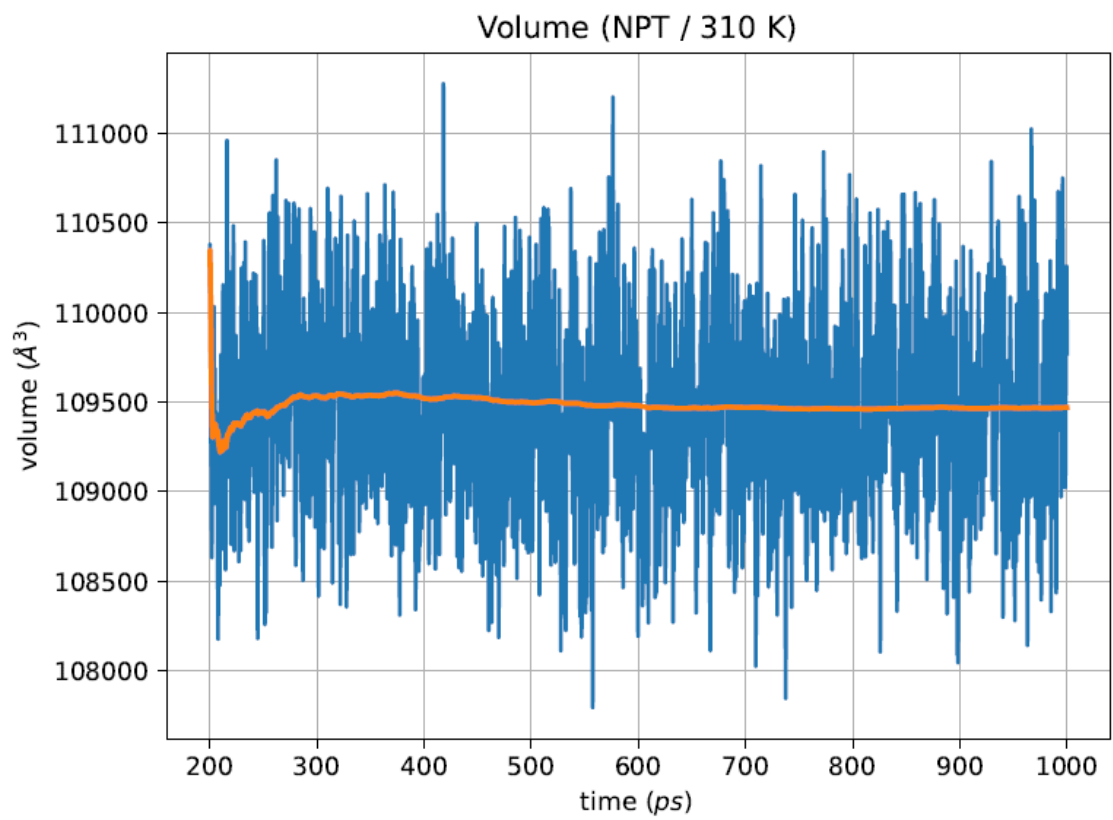


Image A.84:NPT Volume at 310K for H<sub>2</sub>O model2

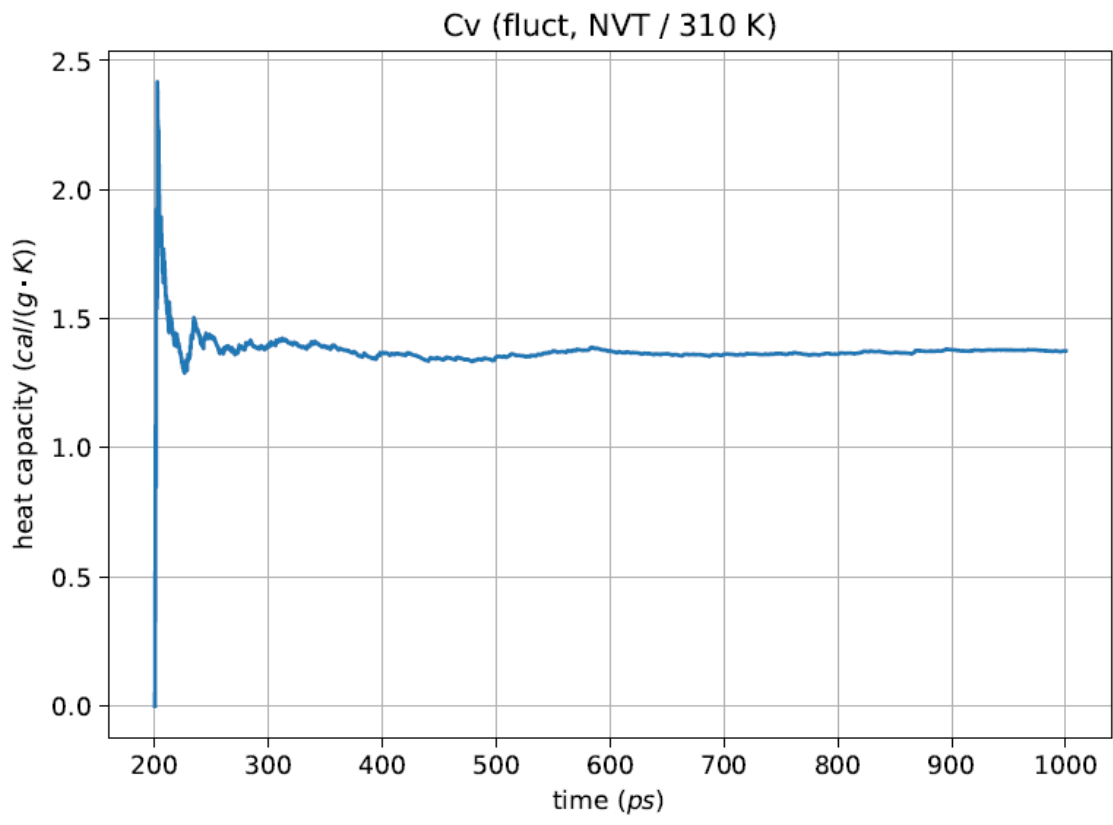


Image A.85:Cv at 310K for H<sub>2</sub>O **model2**

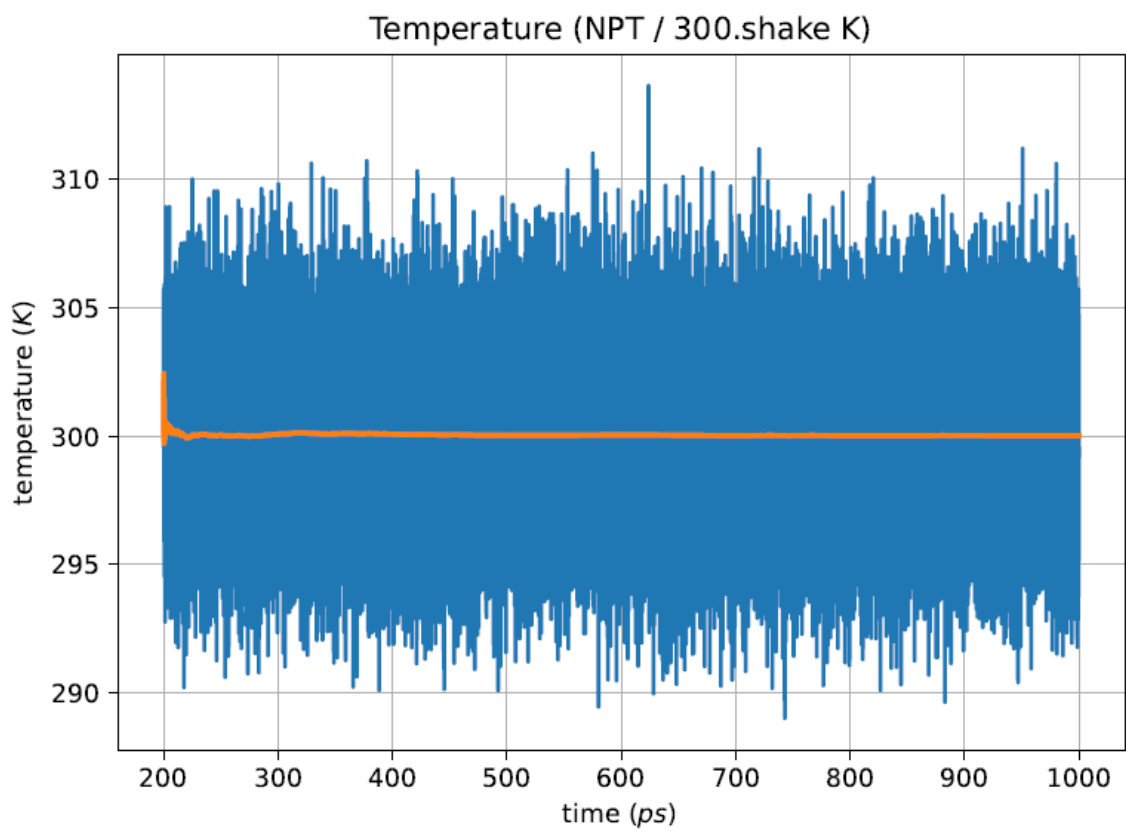


Image A.86:NPT temperature at 300K for H<sub>2</sub>O rigid **model2**

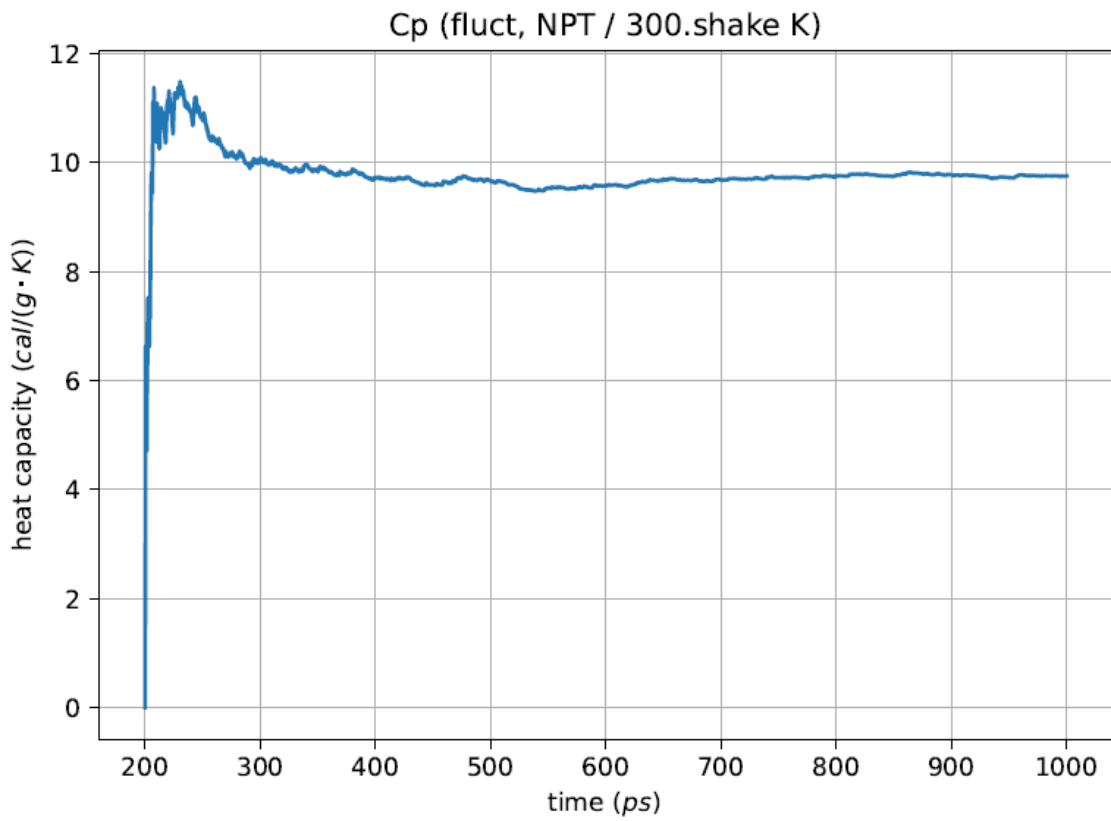


Image A.87:Cp at 300K for H<sub>2</sub>O rigid **model2**

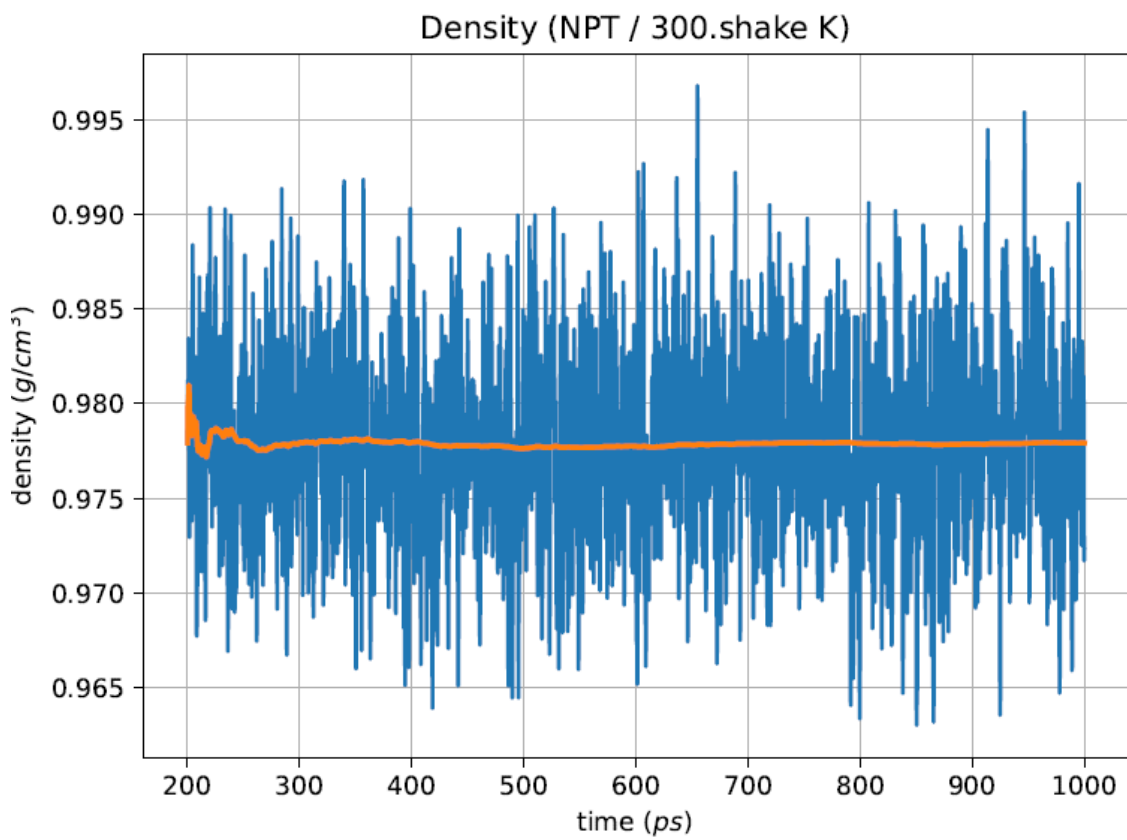


Image A.88:NPT Density at 300K for H<sub>2</sub>O rigid **model2**

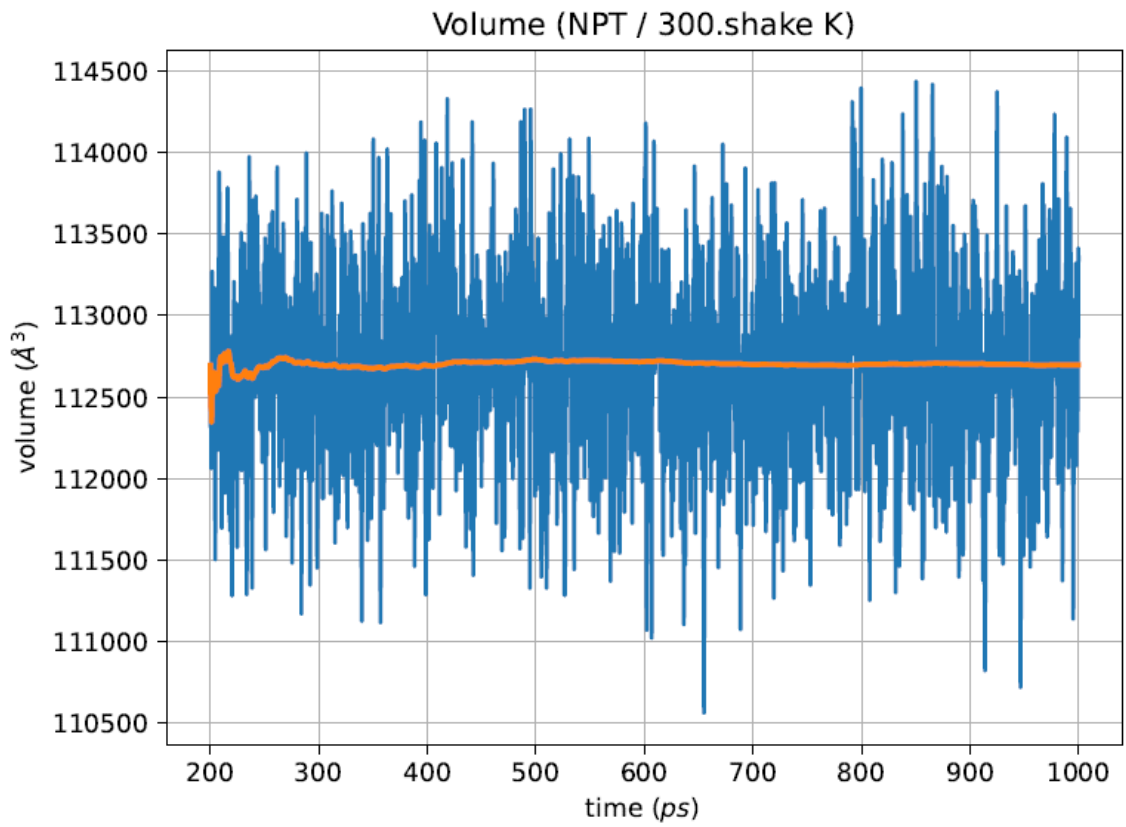


Image A.89:NPT Volume at 300K for H<sub>2</sub>O rigid **model2**

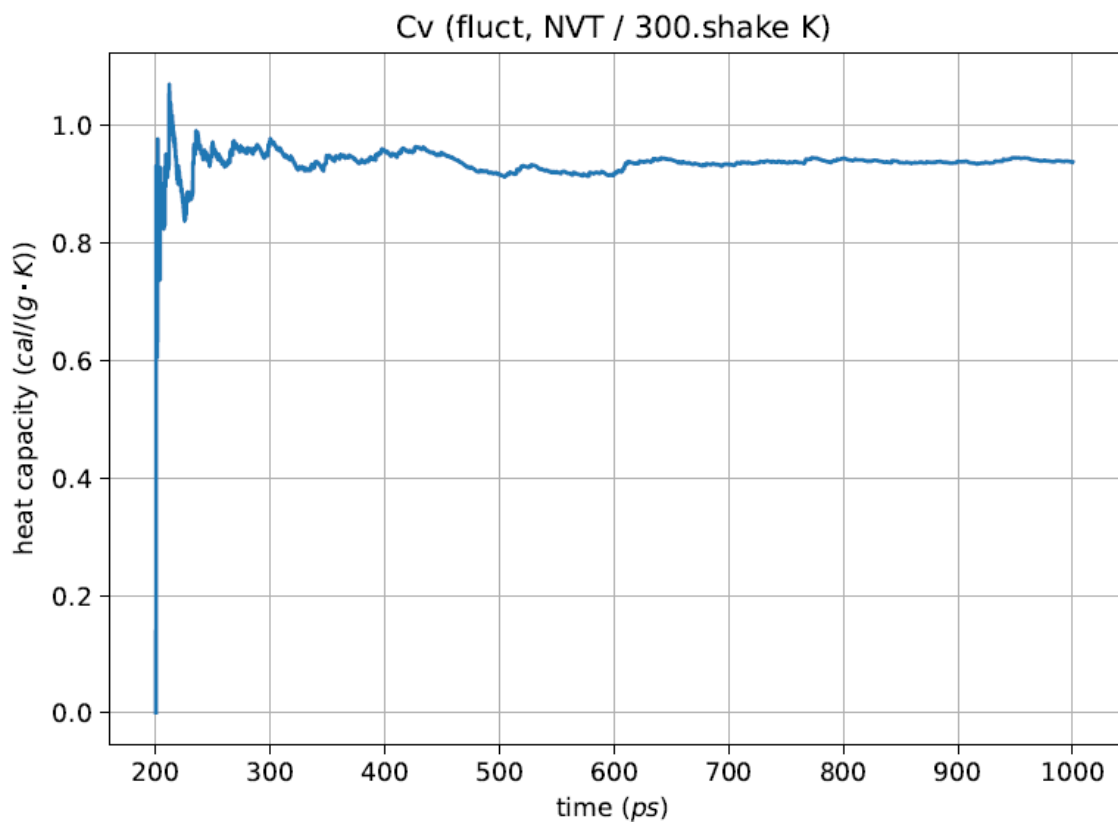


Image A.90:Cv at 300K for H<sub>2</sub>O rigid **model2**

## 5.- H<sub>2</sub>O graphs (model 3)

### Parameters

O 8 0.1521 3.1507

