
Nosé-Hoover thermostat

Material for these lecture notes was compiled from the references below

- ✓ F. [Ercolessi, *A Molecular Dynamics Primer*](#)
- ✓ [MIT's 3.320](#) course notes
- ✓ M. Allen and D. Tildesley, [Computer Simulations of Liquids](#) (Oxford)
- ✓ D. Frenkel and B. Smit, [Understanding Molecular Simulations](#) (Academic) –
Also consult [case studies related to this textbook here](#)

Dynamics Lagrangian style

- Especially in ab initio MD, we use the concept of **extended Lagrangian** or **extended Hamiltonian**. We'll derive the equation of motion from an appropriate functional that includes sometimes exotic degrees of freedom.
- Up to now we have seen Newton's equation of motion. However, there is a more complex and elegant formalism to derive the equation of motion for a system. What you see below is what is called **Lagrangian dynamics**.

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_j} \right) - \frac{\partial L}{\partial q_j} = 0$$

where, $L = T - V$

- **First of all you have to construct your Lagrangian**, i.e. the functional that drives the evolution of your system. Here we just take the kinetic energy of the system, T , and subtract the potential energy of the system.

Dynamics Lagrangian style

- In general the potential energy is a function of position only. So if you have n particles, r_1 to r_n , it is usually written as

$$V(r_1, r_2, \dots, r_n)$$

- This is what is called a conservative field. The work that you are making going from one place to the other is just the integral of the force (which is the gradient of this potential) and it's independent of the trajectory.
- The kinetic energy tends to be a function of the square of the velocities.

$$T(\dot{r}_1, \dot{r}_2, \dots, \dot{r}_n)$$

- In the Lagrangian formulation, we usually don't use the notation for the positions $r_1 \dots r_n$ but instead we use the notation in which the coordinates are given by q_1, q_2, \dots, q_n and the velocities are indicated as $\dot{q}_1, \dot{q}_2, \dots, \dot{q}_n$. The reason we call them q is that we might want to use generalized coordinates.

Generalized coordinates

- Let us assume that we want to study **water molecules as rigid molecules**.
- You want to consider that the angle between the Hydrogen and the Oxygen does not change and that the distance between the Hydrogen and the Oxygen doesn't change. You want to develop dynamics in which what you really move around are not the position of the atoms but **the center of mass of the water molecules and you move around their orientation**. This is very important.
- Water at regular temperature is still a quantum system, is still a system that has most of its vibrational states frozen in their zero-point motion quantum state.
- Thus you actually tend to **describe better liquid water if you describe it as a set of rigid molecules moving around. This is a better approximation of the true dynamics of the system than an approximation in which you let also the internal degrees of freedom change**.

Lagrangian equations of motion

- So, suppose you want to simulate rigid water around, **you need to find out what are the equations of motion for this generalized set of coordinates in which what you move around when you move water is their center of mass and their orientation.**
- It is difficult to do that using Newton's equation of motion with constraints. What you do is use a Lagrangian formalism with generalized coordinates q and generalized velocity \dot{q} .
- What Lagrangian dynamics tells us is that we construct our Lagrangian function, $L=T - V$ and then the Lagrangian equations of motion are given as follows:

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_j} \right) - \frac{\partial L}{\partial q_j} = 0$$

- This focuses us on just constructing the scalar function L , i.e. T and V . Then it's straightforward to derive these equations.

Lagrangian equations of motion in 1D

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_j} \right) - \frac{\partial L}{\partial q_j} = 0$$

- Here is the derivation for the simple case of Newtonian dynamics in 1D for one particle of mass m :

$$T = \frac{1}{2} m v^2, \quad V = V(x)$$

- When you take the partial derivative of the Lagrangian with respect to the generalized velocity, since it's a partial derivative you only need to take the derivative of the kinetic energy with respect to the velocity, with respect to \dot{x} .
- Then you need to take the partial derivatives with respect to the position and there is no position in the KE, so there is only the position in the potential energy.

