

Brief introduction to the thermostats

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1 Motivation for Thermostats

When people do the molecular dynamics(MD) in the canonical ensemble(NVT), a thermostat is introduced to modulate the temperature of a system in some fashion. A variety of thermostat methods are available to add and remove energy from the boundaries of an MD system in a realistic way, approximating the canonical ensemble. Popular techniques to control temperature include the Anderson thermostat, Berendsen thermostat, Nosé-Hoover thermostat, and Langevin (stochastic) thermostat.

What is the goal of a thermostat? Actually, it turns out that the goal is not to keep the temperature constant, as that would mean fixing the total kinetic energy, which would be silly and not the aim of NVT or NPT . Rather, it is to ensure that the average temperature of a system be the desired one.

2 Anderson Thermostat: Stochastic Collision Method

For the canonical ensemble(NVT), the number of particles(N), volume(V) and temperature(T) are constant, and the energy of the simulated system will fluctuate. To simulate the NVT system, Anderson couple the system to a heat bath that imposes the desired temperature. The coupling to a heat bath is represented by stochastic collision that act occasionally on randomly selected particles.

Precisely in Anderson's method, the equations of motion of the N particles in volume V are the Hamiltonian equations with $H = \sum \mathbf{p}_i^2/2m_i + \phi(\mathbf{q})$

$$\frac{d\mathbf{q}_i}{dt} = \frac{\partial H}{\partial \mathbf{p}_i}, \quad \frac{d\mathbf{p}_i}{dt} = -\frac{\partial H}{\partial \mathbf{q}_i} \quad (1)$$

supplemented by a stochastic collision term in the equation for $d\mathbf{p}_i/dt$. Each stochastic collision is an instantaneous event that affects the momentum of one particle. Between stochastic collisions, the state of the system evolves in accordance with (1).

To perform the simulation we introduce two parameters: T and ν . T is the desired temperature of the system. And ν is the frequency of stochastic collisions which determine the strength of the coupling to the heat bath. If successive collisions are uncorrelated, then the distribution of time intervals between two successive stochastic collisions, $P(t; \nu)$, is of Poisson form

$$P(t; \nu) = \nu e^{-\nu t}$$

where $P(t; \nu)dt$ is the probability that the next collision will take place in the interval $[t, t + \Delta t]$.

A constant-temperature simulation is now as the follows. We pick an initial set of positions and momenta $\mathbf{q}^N(0)$ and $\mathbf{P}^N(0)$, and integrate the Hamiltonian equations of motion (1) until the time of the first stochastic collision. Suppose the particle suffering the collision is i . The value of the momentum of

particle i after collision is chosen at random from a Boltzmann distribution at temperature T . The change in momentum takes place instantaneously. All other particles are unaffected by this collision. Then the Hamiltonian equations for the entire collection of particles are integrated until the time of the next stochastic collision. This process is then repeated.

The result of Anderson's constant-temperature MD procedure is a trajectory $(\mathbf{q}^N(t), \mathbf{p}^N(t))$ for N particles in a volume V with periodic boundary conditions. This trajectory can be used to calculate time averages of any quantity $F(\mathbf{q}^N(t), \mathbf{p}^N(t); V)$ according to

$$\bar{F} = \lim_{T \rightarrow \infty} \int_0^T F(\mathbf{q}^N(t), \mathbf{p}^N(t); V(t)) dt$$

The combination of Newtonian dynamics and stochastic collisions turns the MD simulation into a Markov process. Anderson shows that a canonical distribution in phase space is invariant under repeated application of the Anderson's algorithm. Combined with the fact that the Markov chain is also irreducible and aperiodic, this implies that the Anderson's algorithm does generate a canonical distribution. In other words, the time average of any F calculate from a Anderson trajectory is equal to the ensemble average of F for the canonical ensemble in which the temperature is T , i.e. ,

$$\bar{F} = \frac{1}{N!Q(N, V, T)} \int F(\mathbf{q}^N, \mathbf{p}^N; V) e^{-\beta H(\mathbf{q}^N, \mathbf{p}^N; V)} d\mathbf{q}^N d\mathbf{p}^N$$

where

$$Q(N, V, T) = \frac{1}{N!} \int e^{-\beta H(\mathbf{q}^N, \mathbf{p}^N; V)} d\mathbf{q}^N d\mathbf{p}^N$$

is the partition function for canonical ensemble.

A disadvantage of Anderson thermostat is that since the algorithm randomly decorrelates velocities, and messes up dynamics, the dynamics actually is not physical. So if we plan to measure the dynamical properties, Anderson thermostat might not be a good method.