H 1 0.0460 0.4000

O 0.000000 0.000000 0.000000 -0.834

H 0.900000 0.000000 0.000000 0.417

H -0.225340 0.871330 0.000000 0.417

H O 450.0 0.9572

H O H 55.0 104.52

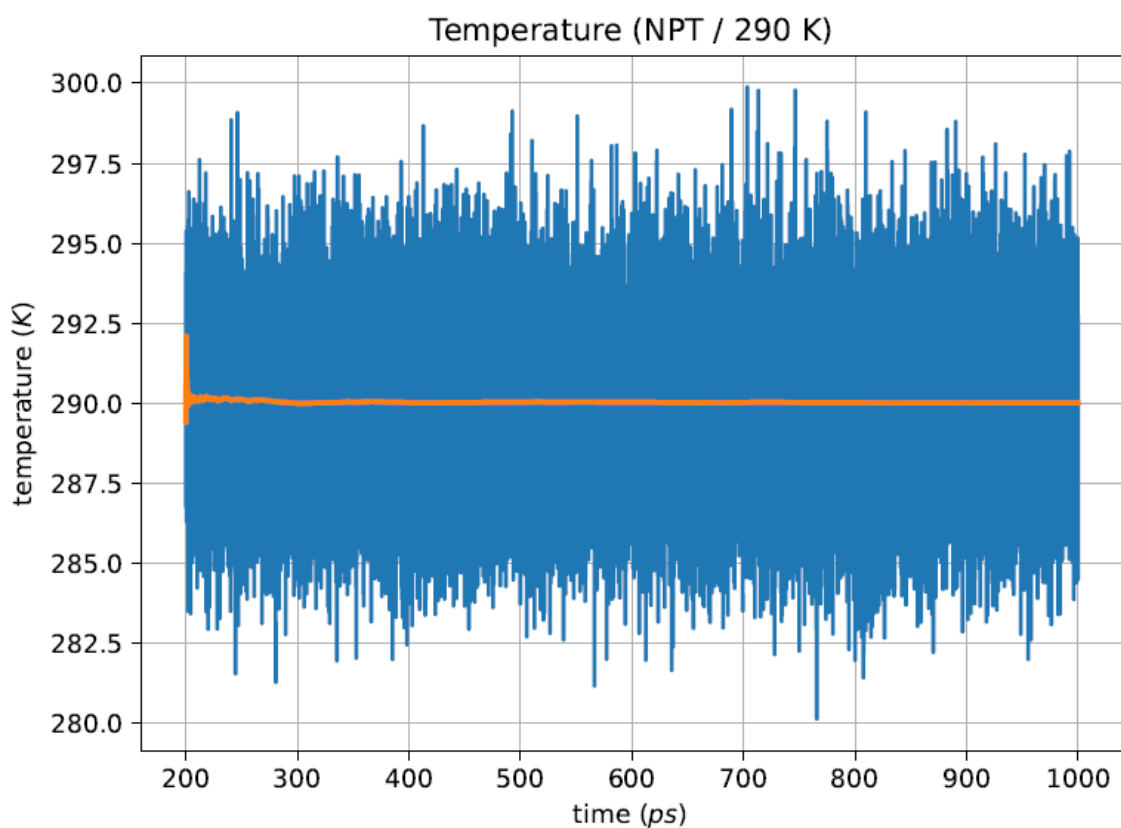


Image A.91:NPT temperature at 290K for H<sub>2</sub>O **model3**

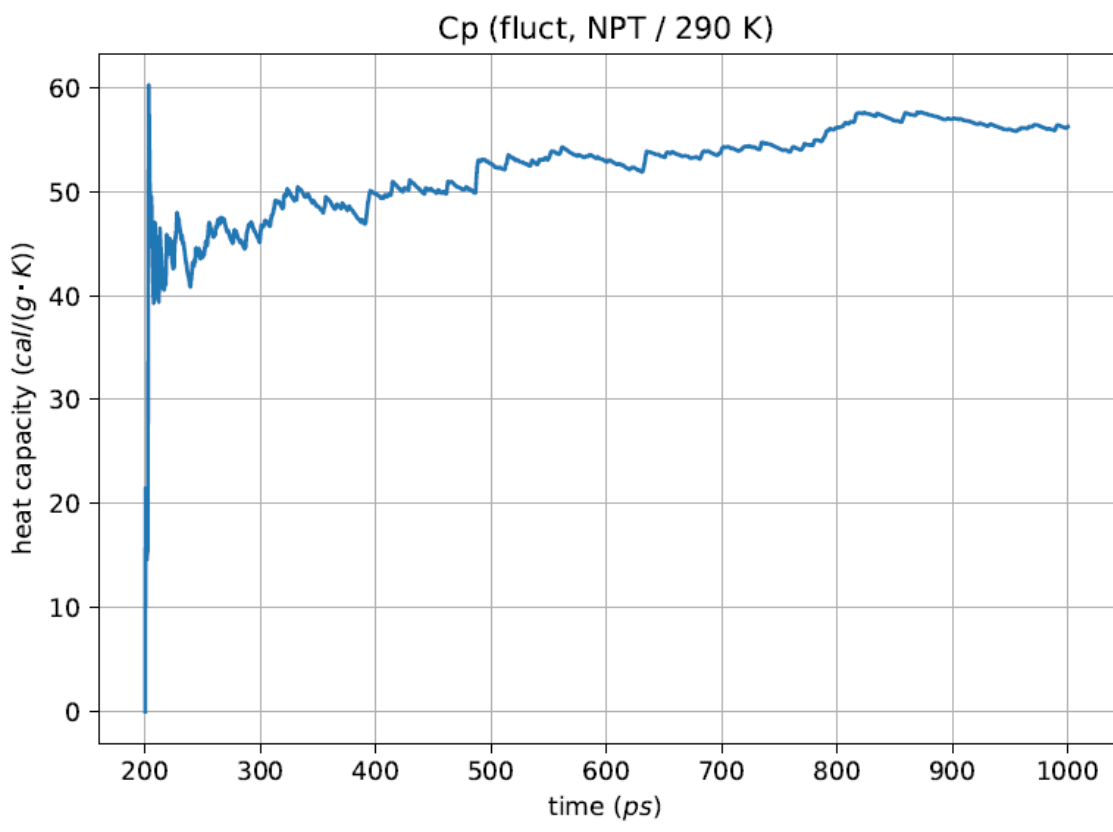


Image A.92:Cp at 290K for H<sub>2</sub>O **model3**

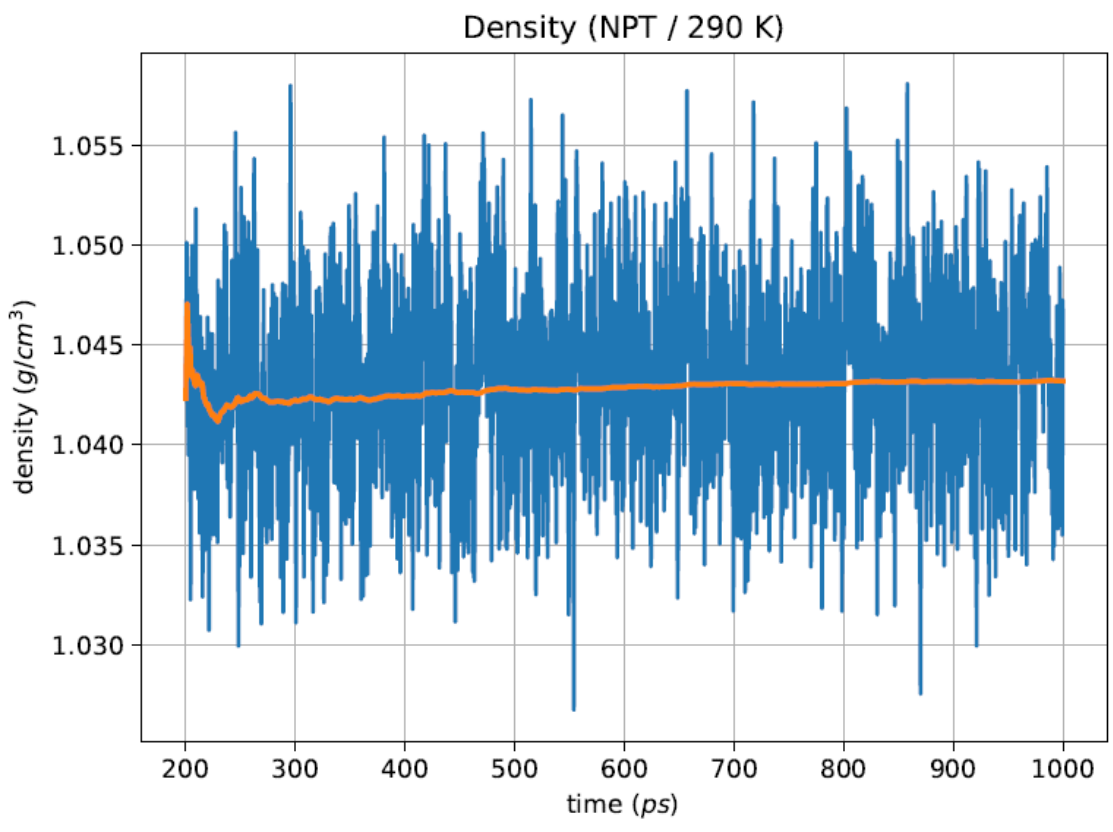


Image A.93:NPT Density at 290K for H<sub>2</sub>O **model3**

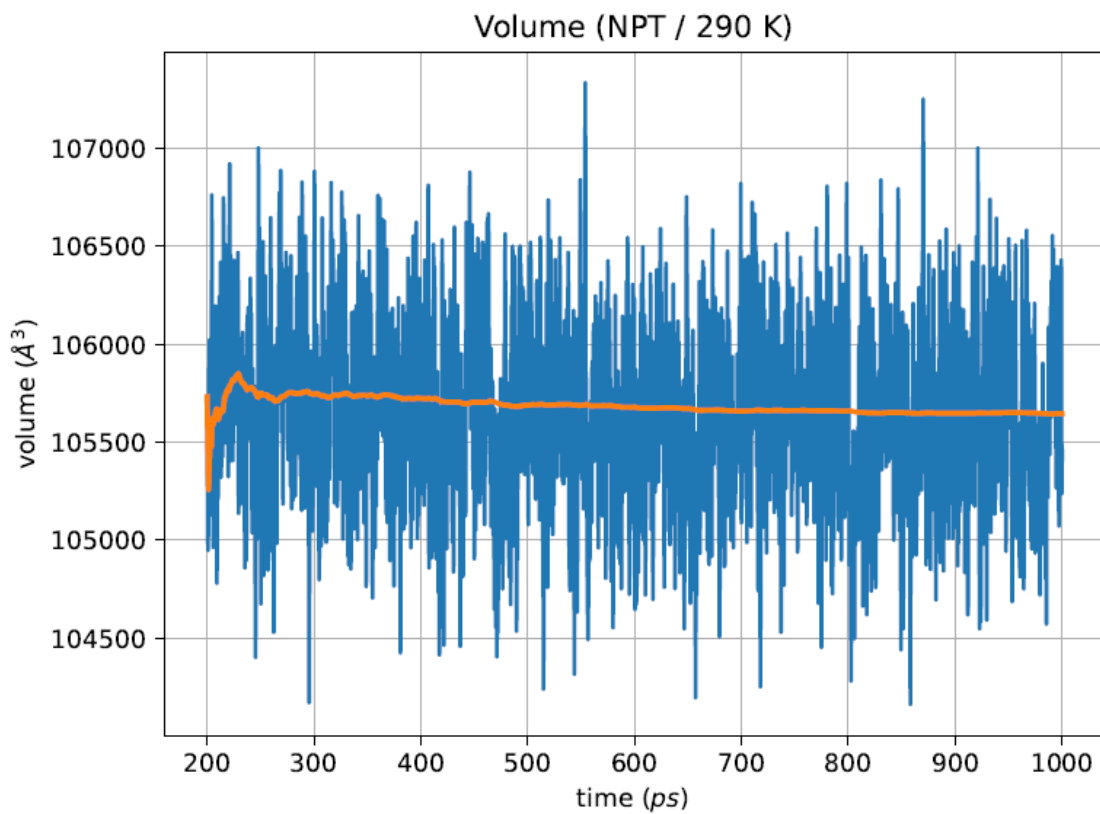


Image A.94:NPT Volume at 290K for H<sub>2</sub>O **model3**

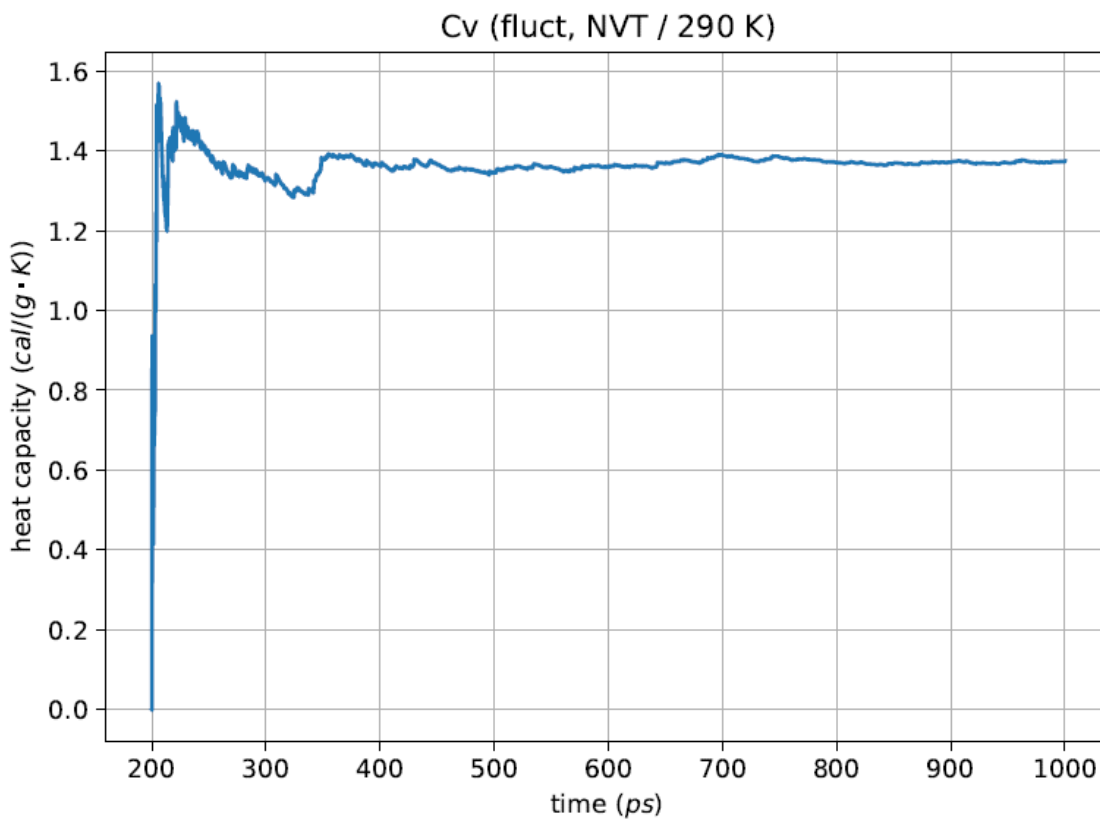


Image A.95:Cv at 290K for H<sub>2</sub>O **model3**

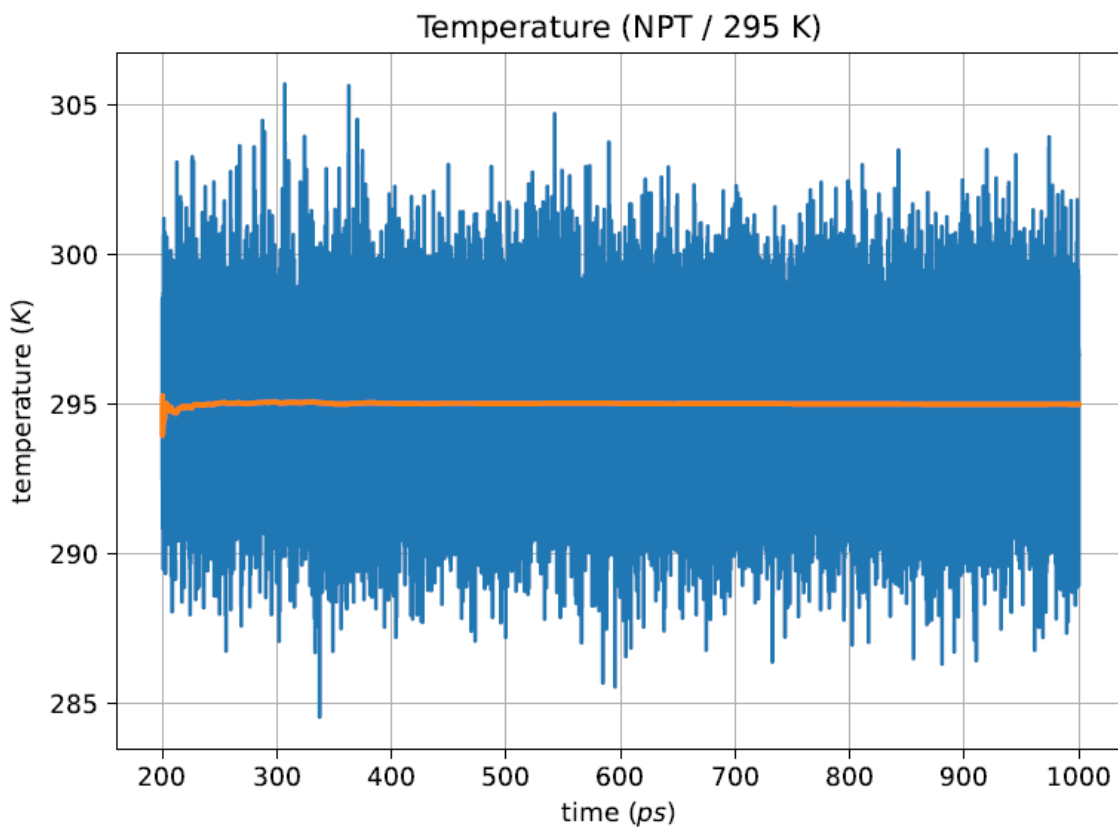


Image A.96:NPT temperature at 295K for H<sub>2</sub>O **model3**