$$\frac{d}{dt} \left(\frac{\partial \left(\frac{1}{2} m \dot{x}^2 \right)}{\partial \dot{x}} \right) + \frac{\partial V}{\partial x} = 0 \quad \Rightarrow \quad \frac{d}{dt} (m \dot{x}) = - \frac{\partial V}{\partial x}$$

Lagrangian equations of motion in 1D

$$\frac{d}{dt}(m\dot{x}) = -\frac{\partial V}{\partial x} \longleftrightarrow F = ma$$

- On the right hand term, you have minus the gradient of your conservative potential field which is nothing else than the force. We have recovered $F = m a$, Newton's equation of motion.
- This is one way of deriving equations of motion that, again, are going to be 2nd order differential equations with respect to time because you are taking the derivative of a kinetic energy with respect to \dot{q} .

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_j} \right) - \frac{\partial L}{\partial q_j} = 0 \quad \text{2nd order ODEs}$$

Hamiltonian formulation

- There is a second formulation of classical mechanics that is called the Hamiltonian formulation. It's easy to see this if you think of the thermodynamic analogy.
- Suppose that you are in the microcanonical ensemble and your thermodynamical functional is the energy. When you look at that thermodynamical ensemble, you are looking at a system that has constant energy E , constant number of particles N and constant volume V .
- However, many times, it becomes appropriate to look at a system that lives at constant pressure or constant temperature. So you transform your thermodynamical functional from the energy to free energy. For example, you do $E - TS$ to obtain a thermodynamical functional that depends on temperature instead of depending on entropy.

$$F = E - TS$$

(for constant T)

$$H = E + pV$$

(for constant p)

Legendre transformations

Legendre transformations, conjugate variables

- This is the concept of **Legendre transformations**. If you have a function that, say, for the Lagrangian was a functional of q and \dot{q} , you can construct a new one that doesn't depend, say, on \dot{q} but depends only on a new variable that we call the conjugate variable to \dot{q} .

So, pressure and volume, temperature and entropy, chemical potential and number of particles are all (work) conjugate variables.

- If you take the Lagrangian and you differentiate it with respect to \dot{q} (remember the Lagrangian is a function of \dot{q}), what you obtain is a conjugate variable that we call a **conjugate momentum**.

$$p_i = \frac{\partial L}{\partial \dot{q}_i}$$

Legendre transformations

$$H(q, p, t) = \sum_i \dot{q}_i p_i - L(q, \dot{q}, t)$$

- This is a typical Legendre transform (by the way the sign doesn't really matter): In this case you sum the product of the conjugate variable time your original variable \dot{q} , **you get a new function that doesn't depend on your original variable but depends only on its conjugate variable p.**
- That's how you remove the dependence, say, on V and you put in the dependence on P making the Legendre transformation $E+pV$ or that's how you move from S to T using free energy $F=E-TS$. This is very simple to do when you take the differential of H because of this relation $p_i = \frac{\partial L}{\partial \dot{q}_i}$ you remove all the dependence in \dot{q} and you put into your system a new dependence on p . Why do we do this?

Legendre transformations

$$H(q, p, t) = \sum_i \dot{q}_i p_i - L(q, \dot{q}, t)$$

- For this new function **H that is called the Hamiltonian**, we can find an alternative set of equations of motion.
- Remember, from the Lagrangian, we had obtained equations of motion, basically, for \dot{q} and q . **In the Hamiltonian formulation we obtain equations of motion for q and for p .**
- Instead of having a 2nd order differential equation from the Lagrangian formulation, now we have double set of differential equations that are only 1st order. Depending on your problem they can actually be easier to solve. They will of course lead to the same trajectories as in the Lagrangian formulation.