3 Nosé-Hoover Thermostat: Extended System Method

3.1 Extended equations of motion

Since the energy of a system of N particles fluctuates at constant temperature, we need some mechanism for introducing the energy fluctuations in order to simulate such a system. Instead of using stochastic collisions on the simulated system, Nosé invent an extended Lagrangian; that is, a Lagrangian containing additional, artificial coordinates and velocities. Actually this extended-Lagrangian method was first introduced by Anderson in the constant-pressure MD simulations. Currently extended-Lagrangian methods are not only for simulations in

ensembles other than constant NVE , but also as a stable and efficient approach to perform simulation in which an expensive optimization has to be carried out at each time step. Since it is now more common to use the Nosé scheme in the formulation of Hoover, MD people usually call the extended-Lagrangian approach Nosé-Hoover Thermostat.

Assume the simulated system is of N particles, with coordinates \mathbf{q}'_i , masses m_i , potential energy $\phi(\mathbf{q}')$, and momenta \mathbf{p}'_i . An additional degree of freedom s is introduced acting as an external system on the simulated system. We also introduce **virtual** variables (coordinates \mathbf{q}_i , momenta \mathbf{p}_i , and time t) which are related to the **real** variable ($\mathbf{q}', \mathbf{p}', t'$) as follows

$$\mathbf{q}'_i = \mathbf{q}_i, \quad \mathbf{p}'_i = \mathbf{p}_i/s, \quad t' = \int_0^t \frac{dt}{s}$$

Then the real velocity is expressed by

$$\frac{d\mathbf{q}'_i}{dt'} = s \frac{d\mathbf{q}'_i}{dt} = s \frac{d\mathbf{q}_i}{dt}$$

Here we can think of the above transformations as time scaling by $dt' = dt/s$. Actually, when Anderson do the constant-pressure MD simulation he use the similar idea.

The Lagrangian of the extended system of the N particles and variable s in terms of the virtual variables is

$$L_{\text{Nosé}} = \sum_{i=1}^N \frac{m_i}{2} s^2 \dot{\mathbf{q}}_i^2 - \phi(\mathbf{q}) + \frac{Q}{2} \dot{s}^2 - gkT \ln s \quad (2)$$

where Q is an **effective mass** associated to s , the parameter g is essentially equal to the number of degrees of freedom of the system. However its exact value will be chosen to satisfy the canonical distribution at equilibrium. And a logarithmic dependence of the potential on the variable s is essential for producing the canonical ensemble. The momenta conjugate to \mathbf{q}_i and s are:

$$\mathbf{p}_i = \frac{\partial L_{\text{Nosé}}}{\partial \dot{\mathbf{q}}_i} = m_i s^2 \dot{\mathbf{q}}_i, \quad p_s = \frac{\partial L_{\text{Nosé}}}{\partial \dot{s}} = Q \dot{s}.$$

This gives the Hamiltonian of the extended system of the N particles and variable s in terms of the virtual variables

$$H_{\text{Nosé}} = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i s^2} + \phi(\mathbf{q}) + \frac{p_s^2}{2Q} + gkT \ln s \quad (3)$$

According to the Hamiltonian formalism, We define the equations of motion

by using the extended Hamiltonian,

$$\frac{d\mathbf{q}_i}{dt} = \frac{\partial H_{\text{Nose}}}{\partial \mathbf{p}_i} = \frac{\mathbf{p}_i}{m_i s^2} \quad (4)$$

$$\frac{d\mathbf{p}_i}{dt} = -\frac{\partial H_{\text{Nose}}}{\partial \mathbf{q}_i} = -\frac{\partial \phi}{\partial \mathbf{q}_i} \quad (5)$$

$$\frac{ds}{dt} = \frac{\partial H_{\text{Nose}}}{\partial p_s} = \frac{p_s}{Q} \quad (6)$$

$$\frac{dp_s}{dt} = -\frac{\partial H_{\text{Nose}}}{\partial s} = \frac{\sum \frac{\mathbf{p}_i^2}{m_i s^2} - gkT}{s} \quad (7)$$

It is obvious that the extended Hamiltonian H_{Nose} is conserved when the extended system evolves by the above equations of motion. Therefore this method produces microcanonical ensemble for the extended system.

3.2 Preserving canonical ensemble

The most important thing of extended Hamiltonian is that we can project the partition function of the extended system onto the original system, and the projection will recover the canonical ensemble. Indeed, the partition function for the extended system is

$$Z = \int \delta \left[H_0 \left(\frac{\mathbf{p}}{s}, \mathbf{q} \right) + \frac{p_s^2}{2Q} + gkT \ln s - E \right] dp_s ds d\mathbf{p} d\mathbf{q} \quad (8)$$

where

$$H_0(\mathbf{p}, \mathbf{q}) = \sum_i \frac{\mathbf{p}_i^2}{2m_i} + \phi(\mathbf{q})$$

is the classic Hamiltonian, and E is the energy prescribed in advance. By change of variables, we can transform the virtual momenta \mathbf{p}_i and coordinates \mathbf{q}_i to the real variables $\mathbf{p}'_i = \mathbf{p}_i/s$, $\mathbf{q}'_i = \mathbf{q}_i$. Then