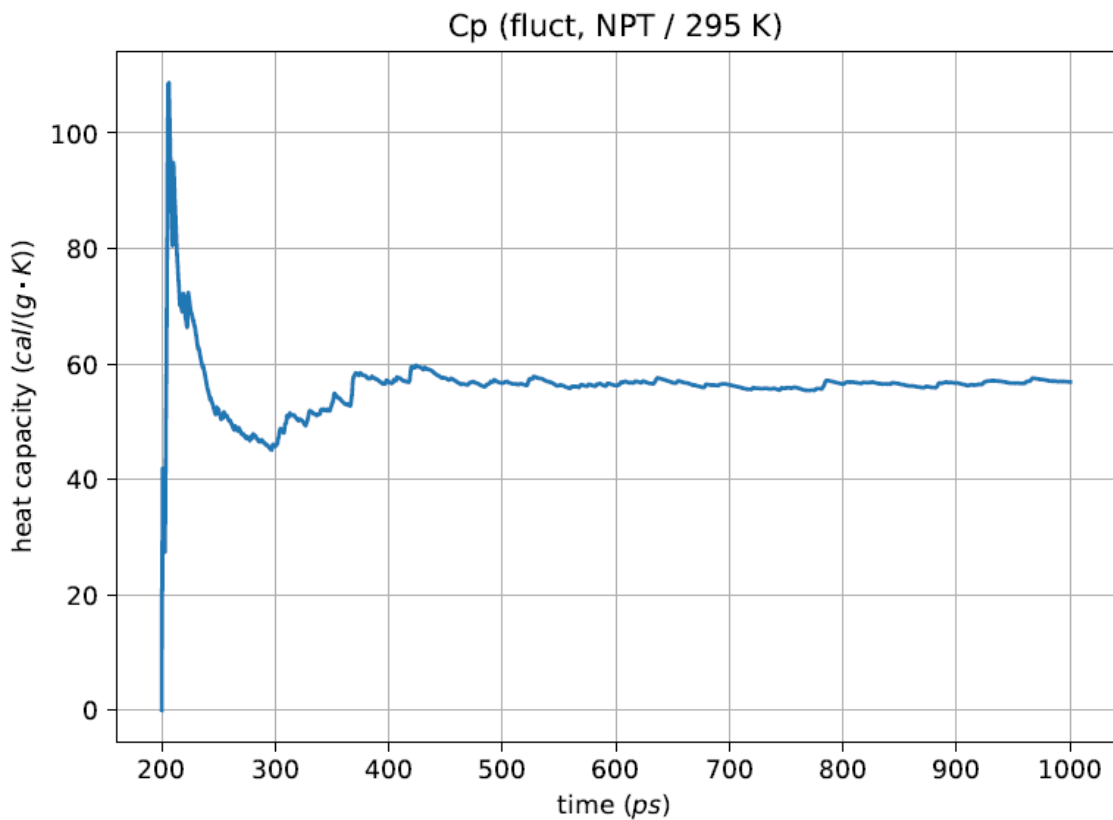


Image A.97: Cp at 295K for H<sub>2</sub>O **model3**



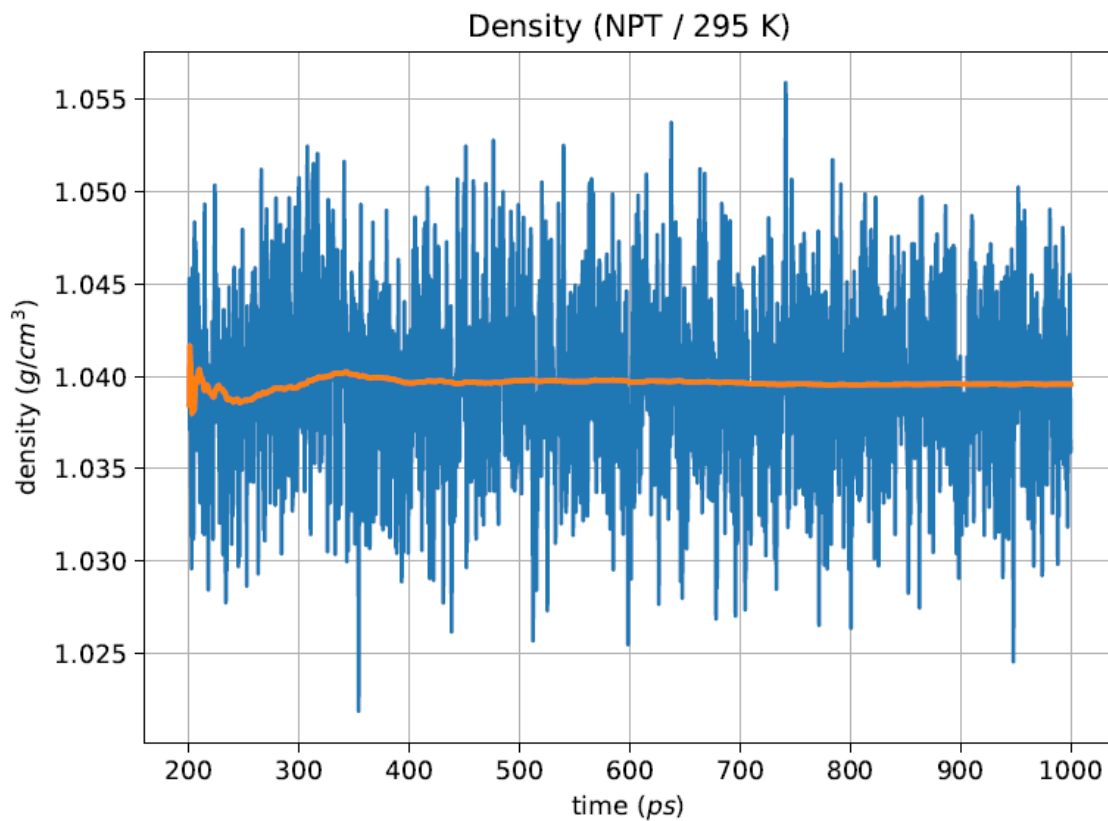


Image A.98:NPT Density at 295K for H<sub>2</sub>O **model3**

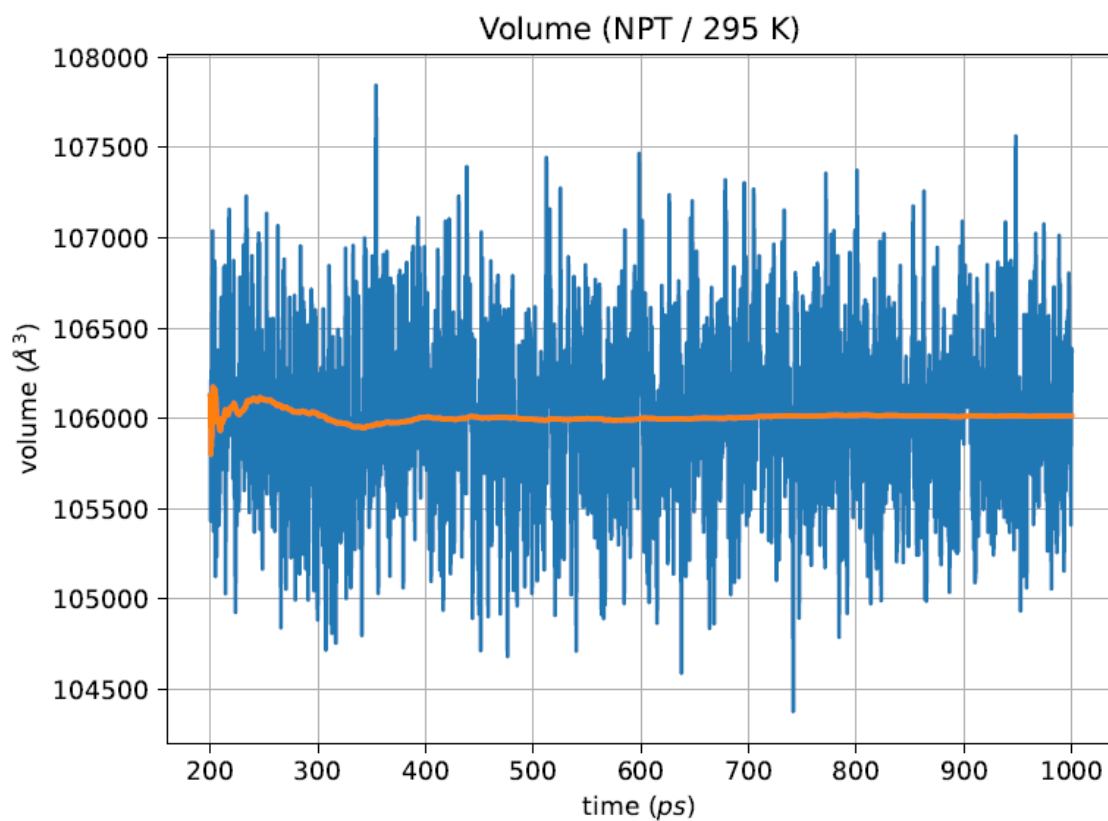


Image A.99:NPT Volume at 295K for H<sub>2</sub>O **model3**

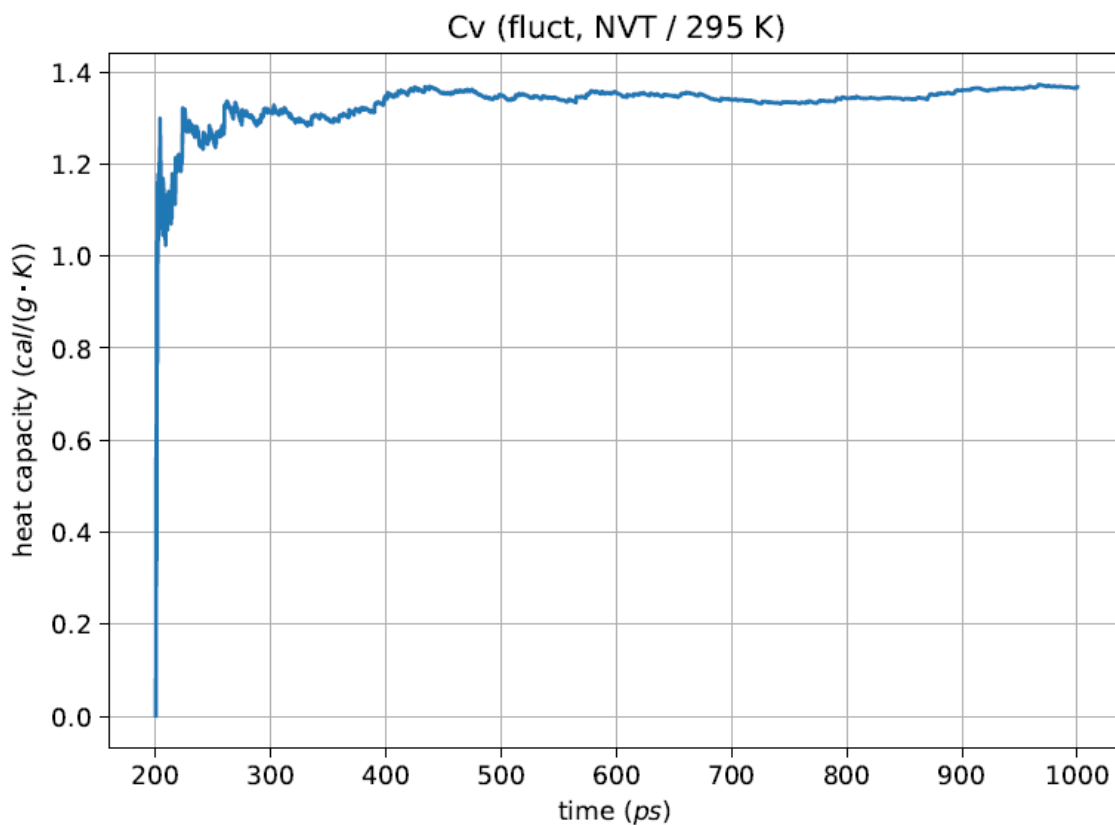


Image A.100:Cv at 295K for H<sub>2</sub>O model3

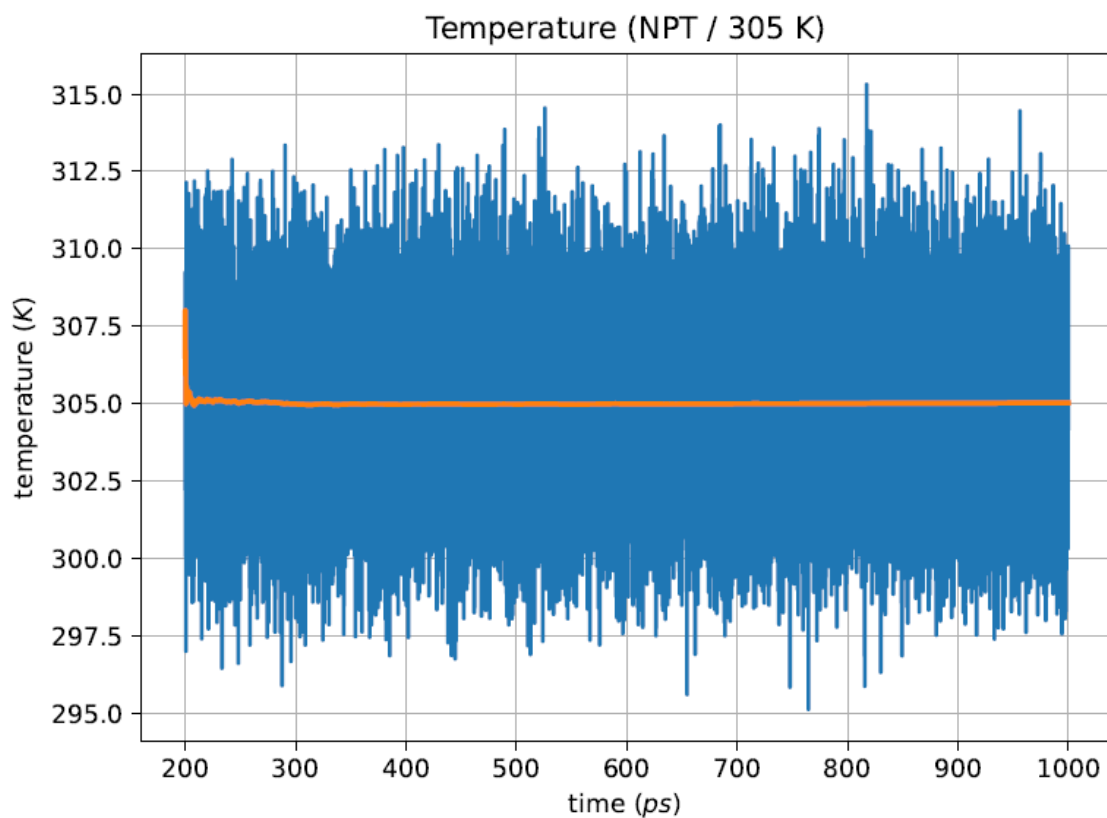


Image A.101:NPT temperature at 305K for H<sub>2</sub>O model3

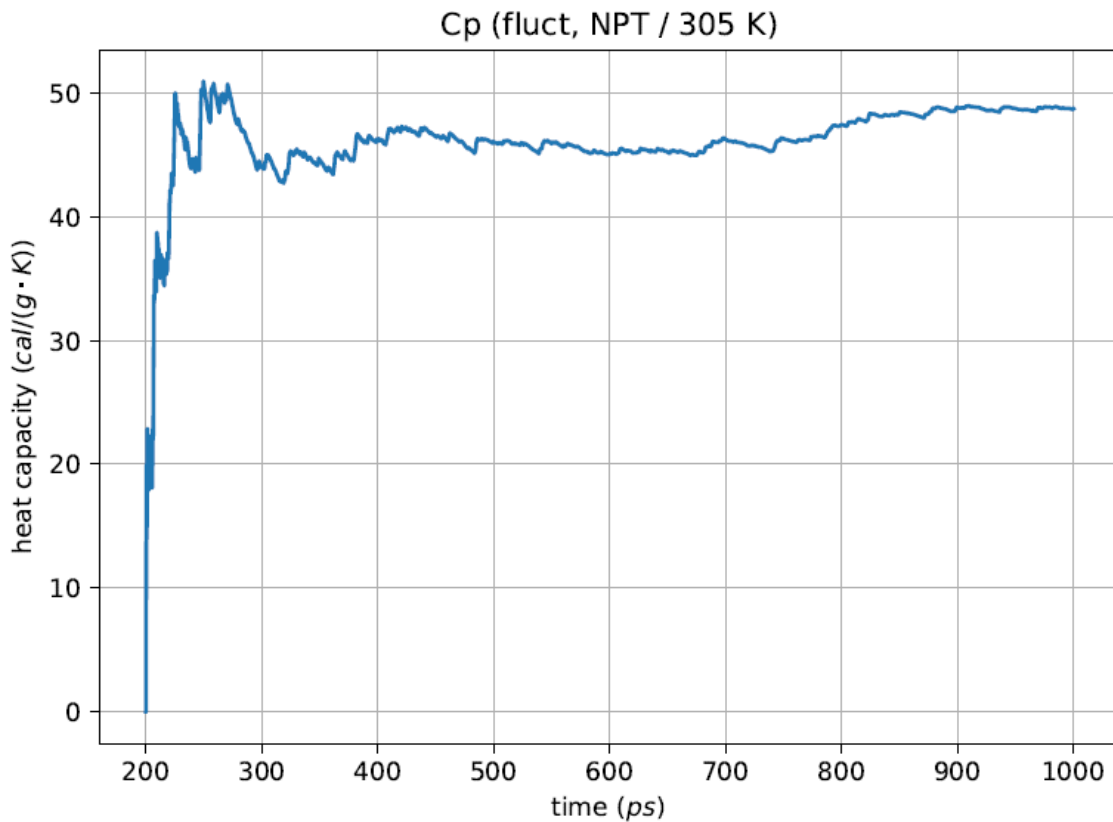


Image A.102:Cp at 305K for H<sub>2</sub>O **model3**

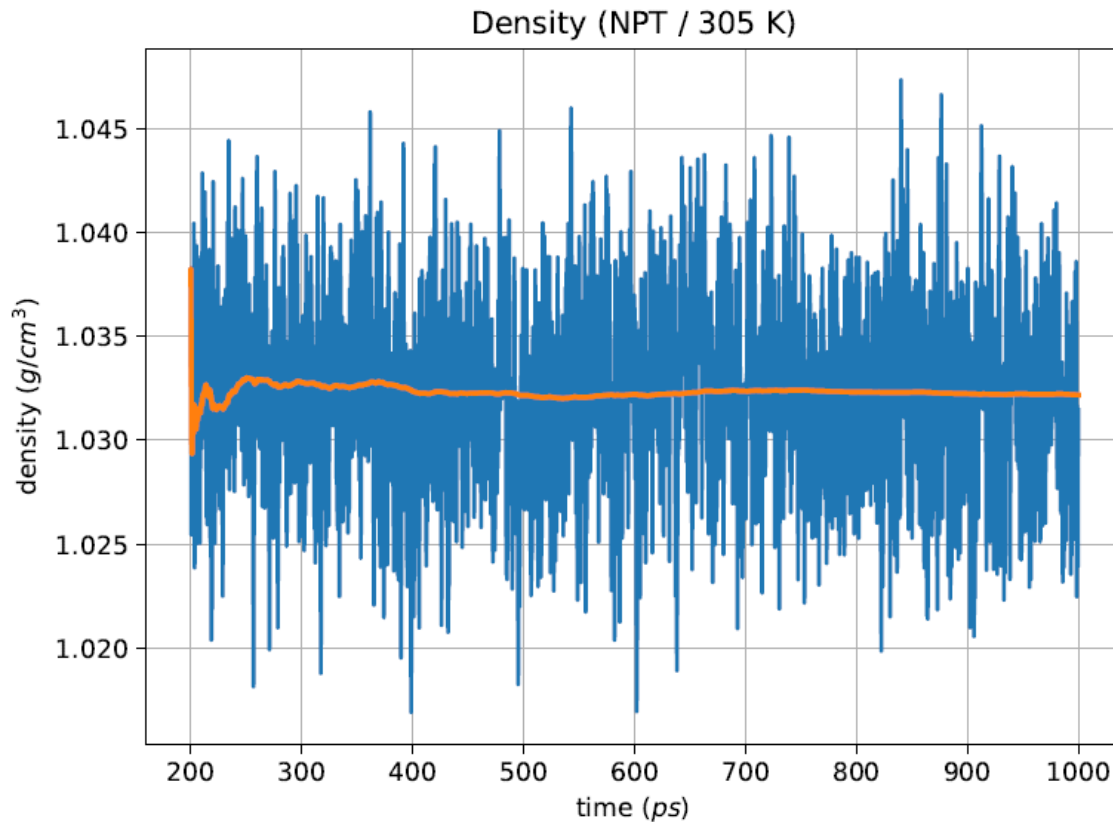


Image A.103:NPT Density at 305K for H<sub>2</sub>O **model3**

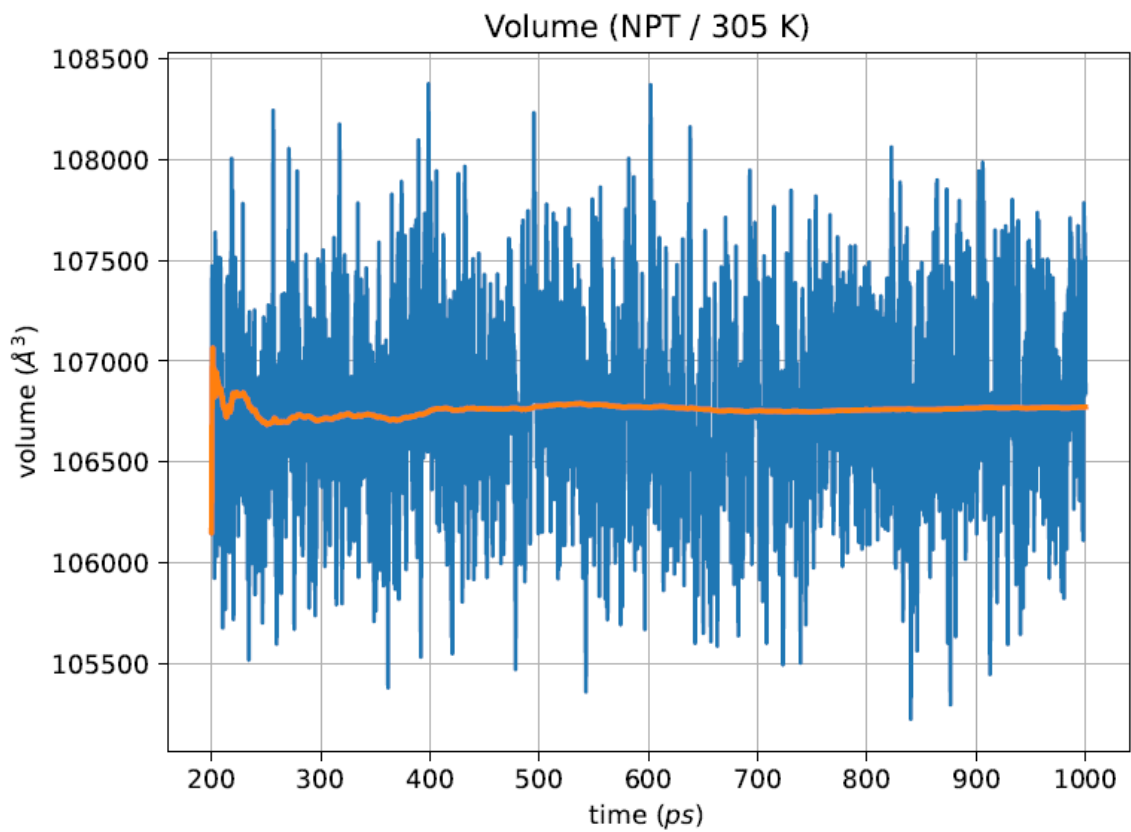


Image A.104:NPT Volume at 305K for H<sub>2</sub>O **model3**