Hamiltonian equation of motion

- All this formalism, of Lagrangian and Hamiltonian, is just a very general way to construct functions, either the Lagrangian ($L=T - V$) or the Hamiltonian via the Legendre transform that gives us equation of motion in q and \dot{q} for the case of the Lagrangian and in q and p for the case of the Hamiltonian.
- If you work this for the case of Newtonian dynamics, you find out that your Hamiltonian is just the kinetic energy plus the potential energy.

$$H = T + V$$

- So you either construct a Lagrangian $L=T - V$ and you have the Lagrangian equation of motion or you construct your Hamiltonian $H=T + V$ and you have **the Hamiltonian equations of motion** which is written below:

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \quad - \quad \dot{p}_i = \frac{\partial H}{\partial q_i}$$

Why do we need this Hamiltonian formalism?

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \quad - \quad \dot{p}_i = \frac{\partial H}{\partial q_i}$$

$$H(q, p, t) = \sum_i \dot{q}_i p_i - L(q, \dot{q}, t)$$

- One of the reasons that we do this is that often we want to simulate the microscopic dynamics not in the microcanonical ensemble but in different thermodynamical ensembles, say, in which we control T or P or the number of particles N or the chemical potential μ . So we need to have some of this formalism to do this effectively.

Canonical simulation – constant T

- There are 3 different approaches in which you can do a canonical simulation, in which you can control the temperature in your system.
 - Stochastic approach
 - Constrained method
 - Extended system
- You could have a **Langevin dynamics**: a stochastic approach in which you randomly kick atoms in order to accelerate them or to slow them down, so that in analogy with a thermal bath, they, on average, have the right kinetic energy.
- You could do a dynamics in which every time you've got new positions, you renormalize those new positions by **renormalizing the velocity of the particle so that the sum of the kinetic energy is actually a constant**. A constraint method would, actually, keep, strictly speaking, the temperature of your system constant with your target value. That can be, actually, very effective to thermalize your system, to bring it very close to your equilibrium distribution.

Nosé HAMILTONIAN

- The velocity rescaling does have some counter effects. That is, if you actually look at what is going to be your equilibrium distribution in positions is really going to be a canonical distribution according to the Boltzmann canonical ensemble. But if you look at your distribution of velocity, it's only pseudocanonical.
- So often people use a most accurate approach by coupling your system to an additional dynamical variable, using an extended Lagrangian or an extended Hamiltonian.
- We've written our Lagrangian or Hamiltonian in terms of generalized coordinates. All of a sudden, you can **add one more generalized coordinate** (you add, if you want, a pseudoparticle in your system with its own kinetic and potential energies). **You can construct the kinetic and potential energy of this pseudoparticle so that this additional dynamical variable interacts with the other dynamical variables, basically exchanging temperature with them so that it brings the average temperature of the real classical particles to the equilibrium distribution.**

$$L_{NOSE} = \sum_i \frac{1}{2} m_i s^2 \dot{r}_i^2 - V + \frac{1}{2} Q \dot{s}^2 - \frac{(3N+1)}{\beta} \ln s$$

Nosé HAMILTONIAN

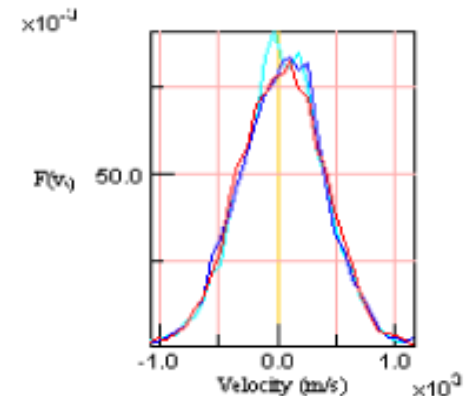
$$L_{NOSE} = \sum_i \frac{1}{2} m_i s^2 \dot{r}_i^2 - V + \frac{1}{2} Q \dot{s}^2 - \frac{(3N+1)}{\beta} \ln s$$

- This is actually how you would write the **extended Lagrangian for the case of a canonical simulation (in which we want to keep the temperature constant)**.
- That's where the power of this generalized system comes to play. You write your kinetic energy and note that there is this \dot{s}^2 and that couples the kinetic energy of your real particles with **the kinetic energy of this new thermostat**, as we call it. So, we have kinetic energy minus potential energy.
- This new particle is described by a generalized position s and a generalized velocity \dot{s} . Its kinetic energy is written in a trivial way, one half our **generalized mass** Q times the square velocity \dot{s} .
- $\frac{(3N+1)}{\beta} \ln s$ is how Nosé figured out the potential energy should look like for a system of N classical particles that you want to keep at an inverse temperature $\beta = 1/\kappa T$.