$$\begin{aligned} Z &= \int s^{3N} \delta \left[H_0(\mathbf{p}', \mathbf{q}') + \frac{p_s^2}{2Q} + gkT \ln s - E \right] ds dp_s d\mathbf{p}' d\mathbf{q}' \\ &= \int \frac{s^{3N+1}}{gkT} \delta \left[s - \exp \left(-\frac{H_0(\mathbf{p}', \mathbf{q}') + p_s^2/2Q - E}{gkT} \right) \right] ds dp_s d\mathbf{p}' d\mathbf{q}' \\ &= \frac{1}{gkT} \int \exp \left(-\frac{3N+1}{gkT} \left[H_0(\mathbf{p}', \mathbf{q}') + p_s^2/2Q - E \right] \right) dp_s d\mathbf{p}' d\mathbf{q}' \\ &= \frac{1}{gkT} \exp \left(\frac{3N+1}{g} \frac{E}{kT} \right) \int \exp \left(-\frac{3N+1}{g} \frac{p_s^2}{2QkT} \right) dp_s \int \exp \left(-\frac{3N+1}{g} \frac{H_0(\mathbf{p}', \mathbf{q}')}{kT} \right) d\mathbf{p}' d\mathbf{q}'. \end{aligned}$$

If we choose $g = 3N + 1$, the partition function of the extended system is equivalent to that of the original system in the canonical ensemble except for a constant factor:

$$Z = C \int e^{-\beta H_0(\mathbf{p}', \mathbf{q}')} d\mathbf{p}' d\mathbf{q}',$$

where $1/\beta = kT$. Then the equilibrium distribution function is

$$\rho(\mathbf{p}', \mathbf{q}') = e^{-\beta H_0(\mathbf{p}', \mathbf{q}')}.$$

Finally with the ergodic hypothesis, we have

$$\bar{F} = \left\langle A\left(\frac{\mathbf{P}}{s}, \mathbf{q}\right) \right\rangle_{\text{extended}} = \left\langle A(\mathbf{p}', \mathbf{q}') \right\rangle_{\text{canonical}}$$

3.3 Nosé-Hoover Thermostat with additional constraints (April 4th)

3.3.1 Equivalent to Gaussian thermostat

Let us consider the extended Hamiltonian (3)

$$H_{\text{Nose}} = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i s^2} + \phi(\mathbf{q}) + \frac{p_s^2}{2Q} + gkT \ln s$$

with condition

$$\frac{\partial H_{\text{Nose}}}{\partial s} = -\frac{1}{s} \left[\sum \frac{\mathbf{p}_i^2}{m_i s^2} - gkT \right] = 0 \quad (9)$$

and

$$\frac{\partial H_{\text{Nose}}}{\partial p_s} = \frac{p_s}{Q} = 0 \quad (10)$$

The constraint (10) is trivial since we can directly ignore the $p_s^2/2Q$ term in the extended Hamiltonian. And the equations of motion for the virtual variable \mathbf{q}_i and \mathbf{p}_i are still:

$$\frac{d\mathbf{q}_i}{dt} = \frac{\partial H_{\text{Nose}}}{\partial \mathbf{p}_i} = \frac{\mathbf{p}_i}{m_i s^2} \quad (11)$$

$$\frac{d\mathbf{p}_i}{dt} = -\frac{\partial H_{\text{Nose}}}{\partial \mathbf{q}_i} = -\frac{\partial \phi}{\partial \mathbf{q}_i} \quad (12)$$

Now we map the virtual equations of motion back to the real equations of motion:

$$\frac{d\mathbf{q}'_i}{dt'} = s \frac{d\mathbf{q}_i}{dt} = \frac{\mathbf{p}_i}{m_i s} = \frac{\mathbf{p}'_i}{m_i} \quad (13)$$

$$\frac{d\mathbf{p}'_i}{dt'} = s \frac{d(\mathbf{p}_i/s)}{dt} = -\frac{\partial \phi}{\partial \mathbf{q}'_i} - \frac{ds}{dt} \mathbf{p}'_i \quad (14)$$

Note that if we differentiate both sides of (9), we have

$$\sum \frac{\mathbf{p}_i}{m_i} \frac{d\mathbf{p}_i}{dt} = gkT s \frac{ds}{dt} \Rightarrow \frac{ds}{dt} = -\frac{1}{gkT} \sum \frac{\partial \phi}{\partial \mathbf{q}'_i} \frac{\mathbf{p}'_i}{m_i} = -\frac{1}{gkT} \frac{d\phi}{dt'}$$

If we set $\alpha = ds/dt$, then the real motion of equation

$$\frac{d\mathbf{q}'_i}{dt'} = \frac{\mathbf{p}'_i}{m_i}, \quad \frac{d\mathbf{p}'_i}{dt'} = -\frac{\partial\phi}{\partial\mathbf{q}'_i} - \alpha\mathbf{p}'_i$$

is actually identical to the Gaussian thermostat which will be introduced in section 4.