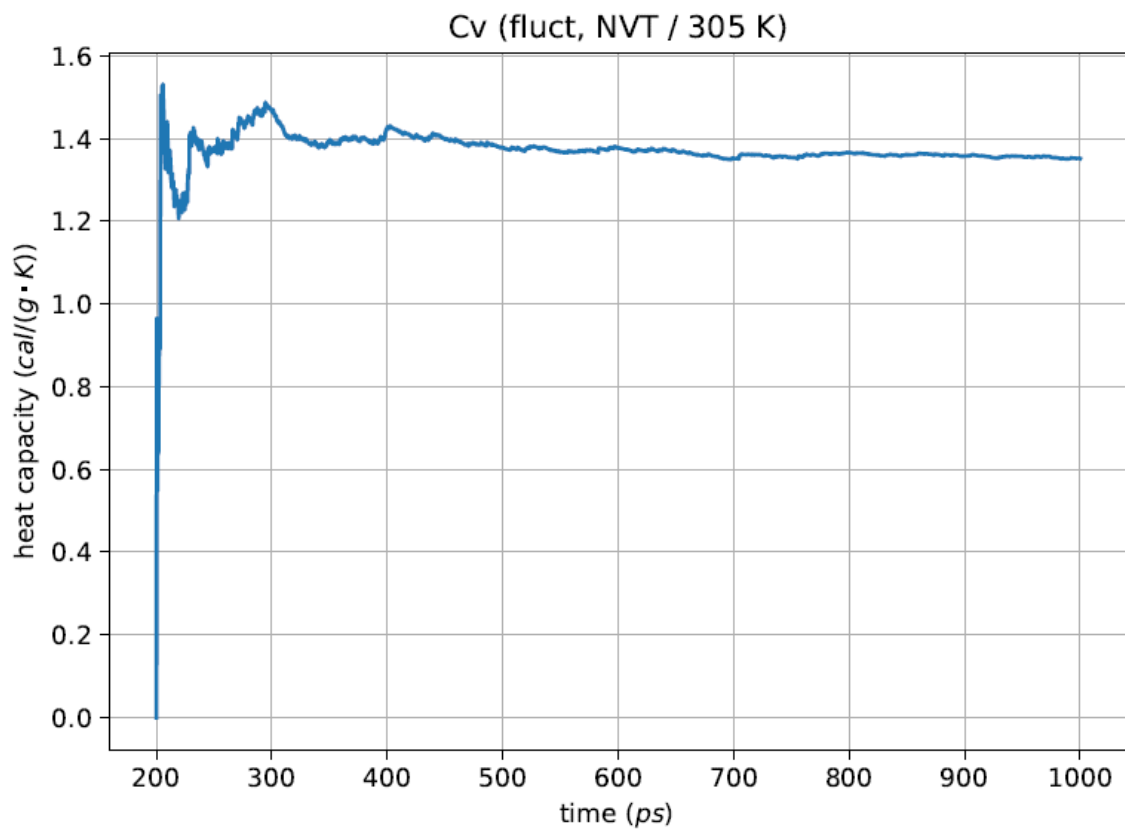


Image A.105: $C_v$  at 305K for H<sub>2</sub>O **model3**

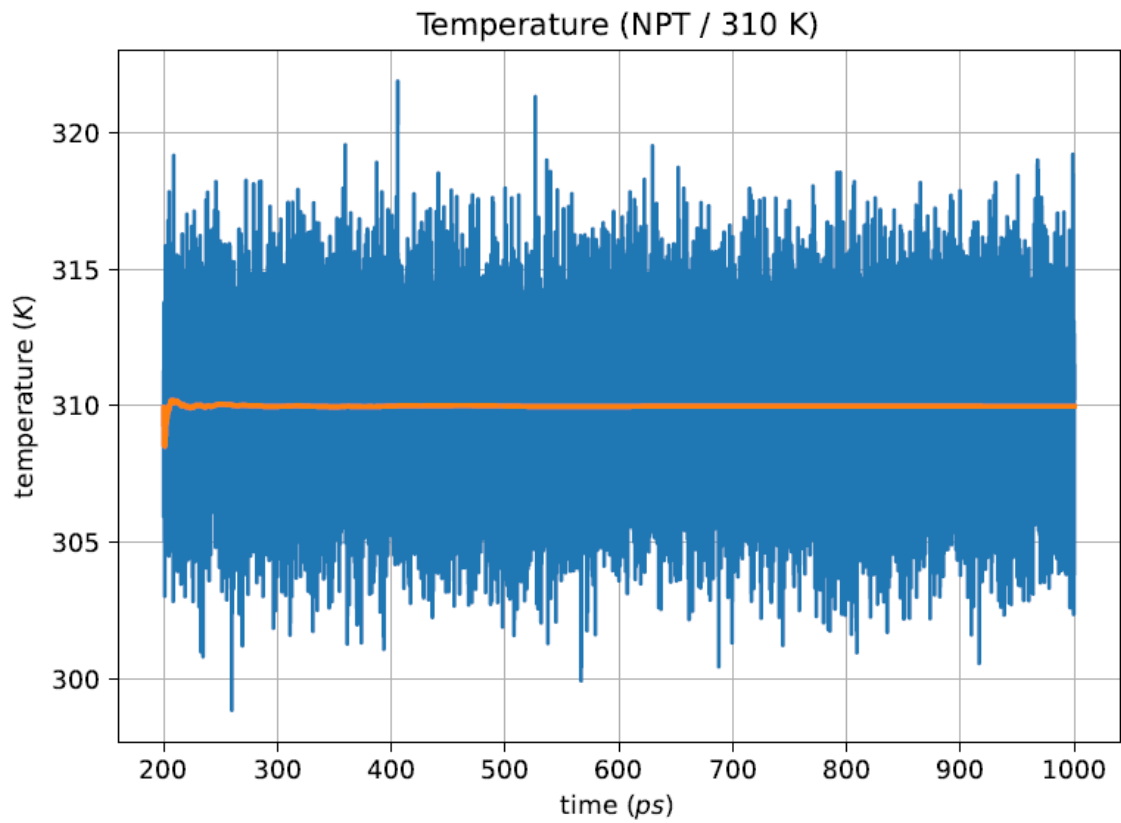


Image A.106:NPT temperature at 310K for H<sub>2</sub>O **model3**

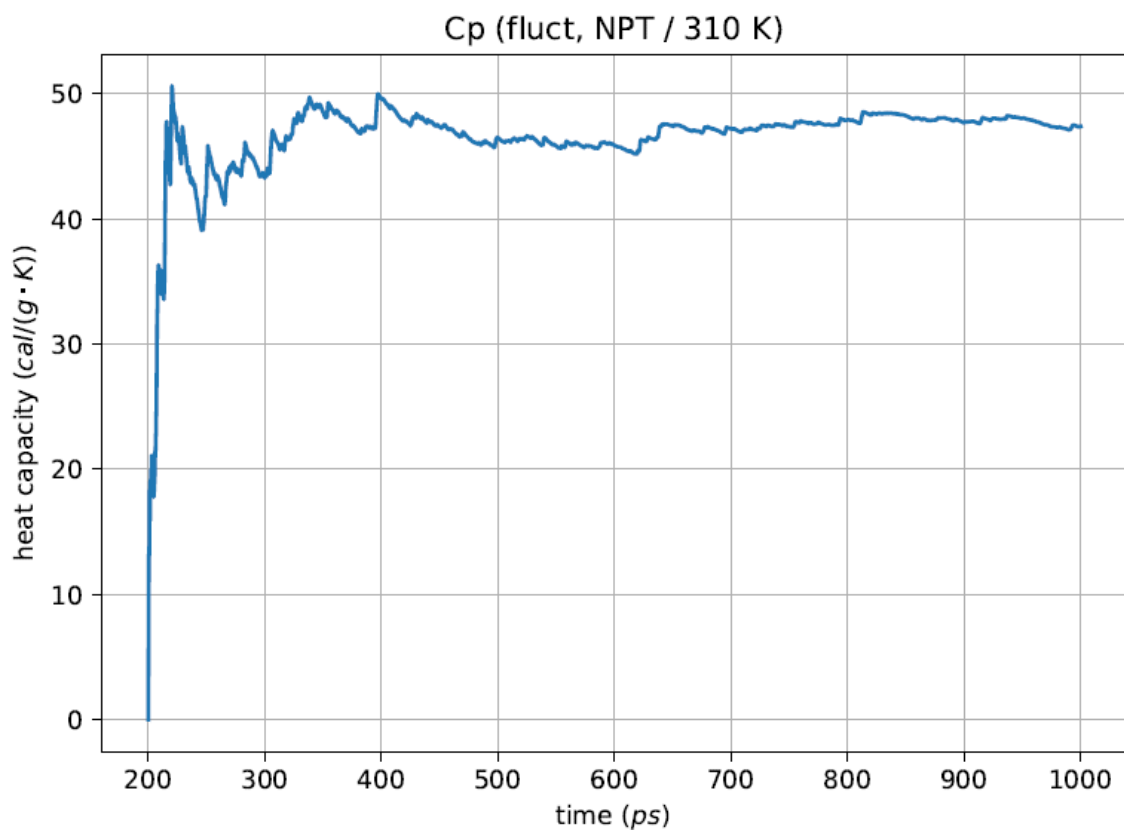


Image A.107:Cp at 310K for H<sub>2</sub>O **model3**

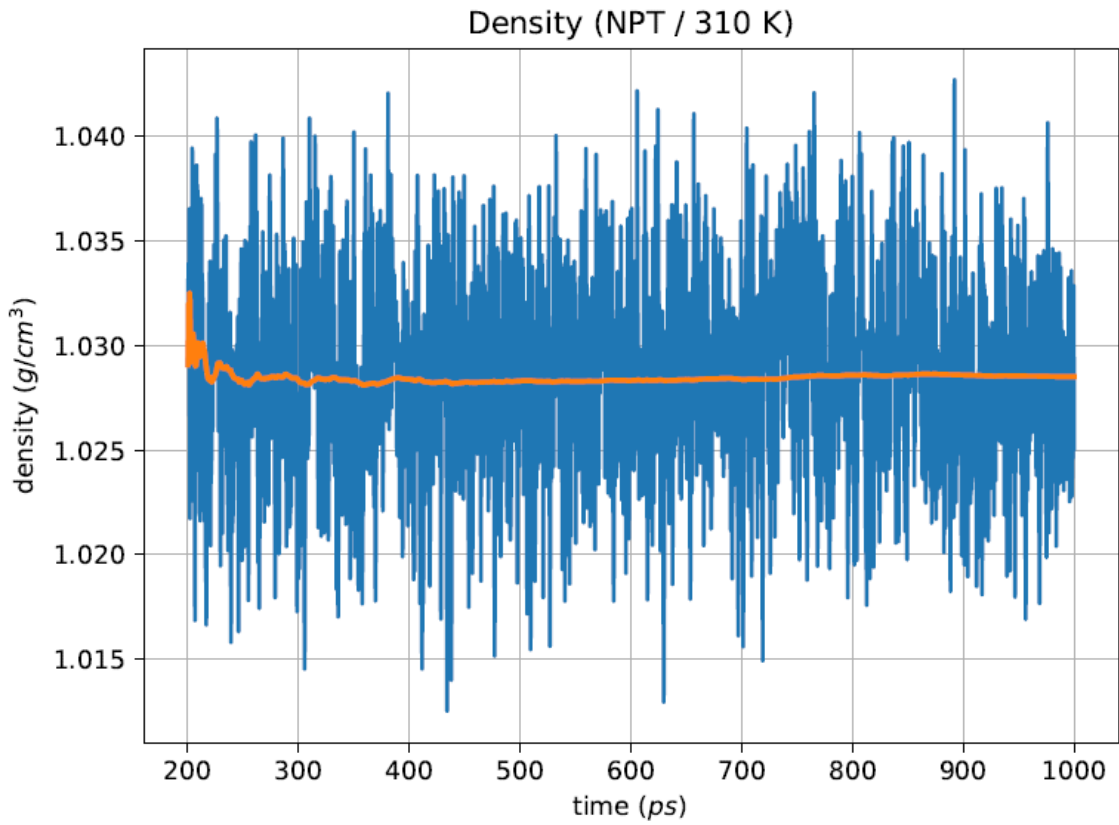


Image A.108:NPT Density at 310K for H<sub>2</sub>O **model3**

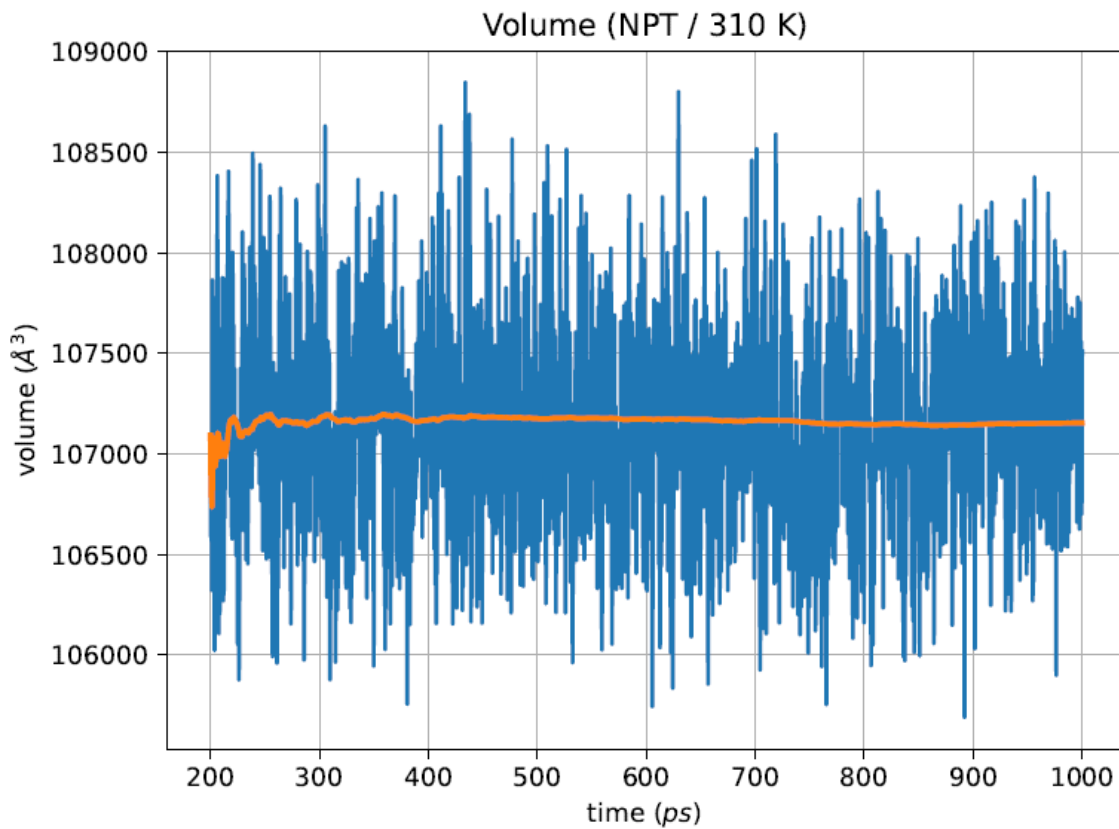


Image A.109:NPT Volume at 310K for H<sub>2</sub>O **model3**

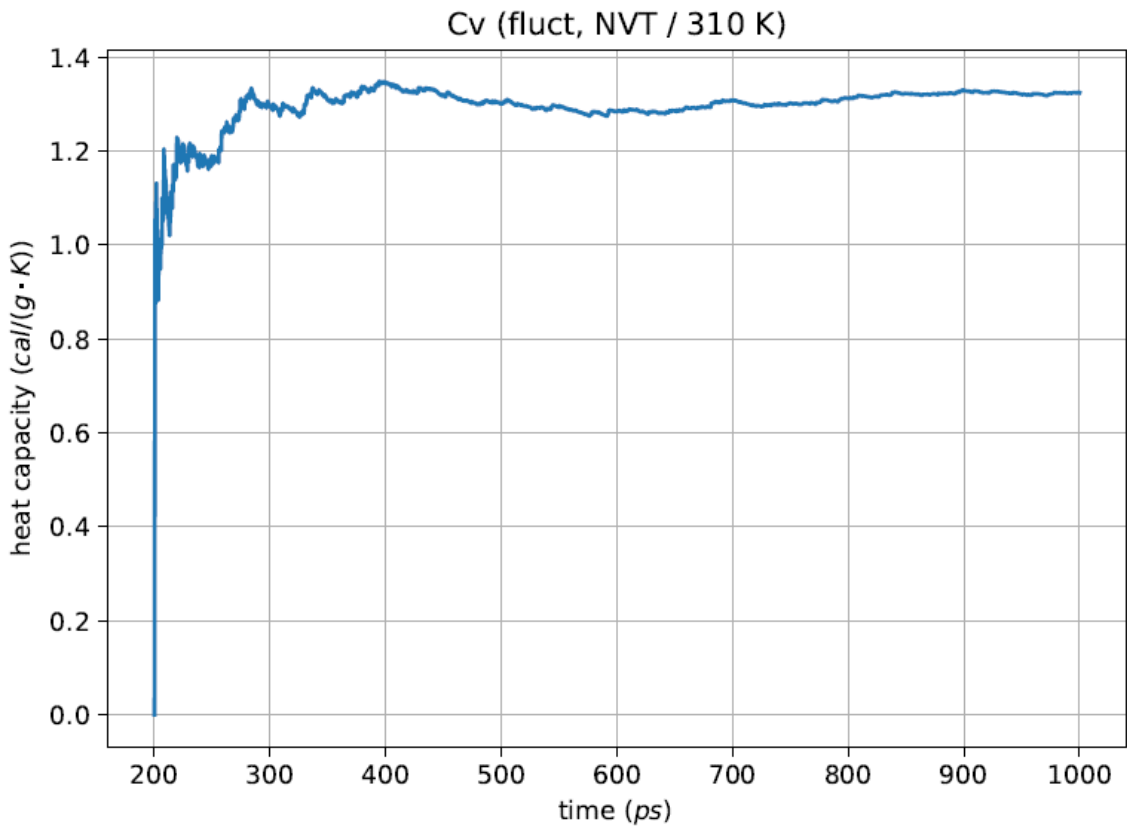


Image A.110:  $C_v$  at 310K for H<sub>2</sub>O **model3**

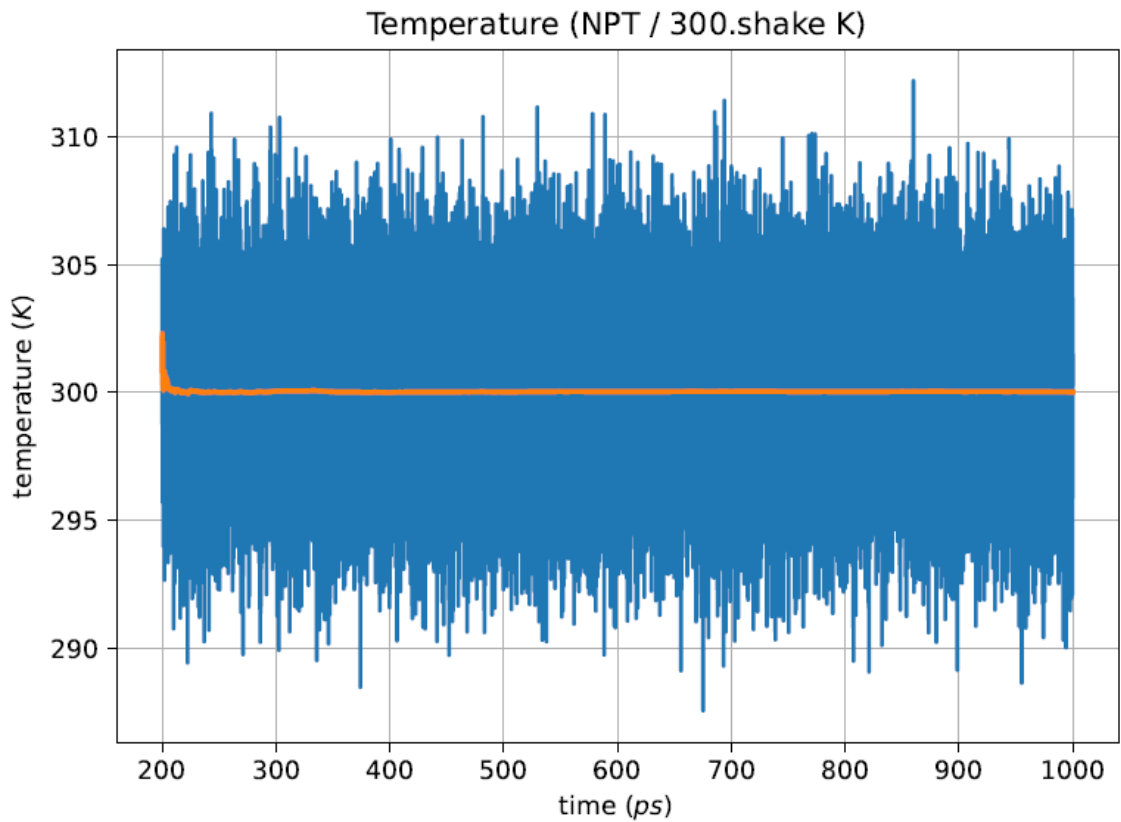


Image A.111: NPT temperature at 300K for H<sub>2</sub>O rigid **model3**

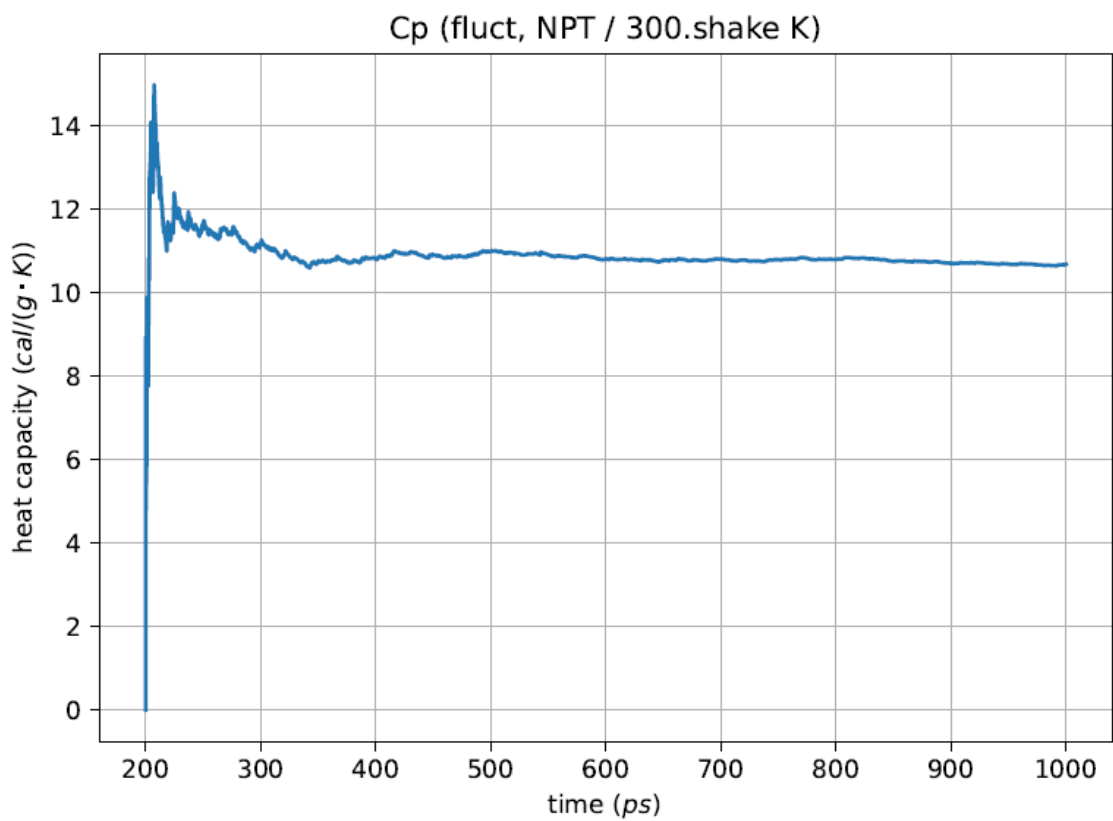