Nosé HAMILTONIAN

$$L_{NOSE} = \sum_i \frac{1}{2} m_i s^2 \dot{r}_i^2 - V + \frac{1}{2} Q \dot{s}^2 - \frac{(3N+1)}{\beta} \ln s$$

- If you use this Lagrangian L_{NOSE} , you can construct the Lagrangian equations of motion, so you'll have equation of motion for your N particles that will be very similar to your standard equation of motion but we'll have in there also terms that contain s . Then you will have an equation of motion for your Nosé-Hoover variable that is an equation of motion for s .
- If you let all this system evolve, the kinetic energies of your classical particles will start to distribute themselves according to a Maxwell-Boltzmann distribution that is according to the canonical ensemble.
- If you take an average from your MD simulation, you see that both the position and the velocity of your classical particles are distributed in the appropriate way.



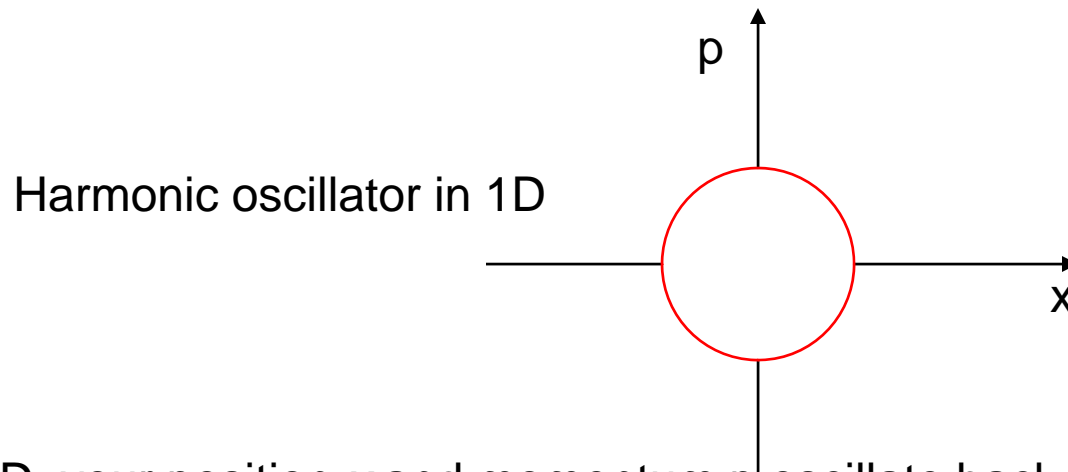
Nosé HAMILTONIAN

$$L_{NOSE} = \sum_i \frac{1}{2} m_i s^2 \dot{r}_i^2 - V + \frac{1}{2} Q \dot{s}^2 - \frac{(3N+1)}{\beta} \ln s$$

- If you want e.g. to calculate the diffusion coefficient from the velocity-velocity autocorrelation function, you need to **have the velocity distributed according to the appropriate thermodynamical ensemble**. Nosé-Hoover is probably the most common way of accurately doing the dynamics and thermostating our problem.
- However, Nosé-Hoover is not the most robust.
 - ❑ This approach gives you the long time thermodynamical properties correctly **but it tends to perform poorly for a system that is very harmonic** (the potential energy of each particle is a quadratic function of the displacement from its equilibrium position).