3.3.2 More constraints

3.4 More on Nosé-Hoover Thermostat (April 4th)

Since the extended system method has more independent variables than the equivalent statistical mechanical ensemble. This is why the extended system method gives correct result for the static quantities, but the time evolution of s are really dependent on the adjustable parameter Q , which is, in some sense, the coupling frequency to the extended system. A frequency with too little overlap with natural frequencies in the original system can lead to very long energy transfer time.

4 Gaussian thermostat: velocity-rescaling (April 4th)

Velocity-rescaling method is actually the first method([14]) proposed to keep the temperature a fixed value during a simulation without allowing fluctuations of T . In this method, the velocities are scaled according to

$$\mathbf{p}_i \rightarrow \sqrt{\frac{T_0}{T}}\mathbf{p}_i$$

where T_0 is the desired temperature, and T the actual temperature calculated from the velocity of the particles.

However, a drawback for the velocity-rescaling is that this method leads to discontinuities in the momentum part of the phase space trajectory due to the rescaling procedure at each time step.

An extension of velocity-rescaling method implies a constraint of the equations of motion (1) to keep the temperature fixed([4],[6],[11]). [Gaussian principle of least constraint](#) states that a force added to restrict a particle motion on a constraint hypersurface should be normal to the surface in a realistic dynamics. From this principle an constraint force term $-\alpha\mathbf{p}_i$ is added to the force term of (1),

$$\frac{d\mathbf{q}_i}{dt} = \frac{\mathbf{p}_i}{m_i}, \tag{15}$$

$$\frac{d\mathbf{p}_i}{dt} = -\frac{\partial\phi(\mathbf{q})}{\partial\mathbf{q}_i} - \alpha\mathbf{p}_i \tag{16}$$

Consequently, the equations are no longer in a canonical form. The parameter α is determined from the requirement that the temperature or the total kinetic energy is constant,

$$\sum \frac{\mathbf{p}_i^2}{2m_i} = \frac{gkT}{2}$$

or

$$\sum \frac{\mathbf{p}_i}{m_i} \frac{d\mathbf{p}_i}{dt} = 0.$$

Thus we obtain

$$\alpha = - \sum \frac{\mathbf{p}_i}{m_i} \frac{\partial \phi}{\partial \mathbf{q}_i} \bigg/ \sum \frac{\mathbf{p}_i^2}{m_i}$$

This method can recover the canonical distribution in coordinate space if we set $g = 3N - 1$ where N is the number of particles. Since Gaussian principle of least constraint is used, this extended velocity-rescaling method is also called [Gaussian thermostat](#).

One important remark is that Gaussian thermostat can actually derived from Nosé-Hoover's extended system method(NH thermostat) by imposing a particular constraint. In other words, Gaussian thermostat is just a special Nosé-Hoover thermostat.

5 Berendsen Thermostat([April 4th](#))

5.1 Motivations for Berendsen thermostat

Notice that one main problem of velocity-rescaling method is that it does NOT allow temperature fluctuations which are present in the canonical ensemble. To overcome this problem, Berendsen introduce([2]) a weak coupling method to an external bath which now is called Berendsen thermostat.

Berendsen thermostat, also called proportional thermostat, is trying to correct the deviations of the actual temperature T from the prescribed one T_0 by multiplying the velocities by a certain factor λ in order to move the system dynamics towards the one corresponding to T_0 . One advantage of Berendsen thermostat is that it allows the temperature fluctuations, thereby not fixing it to a constant value.

The motivation for the Berendsen thermostat is the minimization of local disturbances of a stochastic thermostat while keeping the global effects unchanged.

5.2 Berendsen thermostat: proportional time-rescaling

In Berendsen's method, the velocities are scaled at each time step, such that the rate of change of temperature is proportional to the difference in temperature:

$$\frac{dT}{dt} = \frac{1}{\tau}(T_0 - T) \tag{17}$$

where τ is the coupling parameter, analog of ν in Anderson thermostat, determining how tightly the bath and the system are coupled together. It turns out that Berendsen's method create an exponential decay of the system towards the desired temperature:

$$T = T_0 - Ce^{-t/\tau} \quad (18)$$

Note that from (17) we have

$$\Delta T = \frac{\Delta t}{\tau}(T_0 - T) \quad (19)$$

Thus this lead to a modification of the momenta $\mathbf{p}_i \rightarrow \lambda \mathbf{p}_i$ where λ is the scaling factor:

$$\lambda^2 = 1 + \frac{\Delta t}{\tau_T} \left(\frac{T_0}{T} - 1 \right) \quad (20)$$

where τ_T is coupling time constant which determines the time scale on which the desired temperature is reached.