Image A.112:Cp at 300K for H<sub>2</sub>O rigid **model3**

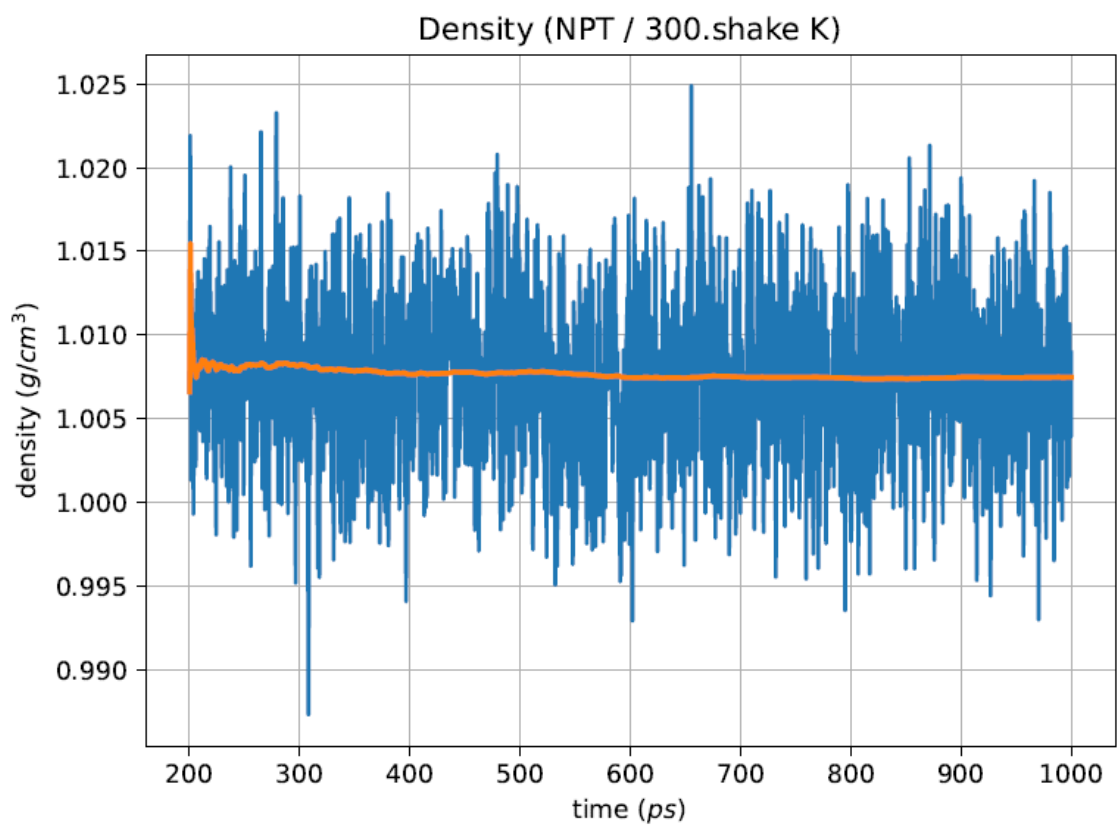


Image A.113:NPT Density at 300K for H<sub>2</sub>O rigid **model3**



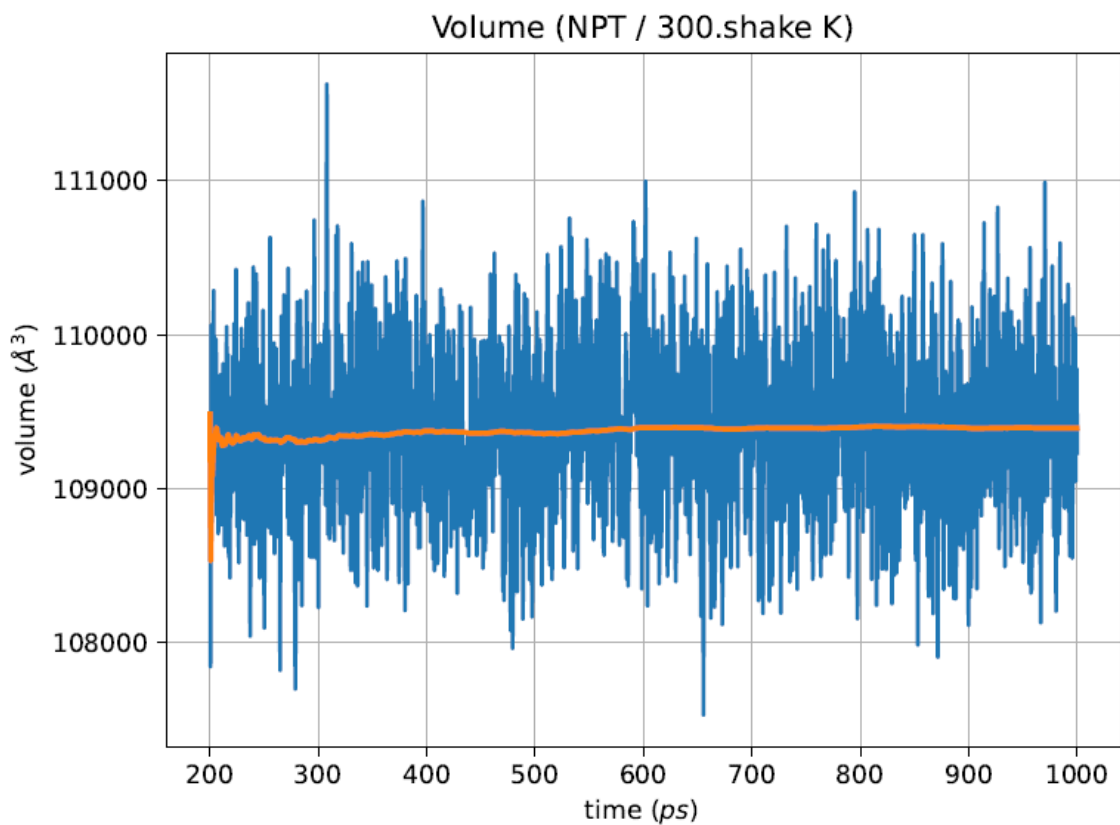


Image A.114:NPT Volume at 300K for H<sub>2</sub>O rigid **model3**

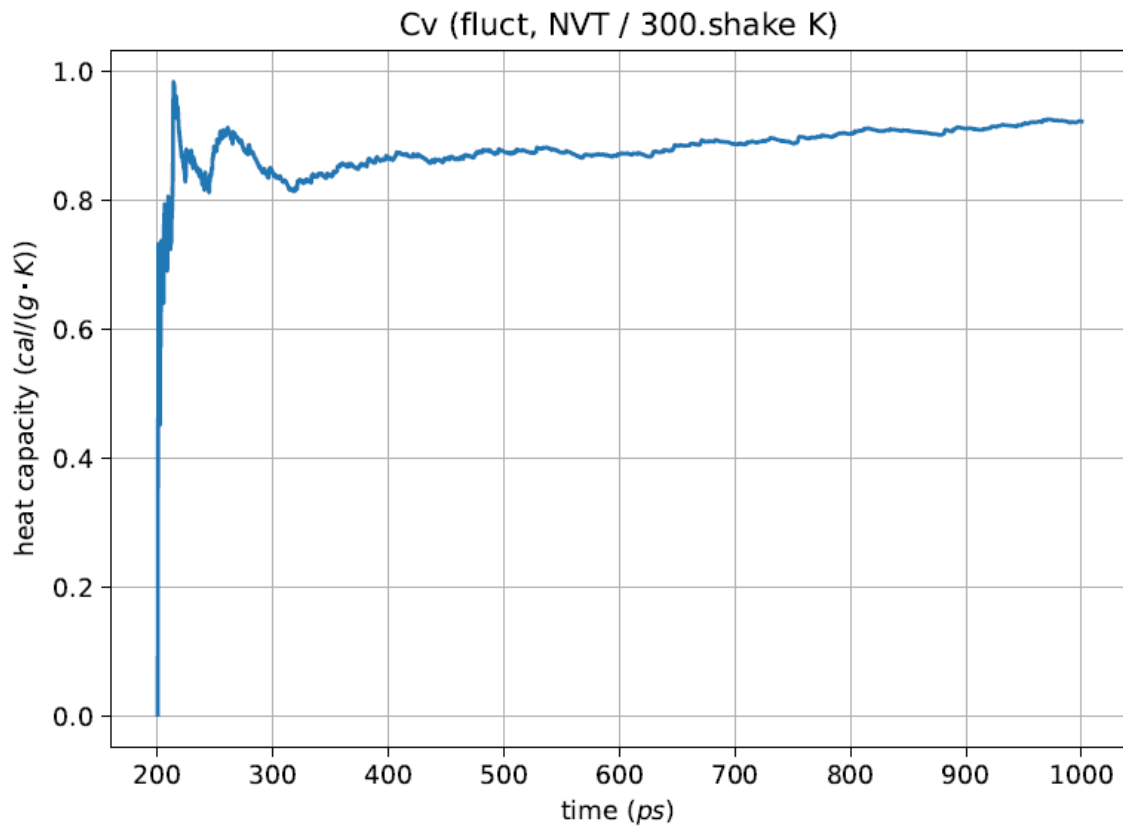


Image A.115: $C_v$  at 300K for H<sub>2</sub>O rigid **model3**

## 6.- H<sub>2</sub>O graphs (model 4)

### Parameters

O 8 0.18937 3.1776

H 1 0.0000 0.0000

O 0.000000 0.000000 0.000000 -0.8450

H 0.900000 0.000000 0.000000 0.4225

H -0.225340 0.871330 0.000000 0.4225

H O 358.51 1.027

H O H 45.77 114.70

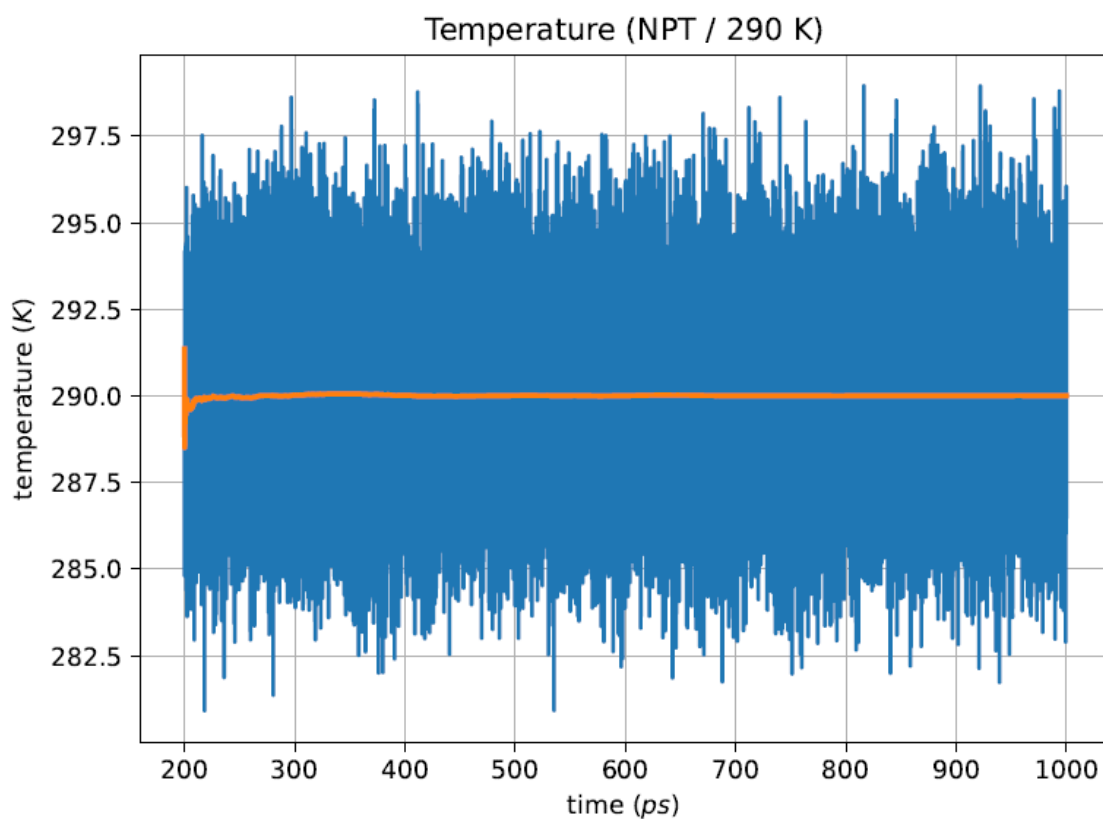


Image A.116:NPT Temperature at 290K for H<sub>2</sub>O model4

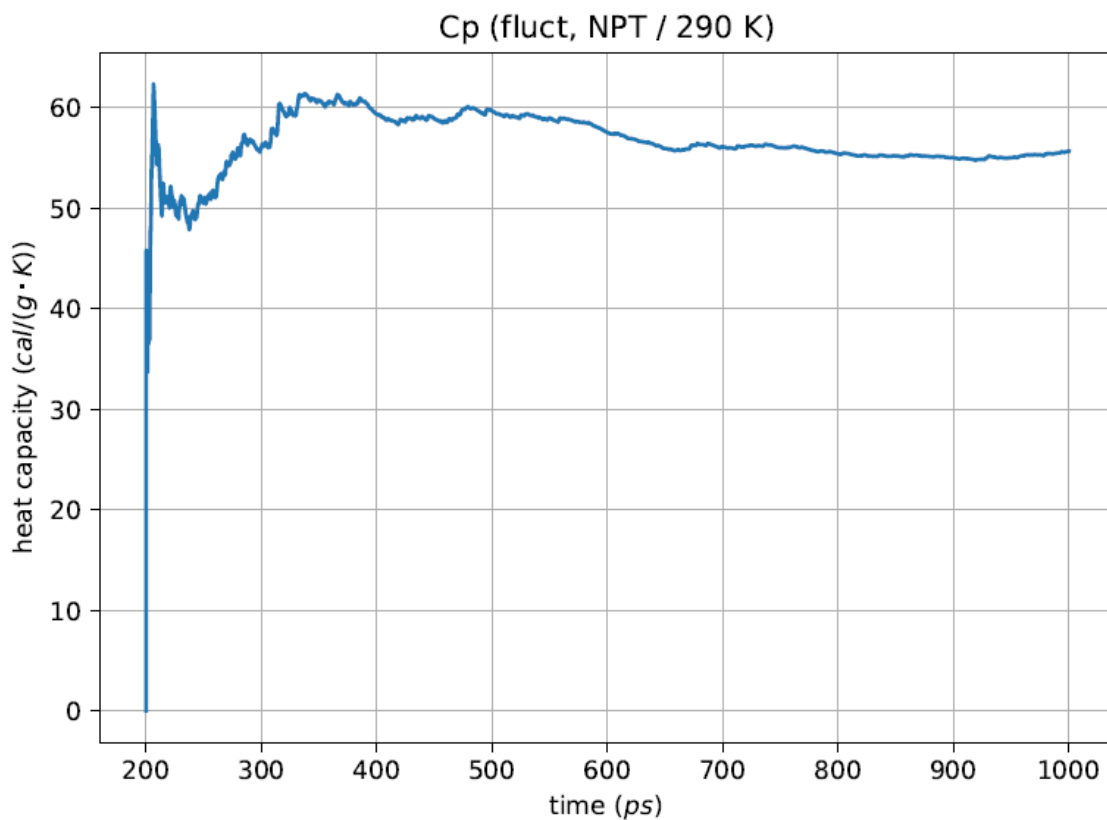