Nosé-Hoover thermostat and harmonic oscillators

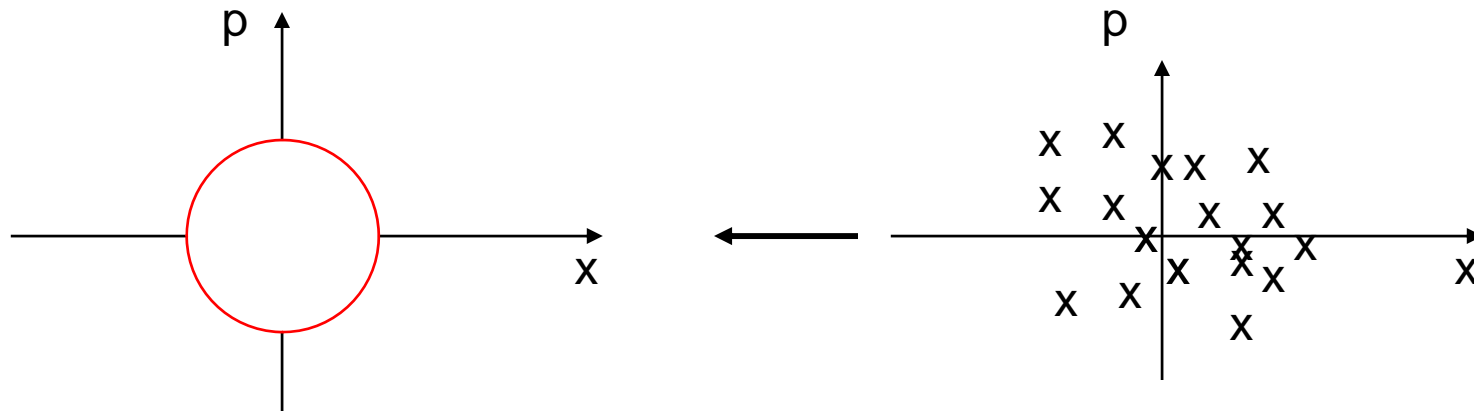
- A system is harmonic when its potential energy is a quadratic function of its coordinate. For example, a single particle in a parabolic well (harmonic oscillator) or a solid at very low temperature is also very harmonic.
- The trajectories in a harmonic oscillator look something like this.



- If 1D, your position x and momentum p oscillate back and forth. x and p will be in phase, e.g. when x is maximal, your momentum is minimum and so on.
- If we are studying a solid at very low temperature, the Nosé-Hoover thermostat would give us something that is very different from the equilibrium distribution.

Nosé-Hoover thermostat and harmonic oscillators

- In the equilibrium canonical distribution of a solid, the momenta and velocity of the particles are distributed. Each atom (i.e. each harmonic oscillator) is going to be talking with its neighbors and so atoms are not going to be all perpetually in phase but they are going to exchange energy between each other. **So a harmonic solid at slightly different from zero temperature, will have a distribution velocity and momentum that doesn't sit in a perfect circle but is distributed around.**



- If you do this with a Nosé-Hoover thermostat, sadly, there will be no exchange of energy i.e. there will be no thermalization between all different atoms. **They are going to be doing perpetually the wrong thing in synchrony.**

Nosé-Hoover thermostat and harmonic oscillators

- Thus the more harmonic your system is, the poorer the equilibration that comes from the Nosé thermostat is.
- For systems at low temperature, one of the usual solutions is using **Nosé-Hoover chains** in which you, actually, have your dynamical system, you have your thermostat and then you have another thermostat that is thermostating your thermostat that thermostats your particles and then you have a 3rd thermostat that thermostats the 2nd thermostat and...
- Harmonic solids are very important because, **in order to calculate the free energy of a system at finite temperature, also you need to do an integration from 0 temperature to the present temperature. So you need to start from a harmonic solid that you need to describe correctly.** So if you don't use the proper thermostatic techniques, this is not going to work out.

A final note

- You really need to be careful because the temperature is a global quantity.
- If you have a system with a 100 particles, you can have a temperature of 300 K by having all particles distributed along the same temperature **but you can also have the same temperature if part of your system is very cold and part of your system is very hot.**
- **The thermostat needs to make sure that the energy flow goes around, i.e. that all parts of your system are really at equilibrium.** This is a difficult thing to achieve than it actually seems.