5.3 Interpolation between the canonical and microcanonical ensemble

A drawback of Berendsen thermostat is that it cannot be mapped onto a specific thermodynamic ensemble. Actually, Morishita([9]) shows that the phase space distribution is

$$\rho(\mathbf{q}, \mathbf{p}) = f(\mathbf{p}) \exp \left(-\beta \left[\phi(\mathbf{q}) - \alpha \beta \frac{|\Delta \phi|^2}{3N} \right] \right) \quad (21)$$

where $\alpha \simeq (1 - \Delta E / \Delta \phi)$ and $\Delta E, \Delta \phi$ are the mean fluctuations of the potential and total energy. $f(\mathbf{p})$ is in general an unknown function of the momenta, so that the full density cannot be determined.

For $\alpha = 0$ which corresponds to $\Delta t = \tau_T$ in (20), the fluctuations in the kinetic energy vanish and the phase space distribution reduces to the canonical energy:

$$\rho(\mathbf{q}, \mathbf{p}) = \delta(T - T_0) \exp(-\beta \phi(\mathbf{q})). \quad (22)$$

On the other hand, if $\tau_T \rightarrow \infty$, it corresponds to an isolated system and the energy should be conserved, which means

$$\Delta E = \Delta K + \Delta \phi = 0, \quad \alpha = 1.$$

In this case, the phase space distribution reduces to the microcanonical distribution. Therefore (19) can be viewed as an interpolation between the canonical and microcanonical ensemble.

6 Langevin Thermostat (April 4th)

6.1 Motivation for Langevin thermostat

When we consider the motion of large particles through a continuum of smaller particles, Langevin equation

$$\ddot{x} = \nabla\phi - \gamma\dot{x} + \sigma\xi$$

or

$$\frac{d\mathbf{q}_i}{dt} = \frac{\mathbf{p}_i}{m_i}, \quad \frac{d\mathbf{p}_i}{dt} = -\frac{\partial\phi(\mathbf{q})}{\partial\mathbf{q}_i} - \gamma\mathbf{p}_i + \sigma\xi_i \quad (23)$$

is taken into account. The smaller particles create a damping force to the momenta, $-\gamma\mathbf{p}_i$, as the large particles push the smaller ones out of the way. The smaller (thermal) particles also move with kinetic energy and give random kicks to the large particles. σ, γ are connected by a fluctuation-dissipation relation

$$\sigma^2 = 2\gamma m_i kT$$

in order to recover the canonical ensemble distribution.

Langevin equation can be used for molecular dynamics equations by assuming that the atoms being simulated are embedded in a sea of much smaller fictional particles. In many instances of solute-solvent systems, the behavior of the solute is desired, and the behavior of the solvent is non-interesting (e.g. proteins, DNA, nanoparticles in solution). In these cases, the solvent influences the dynamics of the solute (typically nanoparticles) via random collisions, and by imposing a frictional drag force on the motion of the nanoparticle in the solvent. And Langevin equation of motion is the way we incorporate these two effects.

6.2 Key idea for Langevin thermostat

At each time step Δt the Langevin thermostat changes the equation of motion so that the change in momenta is

$$\Delta\mathbf{p}_i = \left(\frac{\partial\phi(\mathbf{q})}{\partial\mathbf{q}_i} - \gamma\mathbf{p}_i + \delta p \right) \Delta t$$

where $\gamma\mathbf{p}_i$ damp the momenta and δp is a Gaussian distributed random number with probability

$$\rho(\delta p) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{|\delta p|^2}{2\sigma^2}\right).$$

And standard deviation $\sigma^2 = 2\gamma m_i kT$. The random fluctuating force represents the thermal kicks from the small particles. The damping factor and the random force combine to give the correct canonical ensemble.

6.3 Advantages and disadvantages for Langevin thermostat

Typical advantage for Langevin thermostat is that we need fewer computations per time step since we eliminate many atoms and include them implicitly by stochastic terms. Besides, we can choose a relatively large time step Δt , 2-3 times larger than in MD due to dissipative term, because damping term stabilizes the equations of motion. Furthermore, since Langevin thermostat replace the fastest frequency motions in the real system by stochastic terms, Δt is now chosen to resolve the slower degrees of freedom, and thus Δt is several hundred times larger than in the original MD.

Drawbacks for Langevin thermostat are

- Excluded volume effects of solvent not included(**which I still do NOT understand**)
- Not trivial to implement drag force for non-spherical particles since the friction coefficient γ_i is related to the particle radius

$$\gamma_i = 6\pi\eta r_i/m_i$$

- for the solute-solvent system, solvent molecules must be small compared to the smallest molecules explicitly considered
- the dissipative force describes only the friction with the small particles; we can actually add the drag on neighboring large particles into the dissipative force, which is the dissipative particle dynamics(DPD) thermostat,

7 Dissipative particle dynamics thermostat(**April 13**)

7.1 Description of the technique

Dissipative particle dynamics(DPD) thermostat is typically used in the mesoscale simulations, for instance, the diblock copolymer model where we assume the mesoscopic particles, which are soft spheres, are connected by a spring.