Image A.117:Cp at 290K for H<sub>2</sub>O **model4**

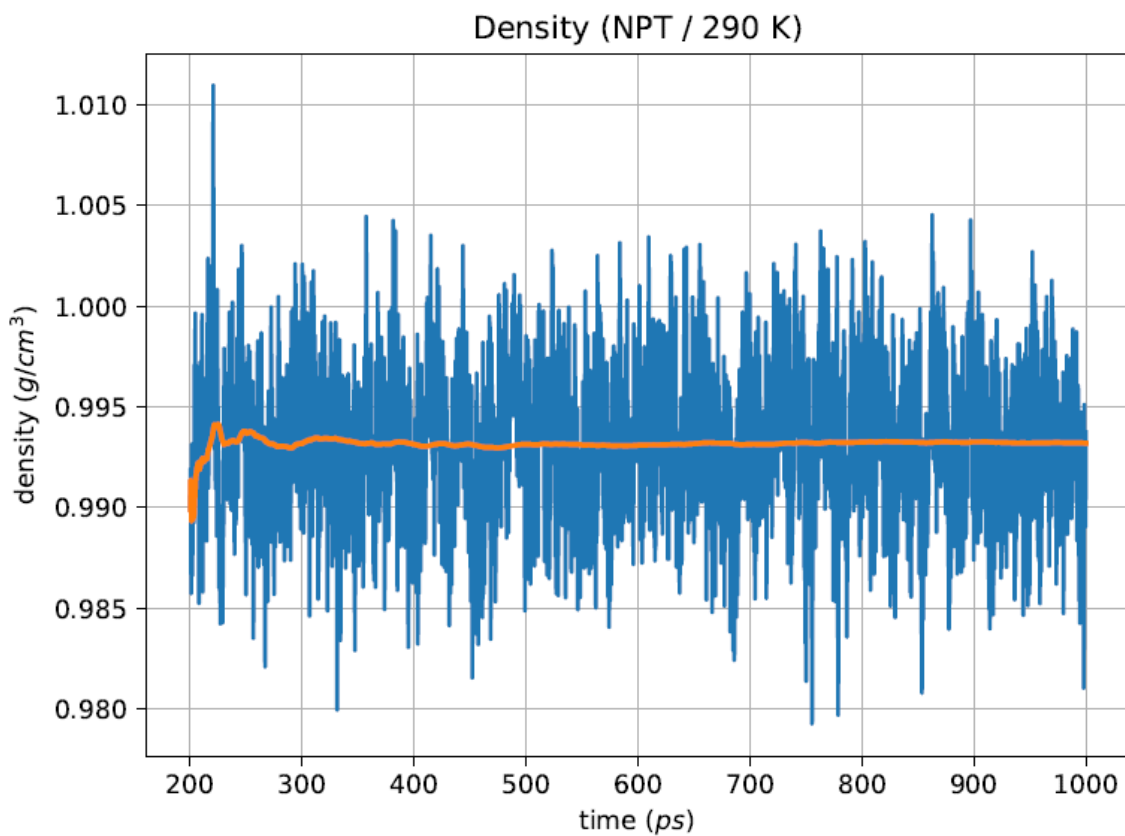


Image A.118:NPT Density at 290K for H<sub>2</sub>O **model4**

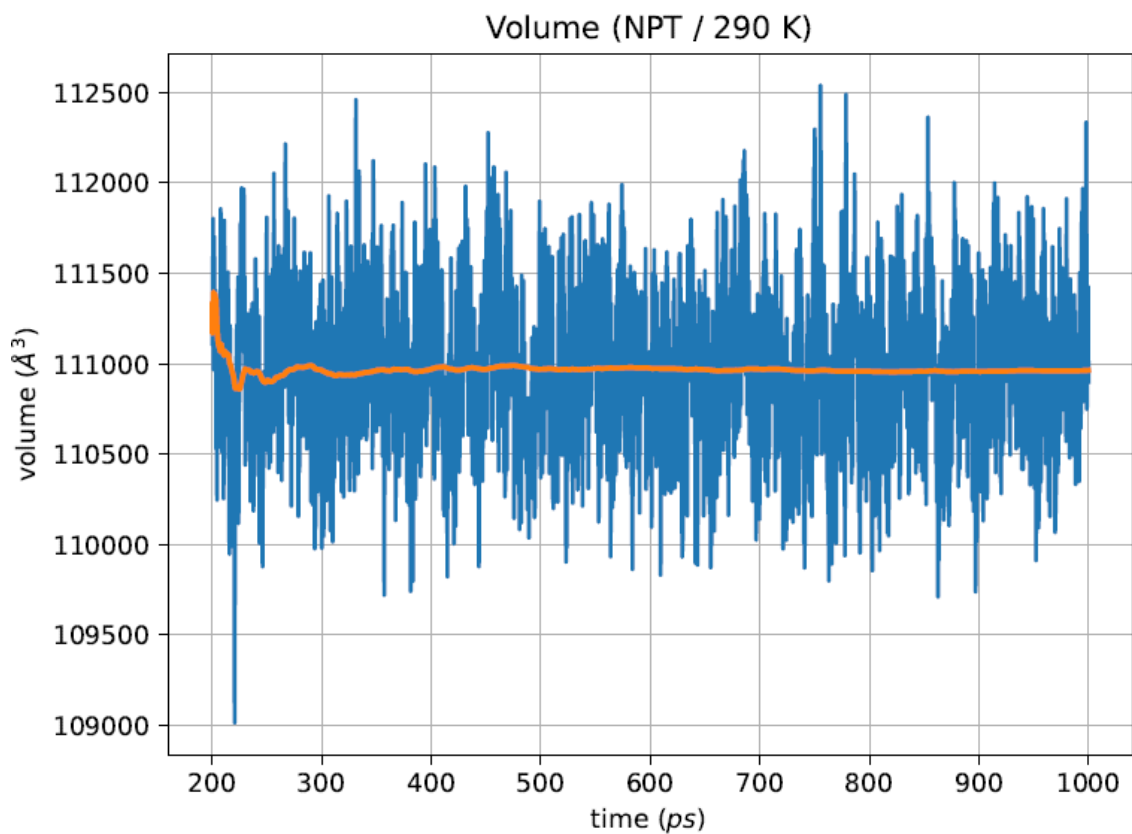


Image A.119:NPT Volume at 290K for H<sub>2</sub>O **model4**

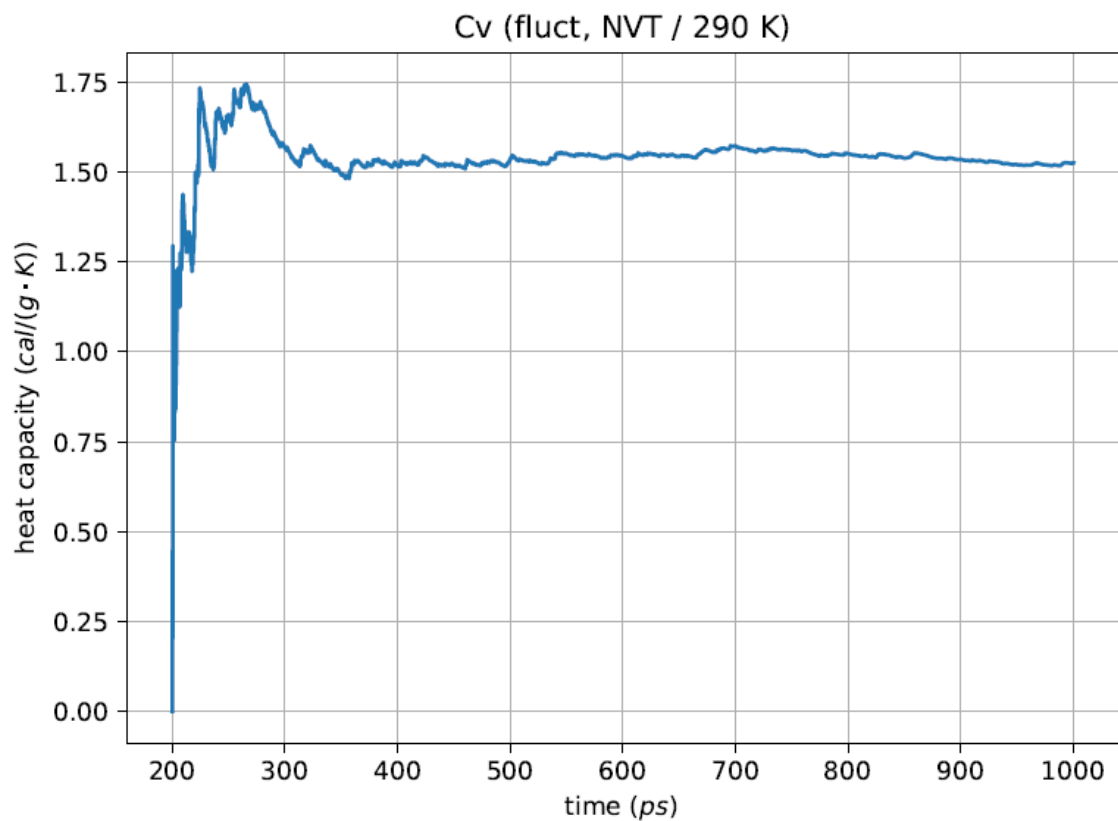


Image A.120:Cv at 290K for H<sub>2</sub>O **model4**

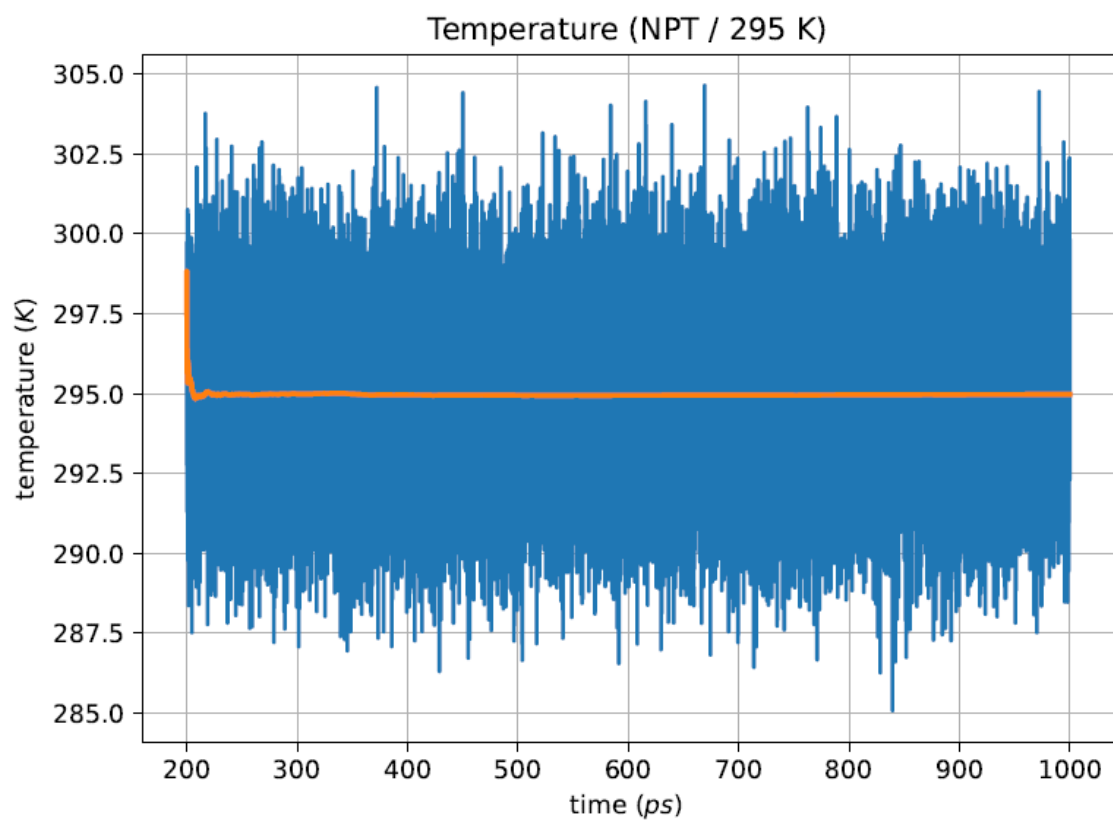


Image A.121:NPT Temperature at 295K for H<sub>2</sub>O **model4**

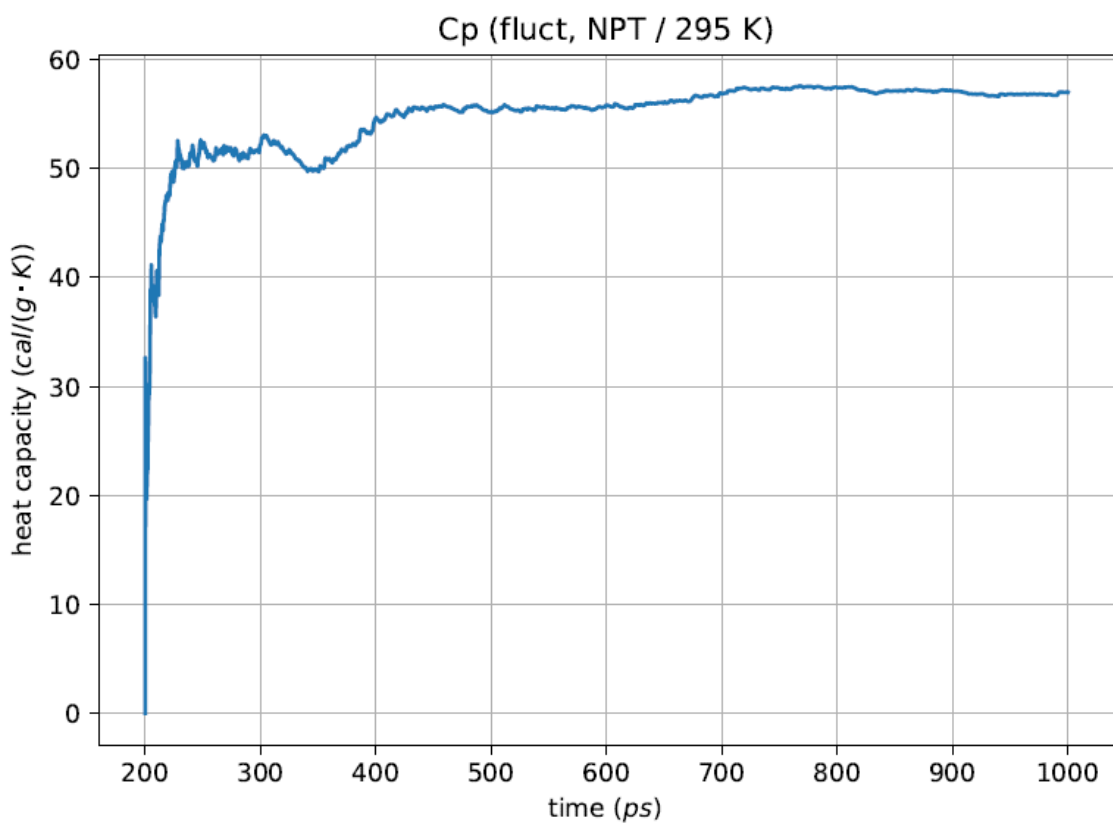


Image A.122:Cp at 295K for H<sub>2</sub>O **model4**

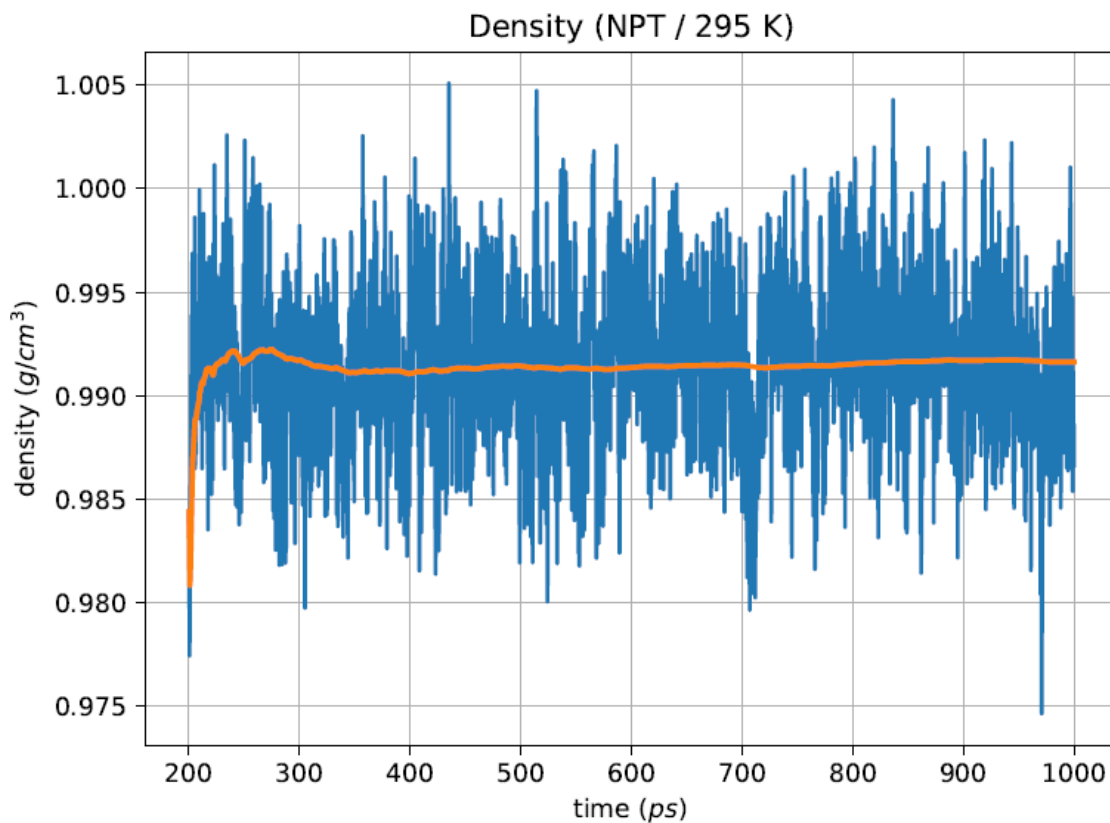


Image A.123:NPT Density at 295K for H<sub>2</sub>O **model4**

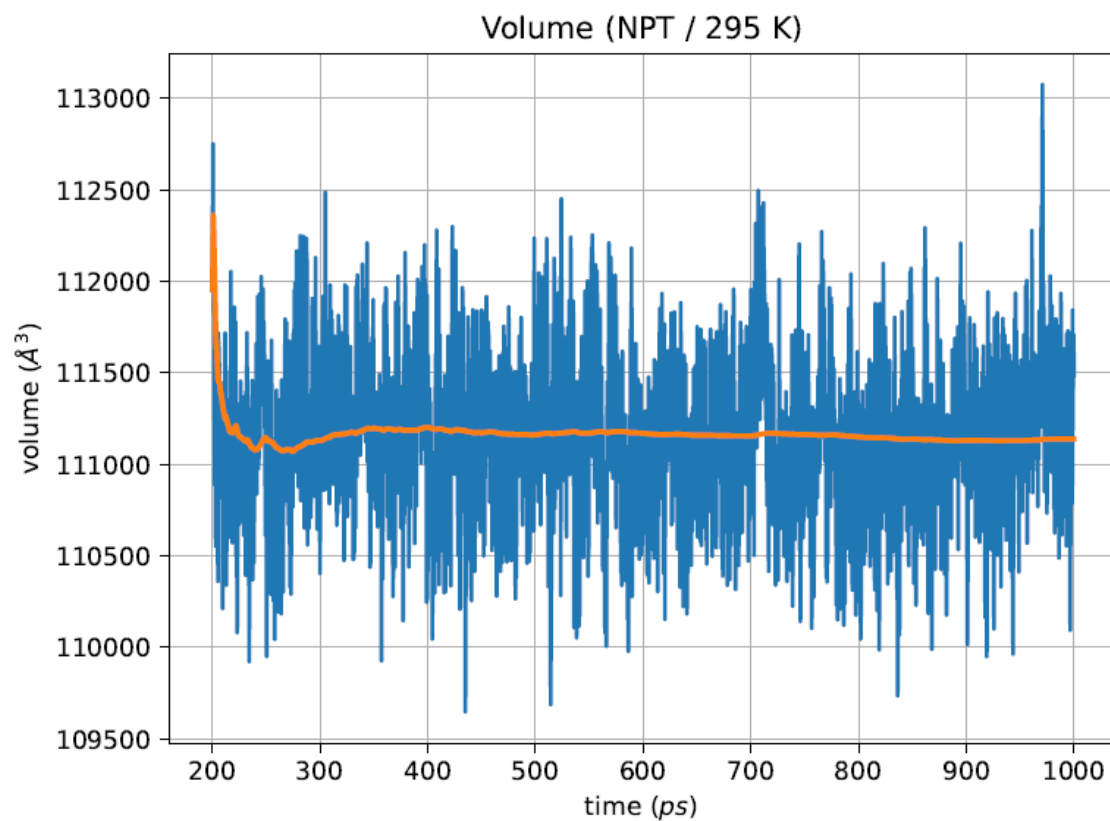


Image A.124:NPT Volume at 295K for H<sub>2</sub>O **model4**

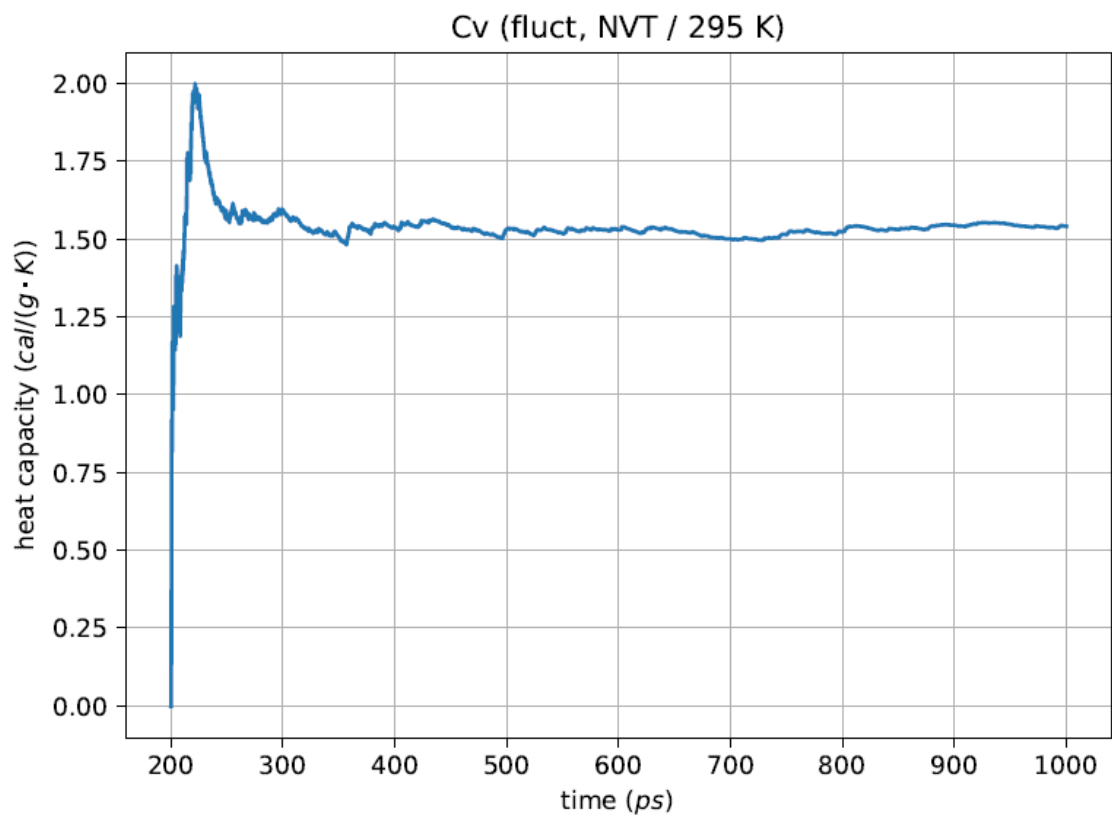


Image A.125:Cv at 295K for H<sub>2</sub>O **model4**

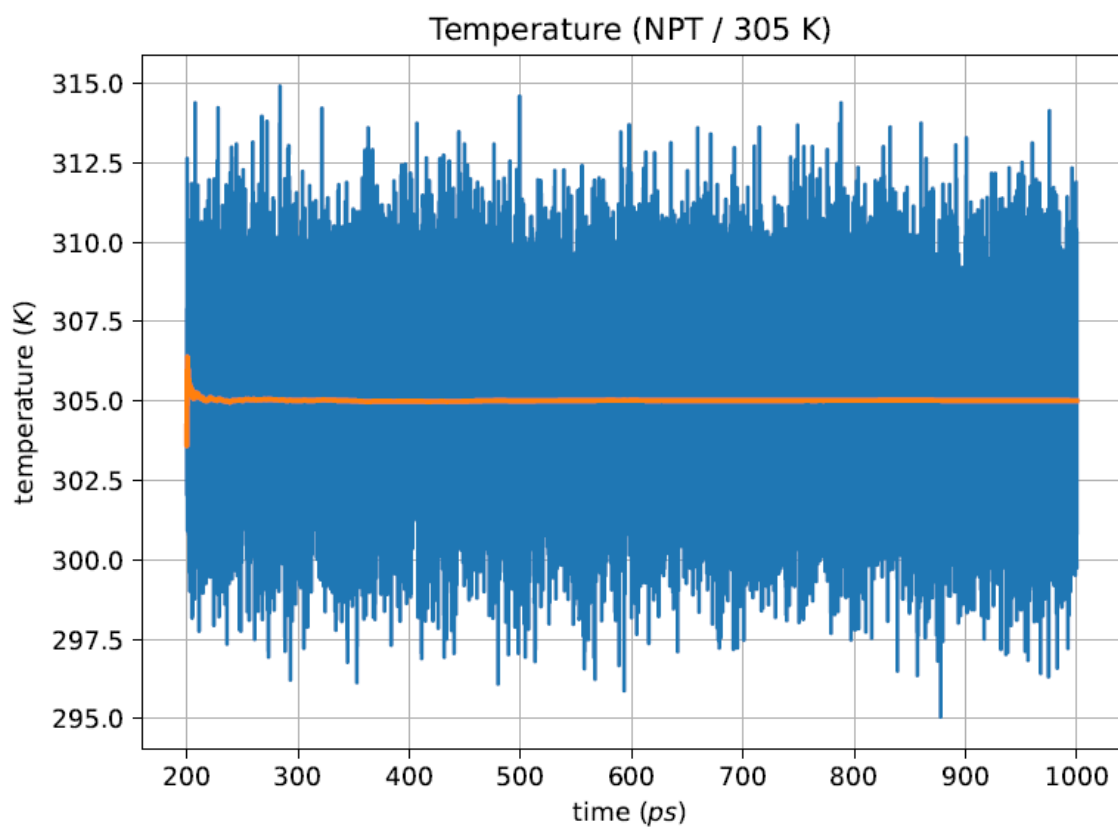


Image A.126:NPT Temperature at 305K for H<sub>2</sub>O **model4**

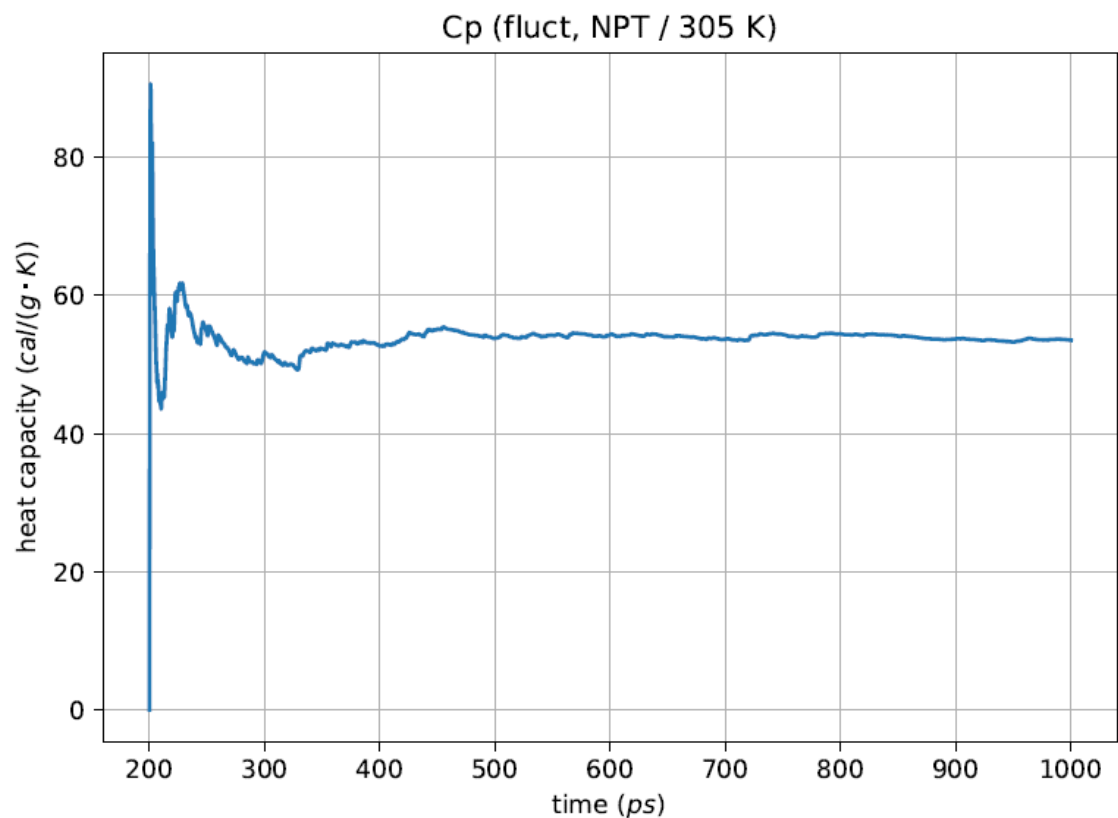


Image A.127:Cp at 305K for H<sub>2</sub>O **model4**

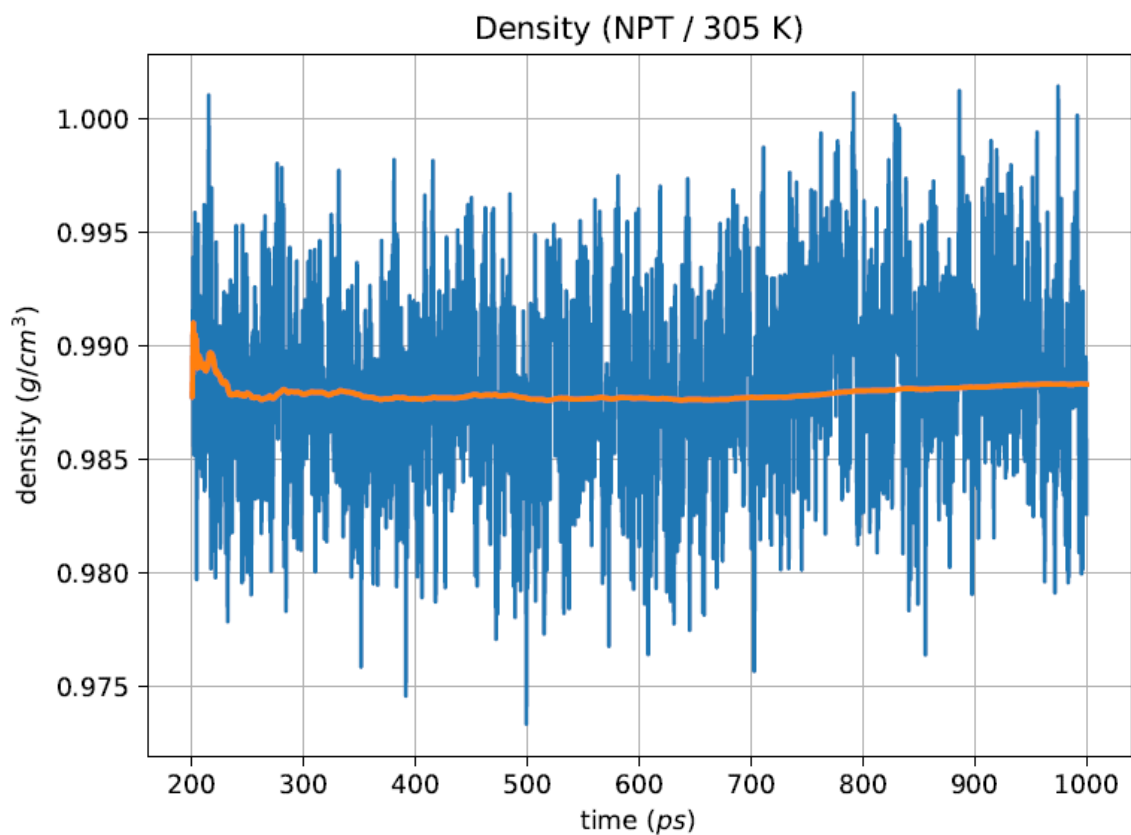


Image A.128:NPT Density at 305K for H<sub>2</sub>O **model4**



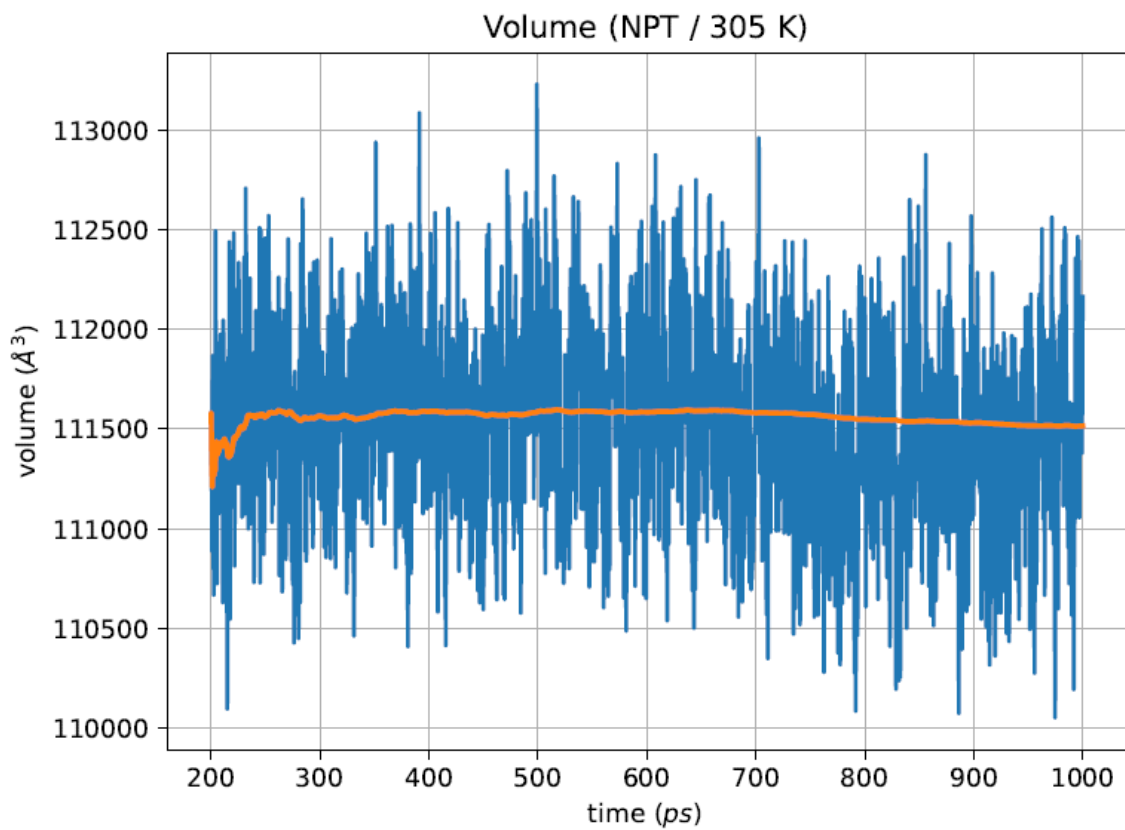


Image A.129:NPT Volume at 305K for H<sub>2</sub>O **model4**

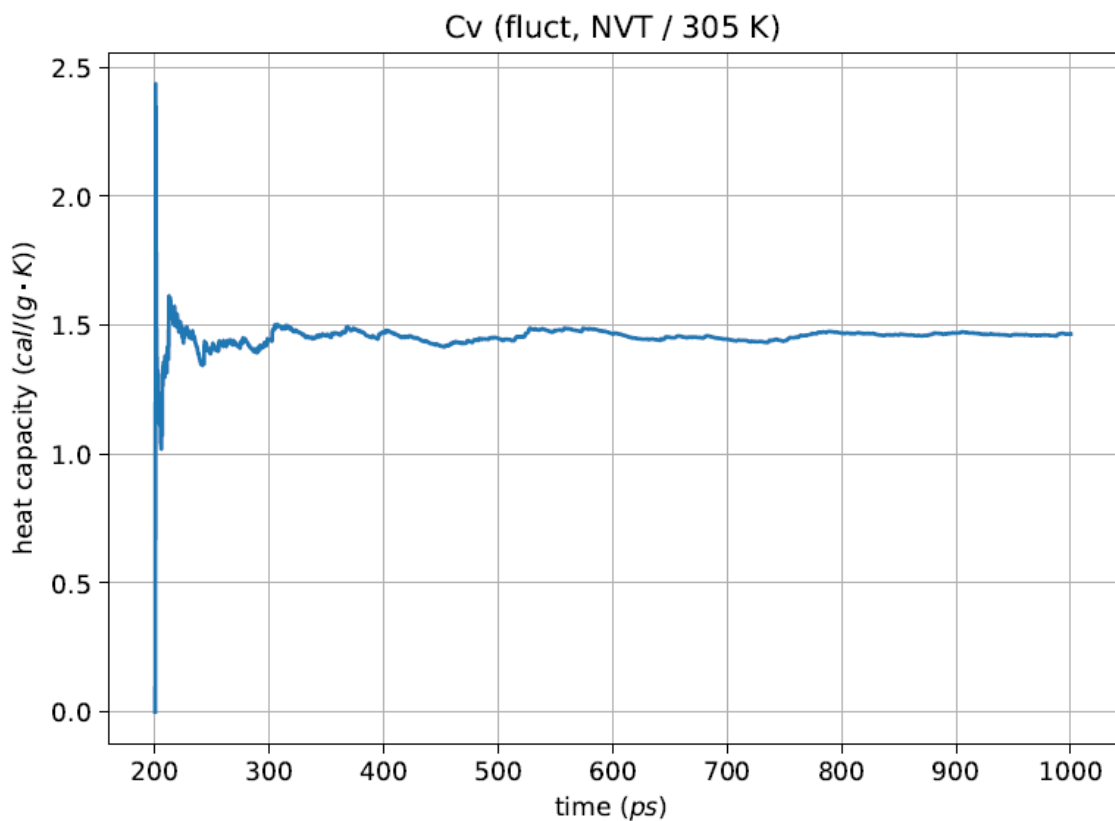


Image A.130:Cv at 305K for H<sub>2</sub>O **model4**

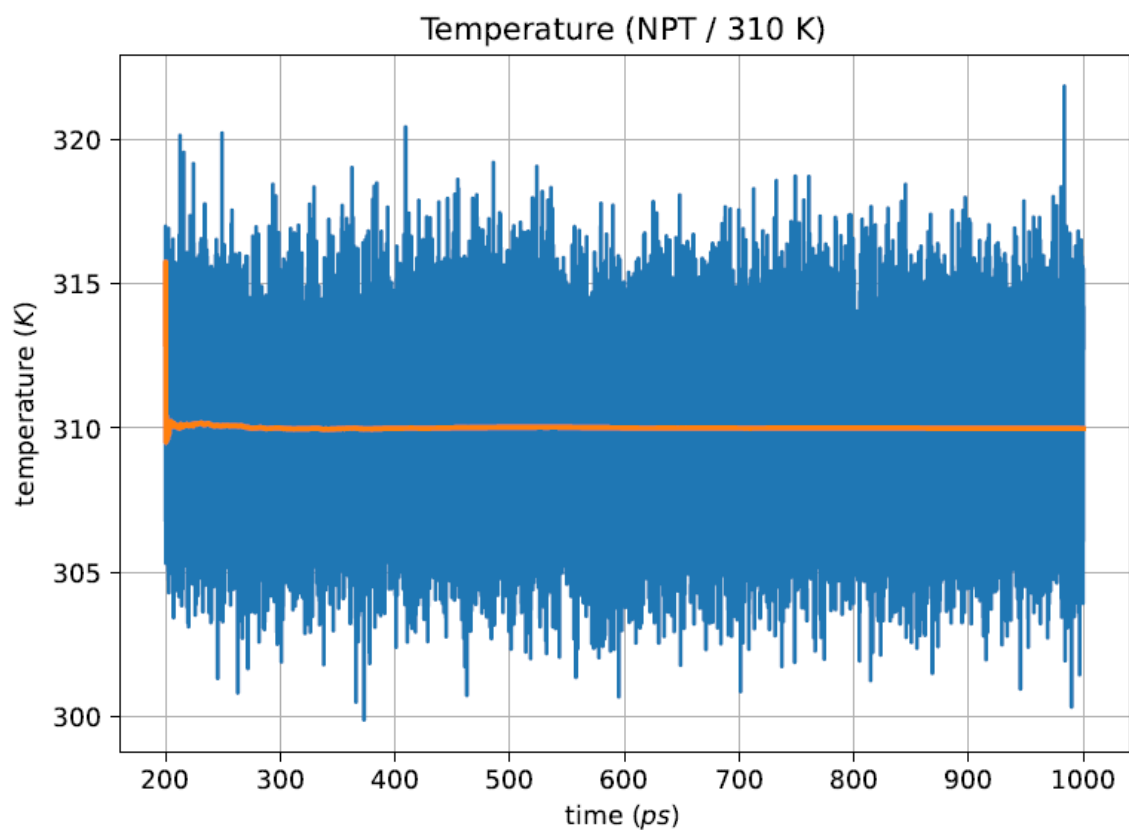


Image A.131:NPT Temperature at 310K for H<sub>2</sub>O **model4**

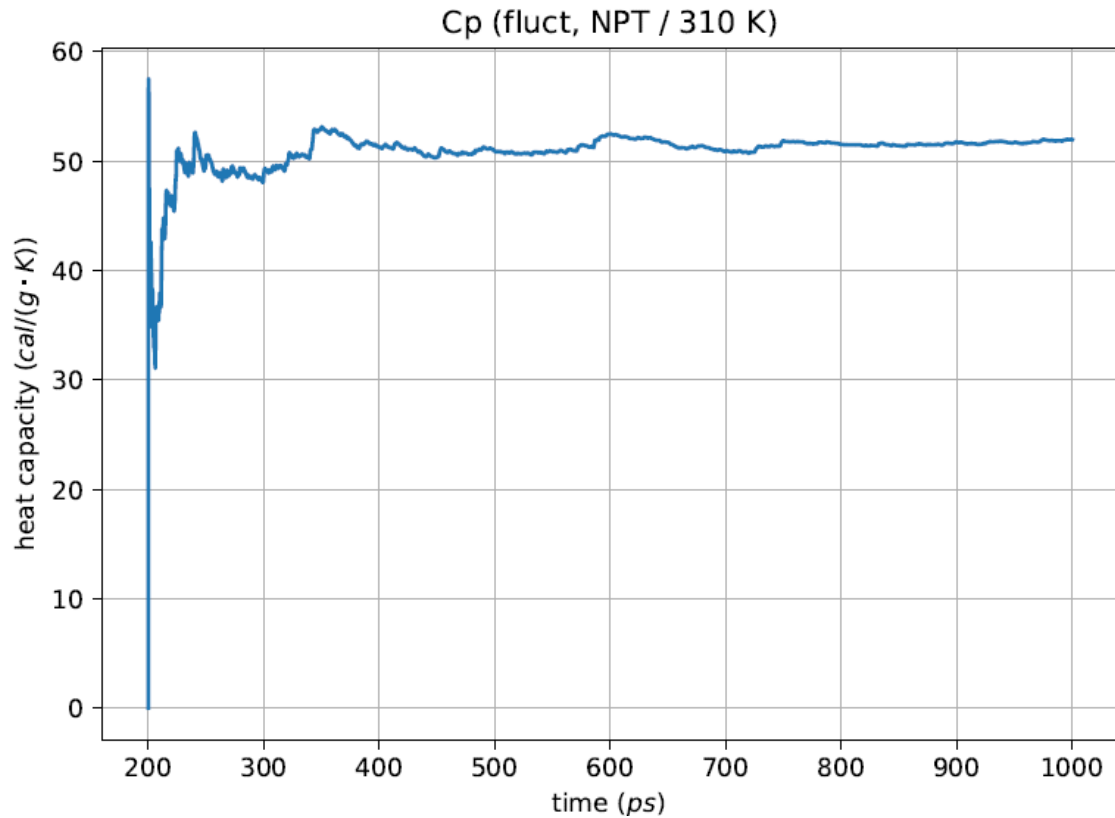


Image A.132:Cp at 310K for H<sub>2</sub>O **model4**

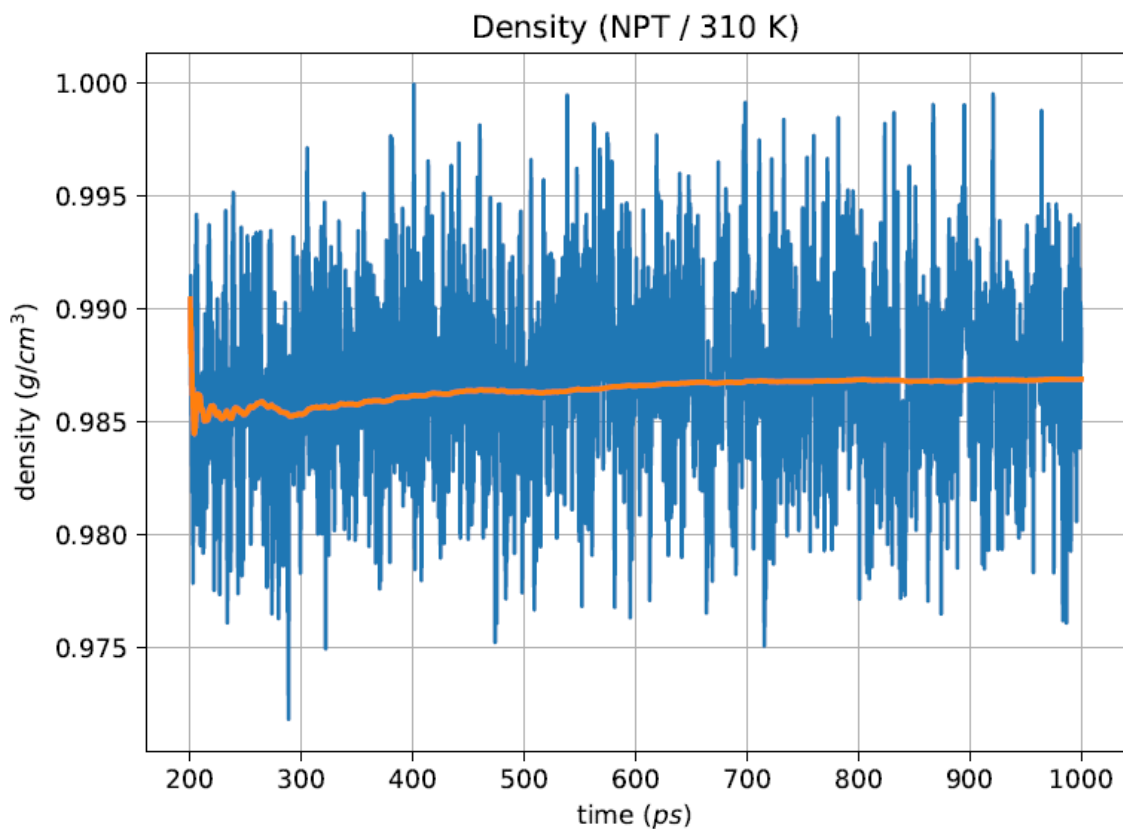