For the DPD thermostat, we adds the pairwise random and dissipative forces to the force term of the Hamiltonian equations of motion:

$$\frac{d\mathbf{q}_i}{dt} = \frac{\mathbf{p}_i}{m_i}, \quad \frac{d\mathbf{p}_i}{dt} = \mathbf{f}_i(t) = \sum_{i \neq j} (F_{ij}^C + F_{ij}^D + F_{ij}^R) \quad (24)$$

where F^C represents the conservative forces, F^D represents the dissipative forces, and F^R represents the random forces.

More precisely, we define F^C, F^D, F^R as follows. The conservative forces is a sum of the harmonic springs and the soft repulsions:

$$F_{ij}^C = F_{ij}^{C_s} + F_{ij}^{C_r}$$

with

$$F_{ij}^{Cs} = -K(r_{ij} - r_0)\hat{\mathbf{r}}_{ij}, \quad F_{ij}^{Cr} = \begin{cases} a_{ij} \left(1 - \frac{r_{ij}}{r_c}\right) \hat{\mathbf{r}}_{ij}, & r_{ij} < r_c \\ 0 & r_{ij} \geq r_c \end{cases}$$

where r_c is a cut-off radius and

$$\hat{\mathbf{r}}_{ij} = \frac{\mathbf{r}_{ij}}{|\mathbf{r}_{ij}|}.$$

The dissipative(friction) forces are defined as

$$F_{ij}^D = -\gamma\omega^D(r_{ij})(\mathbf{v}_{ij} \cdot \hat{\mathbf{r}}_{ij})\hat{\mathbf{r}}_{ij},$$

where γ is the friction constant, ω^D is a cut-off function for the force as a function of the scalar distance between i and j which simply limits the interaction range of the dissipative forces:

$$\omega^D(r) = \begin{cases} \left(1 - \frac{r}{r_c}\right)^2, & r < r_c \\ 0. & r \geq r_c \end{cases}$$

$\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$ is the relative velocity of i to j . The random forces are defined as

$$F_{ij}^R = \sigma\omega^R(r_{ij})\zeta_{ij}\hat{\mathbf{r}}_{ij}$$

where σ is the strength of the random force which, similar as we discuss in section 6.1, is connected with the friction constant γ by the fluctuation-dissipation relation

$$\sigma^2 = 2\gamma kT,$$

and ω^R is cut-off function related to ω^D by

$$[\omega^R(r)]^2 = \omega^D(r),$$

and ζ_{ij} is a Gaussian random number with zero mean and unit variance with $\zeta_{ij} = \zeta_{ji}$.

7.2 Implementation of the method

A DPD simulation can be implemented in any working MD program. The only subtlety is in the integration of the equations of motion. As the forces between the particles depend on their relative velocities, the standard velocity-Verlet scheme cannot be used.

The update of velocities and position uses the new forces:

$$\begin{aligned} \mathbf{v}_i(t + \Delta t) &= \mathbf{v}_i(t) + \frac{\Delta t}{m}(F_i^C + f_i^D) + \frac{\sqrt{\Delta t}}{m}F_i^R, \\ \mathbf{r}_i(t + \Delta t) &= \mathbf{r}_i(t) + \Delta t\mathbf{v}_i(t + \Delta t). \end{aligned}$$

Note that since all forces are pair-interactions, Newton's 3rd law is obeyed! This is not the case in the Langevin thermostat. As a result, DPD thermostat looks more like MD.

One advantage of DPD over atomistic MD is that DPD involves a coarse-grained model. This makes the technique useful when studying the mesoscopic structure of complex liquids. However if we are only interested in static properties, we could use standard MC or MD on a model with the same conservative forces F^C , but without dissipation F^D . The real advantage of DPD shows up when we try to model the dynamics of complex liquids.

We can even compare the DPD thermostat with the Langevin thermostat. In the Langevin thermostat, the dissipative force describes only friction with the small particles, but in DPD thermostat, the friction generates a drag on neighboring DPD particles, mediated by the small particles. For the DPD thermostat, since all interactions are pair-interactions, the momentum is conserved which is not true for Langevin thermostat.