Image A.133:NPT Density at 310K for H<sub>2</sub>O **model4**

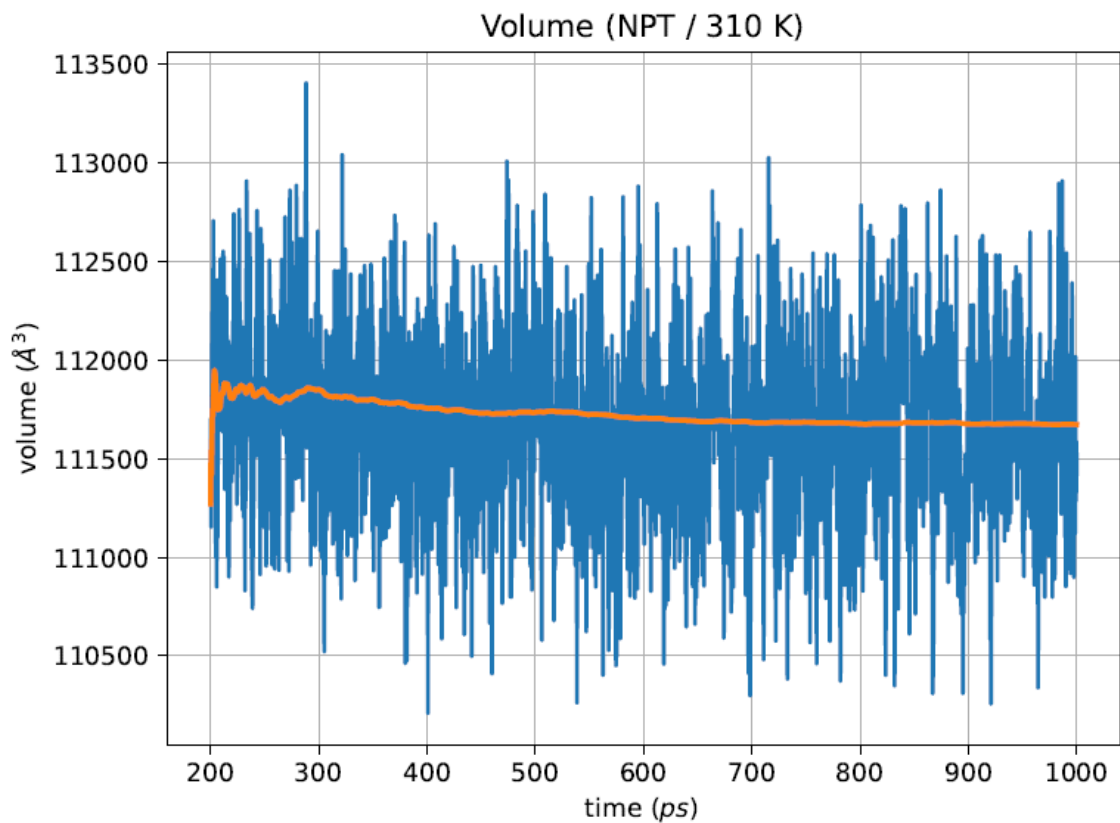


Image A.134:NPT Volume at 310K for H<sub>2</sub>O **model4**

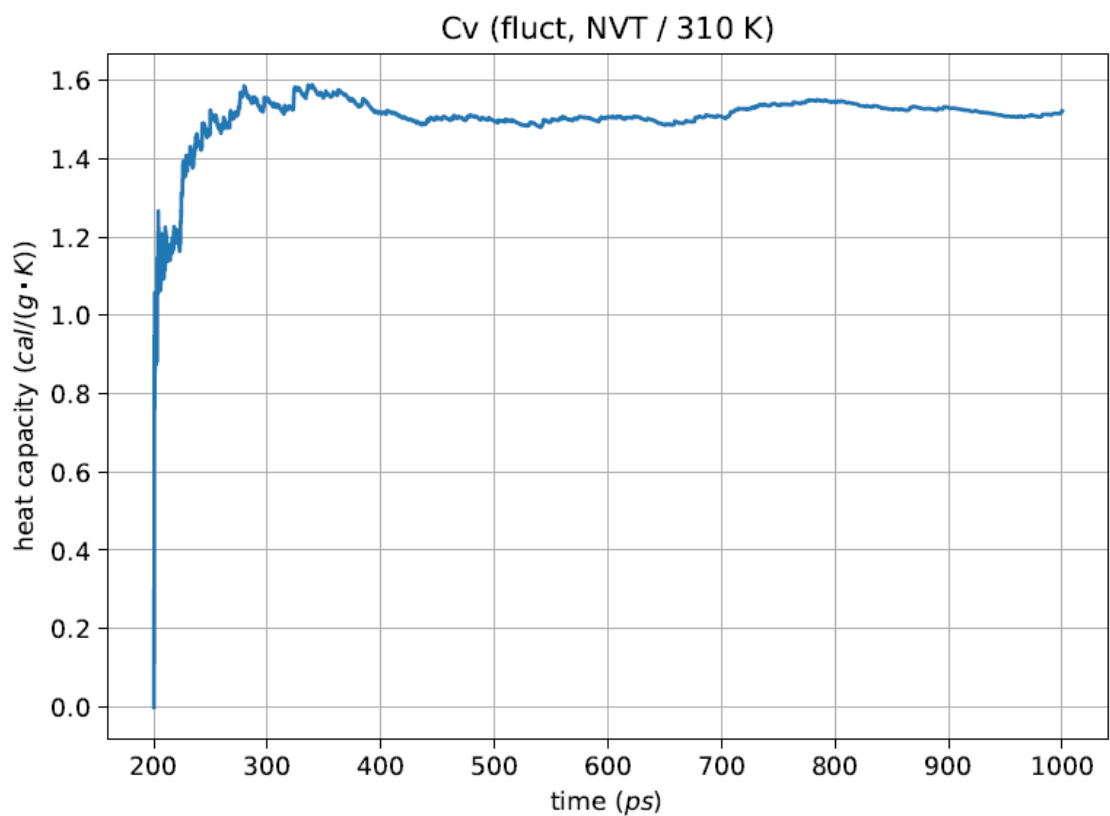


Image A.135:  $C_v$  at 310K for H<sub>2</sub>O **model4**

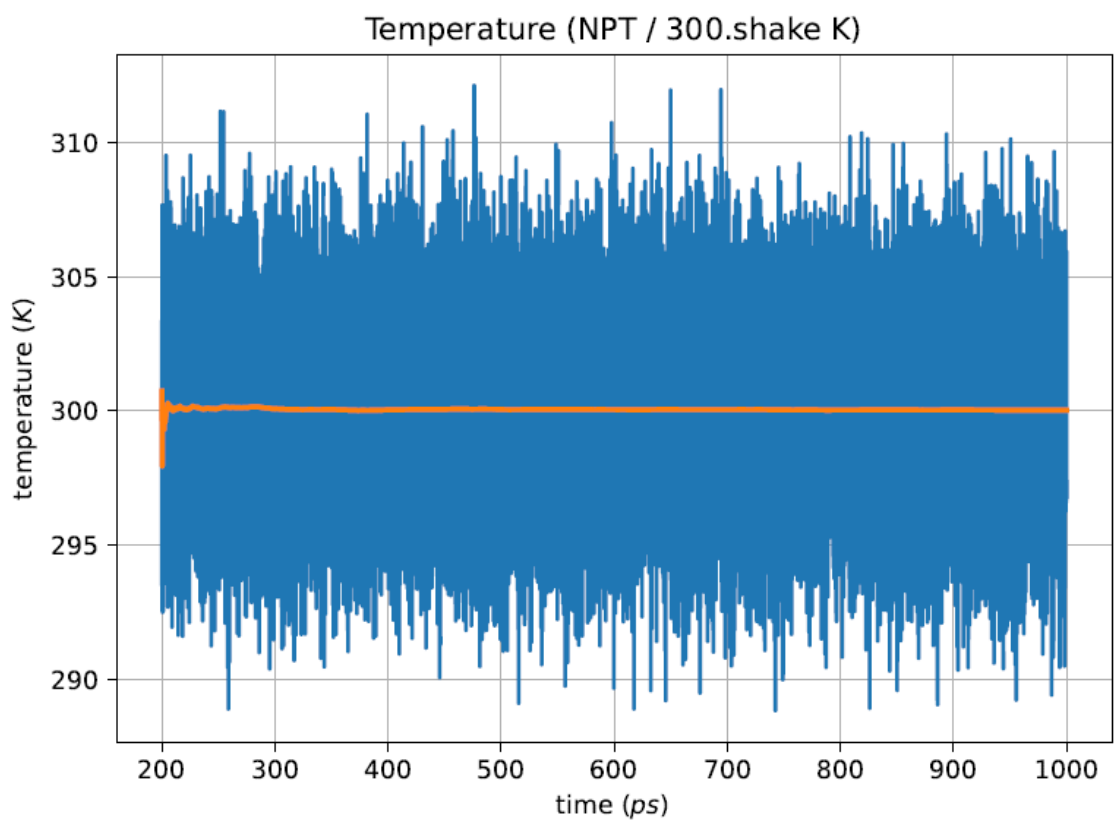


Image A.136: NPT Temperature at 300K for H<sub>2</sub>O **model4**

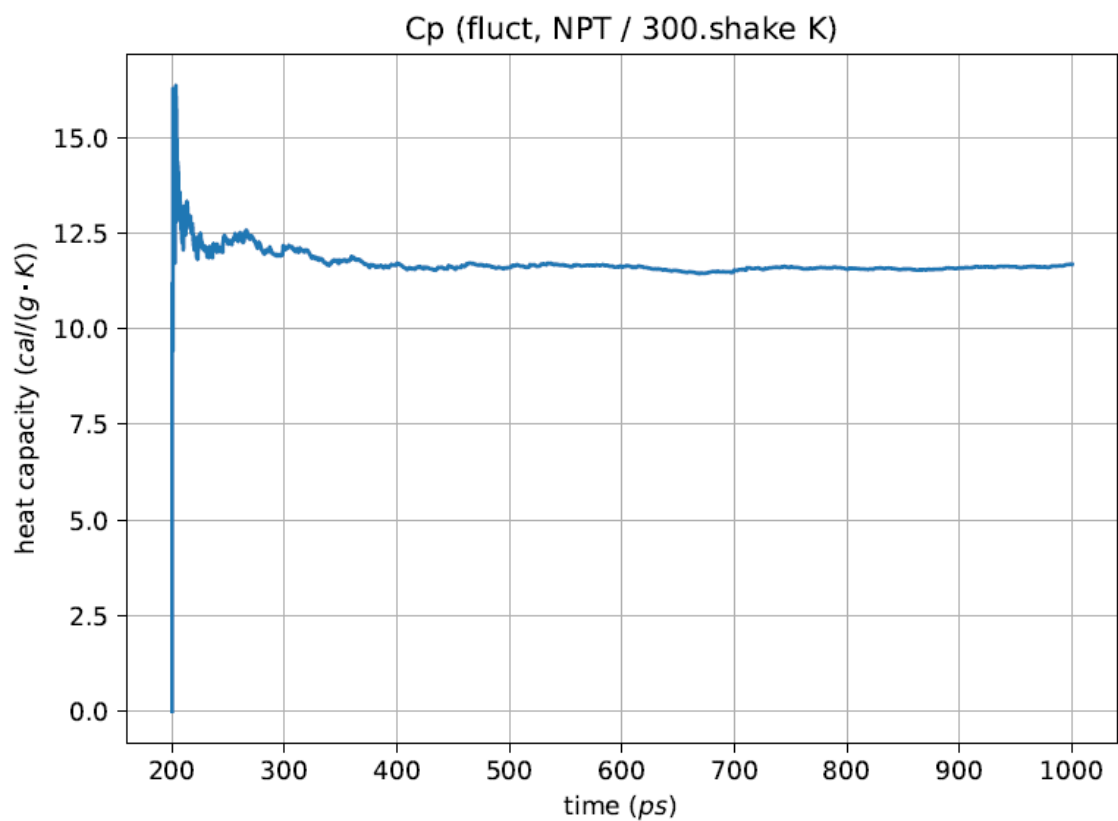


Image A.137:Cp at 300K for H<sub>2</sub>O **model4**

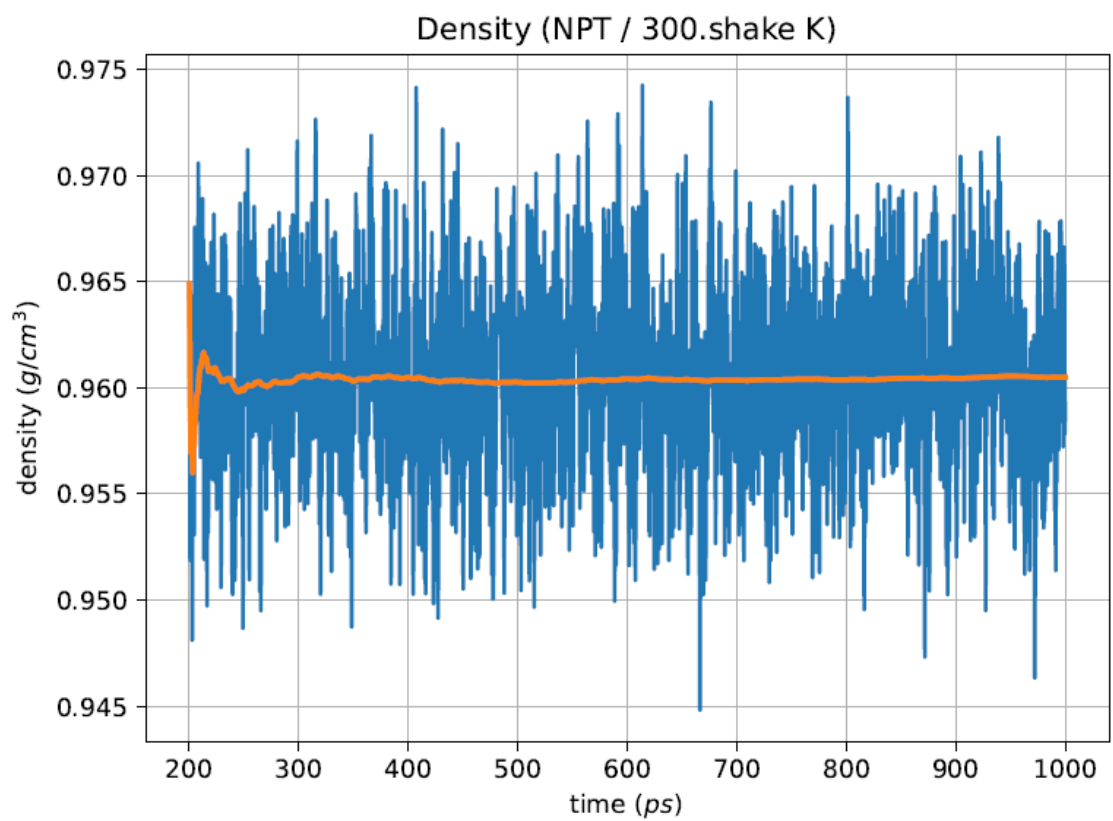


Image A.138:NPT Density at 300K for H<sub>2</sub>O **model4**

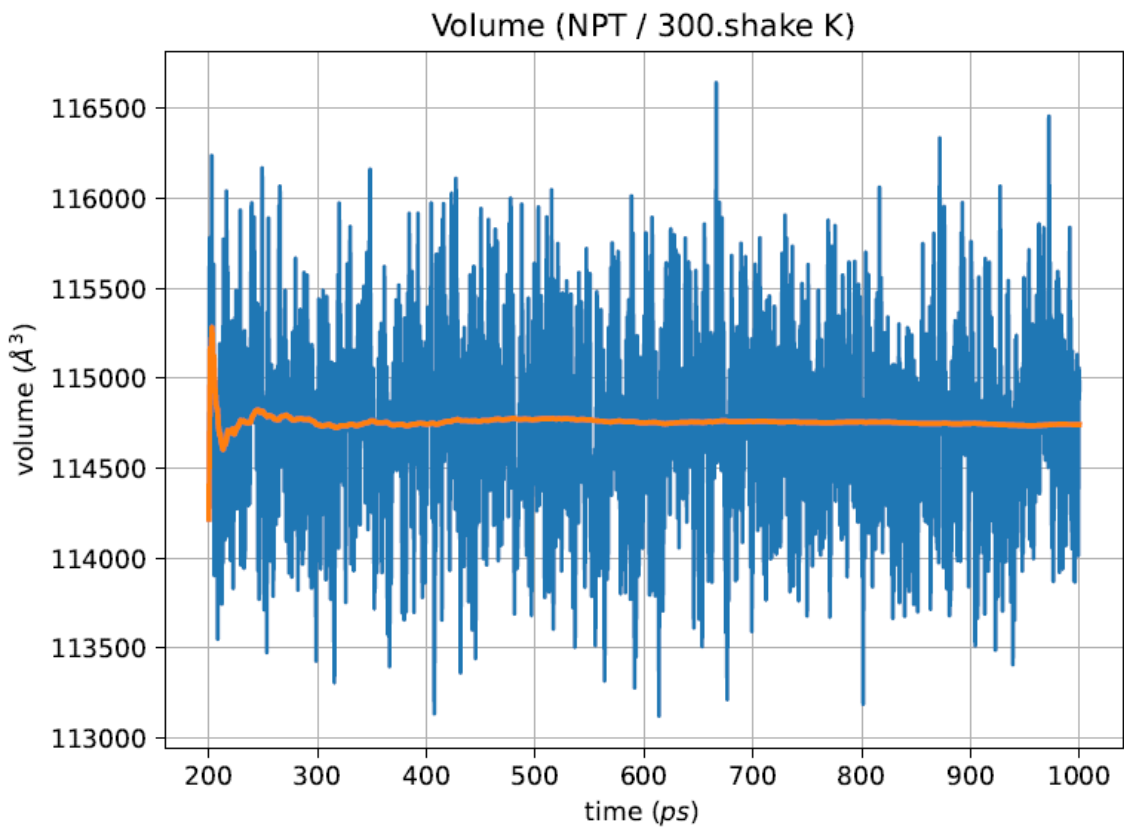


Image A.139:NPT Volume at 300K for H<sub>2</sub>O **model4**

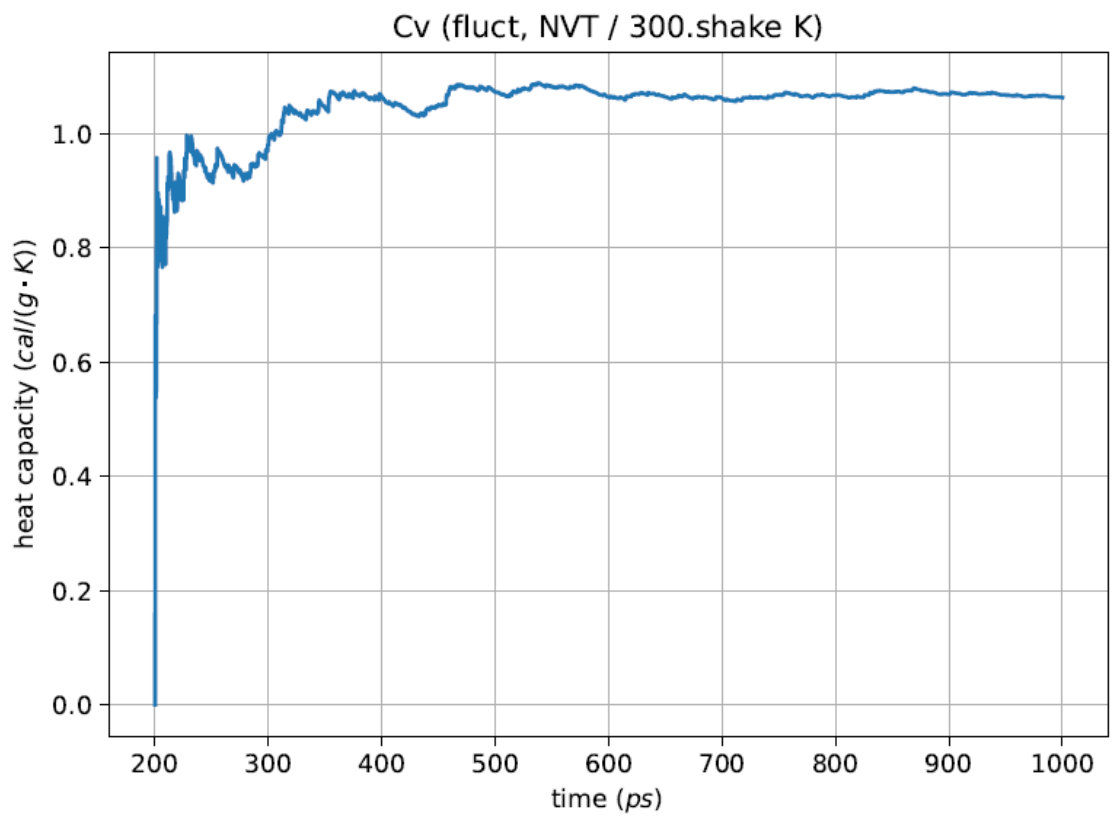


Image A.140:Cv at 300K for H<sub>2</sub>O **model4**