8 Anisotropic Willmore cont'(April 20)

I am still considering the regularized ODE system

$$\begin{aligned} & \dot{Q} + \frac{\cos t}{\sin t} Q + 2H(H^2 - K) - (2\mu H + p) \\ & + 2\eta \left\{ \frac{1}{\sin t} \left[\left(\frac{k_1(k_1 - k_2) + \epsilon/2}{\sqrt{|k_1 - k_2|^2 + \epsilon}} \right) \cdot \frac{x^2}{\sin t} \right] + \frac{1}{\sin t} \left[\frac{(k_1^2 - k_2^2) \cos \phi}{\sqrt{|k_1 - k_2|^2 + \epsilon}} \right] \right. \\ & \quad \left. + \left[(k_1^2 + k_2^2)((k_1 - k_2)^2 + \epsilon) - (k_1 + k_2)^2 \cdot \epsilon \right] \frac{1}{\sqrt{|k_1 - k_2|^2 + \epsilon}} \right\} \\ & + 4\eta^2 \left[\dot{Q} + \frac{\cos t}{\sin t} Q + 2H(H^2 - K) \right] = 0 \end{aligned}$$

with the boundary conditions

$$\begin{aligned} Q(0) = 0, \phi(0) = 0, x(0) = 0, y(0) = 0, V(0) = 0, \\ Q(\pi) = 0, \phi(\pi) = \pi, \quad V(\pi) = \text{Volume}. \end{aligned}$$

The difficulty here is to compute all the derivatives and represent all of them by Q, H, ϕ, x .

9 Gauss's principle of least constraint and thermostat (April 26)

9.1 Main question for the thermostats

Let us consider the continuous thermostats, for instance, Gaussian thermostat or Berendsen thermostat. Gaussian thermostat describes the following dynamics

for the system of N particles:

$$\frac{d\mathbf{q}_i}{dt} = \frac{\mathbf{p}_i}{m_i}, \quad (25)$$

$$\frac{d\mathbf{p}_i}{dt} = -\frac{\partial\phi(\mathbf{q})}{\partial\mathbf{q}_i} - \alpha\mathbf{p}_i \quad (26)$$

where

$$\alpha = -\frac{\sum \frac{\mathbf{p}_i}{m_i} \frac{\partial\phi}{\partial\mathbf{q}_i}}{\sum \frac{\mathbf{p}_i^2}{m_i}}.$$

And Berendsen thermostat gives the dynamics:

$$m_i \dot{v}_i = F_i + m_i \gamma \left(\frac{T_0}{T} - 1 \right) v_i \quad (27)$$

where F_i is the conservative force, or if we use the (\mathbf{q}, \mathbf{p}) language as Gaussian thermostat, then the Berendsen dynamics reads as:

$$\frac{d\mathbf{q}_i}{dt} = \frac{\mathbf{p}_i}{m_i}, \quad (28)$$

$$\frac{d\mathbf{p}_i}{dt} = -\frac{\partial\phi(\mathbf{q})}{\partial\mathbf{q}_i} - \gamma \left(\frac{T_0}{T} - 1 \right) \mathbf{p}_i \quad (29)$$

Now if we observe the Gaussian and Berendsen dynamics, they are just the Hamiltonian dynamics with extra terms

$$\alpha\mathbf{p}_i \quad \text{or} \quad \gamma \left(\frac{T_0}{T} - 1 \right) \mathbf{p}_i$$

So there is a natural question saying that if we can think of the Gaussian and Berendsen dynamics as minimization problems with constraints

$$\sum \frac{\mathbf{p}_i^2}{2m_i} = \frac{gkT}{2} \quad \text{or} \quad \frac{dT}{dt} = 2\gamma(T_0 - T)$$

since the classic Hamiltonian system can be derived from least action principle.

9.2 Least action principle with constraints

We can investigate the least action principle with constraints, and see if we can recover, for instance, the Gaussian dynamics,

$$\begin{aligned} \frac{d\mathbf{q}_i}{dt} &= \frac{\mathbf{p}_i}{m_i}, \\ \frac{d\mathbf{p}_i}{dt} &= -\frac{\partial\phi(\mathbf{q})}{\partial\mathbf{q}_i} - \alpha\mathbf{p}_i. \end{aligned}$$

Let us consider the minimization problem

$$\min \int_0^T \sum \frac{m_i}{2} \left(\frac{d\mathbf{q}_i}{dt} \right)^2 - U(\mathbf{q}) dt$$

s.t.

$$\sum \frac{m_i}{2} \left(\frac{d\mathbf{q}_i}{dt} \right)^2 = \frac{gkT}{2}$$

If we apply the Lagrange multiplier method as usual, the equilibrium system will be

$$(1 - \lambda) \frac{d\mathbf{p}_i}{dt} = - \frac{\partial \phi(\mathbf{q})}{\partial \mathbf{q}_i}$$

This equilibrium system is not the Gaussian dynamics since the extra force in Gaussian dynamics is proportional to the velocity rather than the acceleration.

Hence the argument of least action principle with constraints can not be used to recover the Gaussian or Berendsen dynamics.

9.3 Gauss's principle of least constraint

Gauss formulated a mechanics over 170 years ago which is more general than Newton's. Gauss's formulation applies to systems which are subject to constraints, either holonomic (coordinate-dependent only) or nonholonomic (coordinate and velocity dependent). Gauss's principle stated that the trajectories actually followed would deviate as little as possible, in a least squares sense, from the unconstrained Newtonian trajectories.

Mathematically, Gauss's principle of least constraint state that the true motion of a mechanical system of N masses is the minimum of the quantity

$$\sum_{i=1}^N \frac{1}{m_i} \left| \frac{d\mathbf{p}_i}{dt} - F_i \right|^2$$

for all trajectories satisfying any imposed constraints. For our case, it turns out to be a minimization problem

$$\min \sum_{i=1}^N \frac{1}{m_i} \left| \frac{d\mathbf{p}_i}{dt} + \frac{\partial \phi}{\partial \mathbf{q}_i} \right|^2 \quad (30)$$

This is a statement of Gauss's principle of least constraint that I find in [2],[5],[8], however the minimization problem (30), in my understanding, does not make sense since the minimized quantity is a function of time t rather than a constant.

If we modify the minimization problem as

$$\min \int_0^T \sum_{i=1}^N \frac{1}{m_i} \left| \frac{d^2 \mathbf{q}_i}{dt^2} + \frac{\partial \phi}{\partial \mathbf{q}_i} \right|^2 dt \quad (31)$$

s.t.

$$\sum \frac{m_i}{2} \left(\frac{d\mathbf{q}_i}{dt} \right)^2 = \frac{gkT}{2}$$

we can still not cover the Gaussian dynamics since the term containing the Lagrange multiplier is proportional to the acceleration.

Although Berendsen mentioned in [2] that Berendsen proportional scaling gives a least squares local disturbance satisfying a global constraint, meaning, discretely at each time step, Berendsen proportional scaling method is a minimizer of

$$\min \sum m_i (v_i(t + \Delta t) - v_i(t))^2$$

s.t.

$$\sum \frac{1}{2} m_i v_i(t + \Delta t)^2 - \sum \frac{1}{2} m_i v_i(t)^2 = \frac{3N}{2} K \frac{\Delta t}{\tau} (T_0 - T(t)).$$

But a global minimization description is still not given to recover the Gaussian and Berendsen dynamics. Furthermore, Parrinello's dynamics in [3] is also derived from the minimization of the local disturbance on the trajectory without any global consideration.

Now the main point in this section is how to understand the Gauss's principle of least constraint from the variational point of view and recover the Gauss and Berendsen dynamics. I will keep working on it in the next couple of weeks.

10 Fokker-Planck equation and energy laws (June 22))

10.1 Fundamental question

The fundamental question we are considering is that how Langevin equation (1D case)

$$\epsilon \ddot{x} + \dot{x} + \nabla U = \sqrt{2}\xi \quad (32)$$

converges to the first order stochastic differential equation

$$\dot{x} + \nabla U = \sqrt{2}\xi. \quad (33)$$

One way to prove the convergence is the so-called Smoluchowski-Kramers approximation, which has been known very well. Another possible method is that we consider relation between the associated Fokker-Planck equations for, namely, how the solution of the Kramers equation

$$\frac{\partial W}{\partial t} = -\frac{\partial}{\partial x}(vW) + \frac{1}{\epsilon} \frac{\partial}{\partial v}(v + \nabla U)W + \frac{1}{\epsilon^2} \frac{\partial^2}{\partial v^2} W \quad (34)$$

converges to the solution of the Smoluchowski equation

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial x}(P\nabla U) + \frac{\partial^2}{\partial x^2} P \quad (35)$$

10.2 Possible approach

As what we discussed before, we can find the energy law for the Smoluchowski equation (35), but the difficulty is the energy law for the Kramers equation (34). Now I am thinking why don't we avoid the energy law, and try to prove

the convergence directly. In this case, what we need to do is to pick a suitable weight function

$$F := F(x, v, \epsilon)$$

such that

$$Q(x, t, \epsilon) \rightarrow P(x, t), \quad \text{as } \epsilon \rightarrow 0$$

where

$$Q(x, t, \epsilon) := \int_{-\infty}^{+\infty} F(x, v, \epsilon) W(x, v, t, \epsilon) dv. \quad (36)$$

First of all, one notices that the Kramers equation

$$\frac{\partial W}{\partial t} = -\frac{\partial}{\partial x}(vW) + \frac{1}{\epsilon} \frac{\partial}{\partial v}(v + \nabla U)W + \frac{1}{\epsilon^2} \frac{\partial^2}{\partial v^2} W$$

has coefficients $1/\epsilon, 1/\epsilon^2$ which will blow up when ϵ goes to zero, one possible choice for the weight function might be

$$F(x, v, \epsilon) := \exp[c(\epsilon)f(x, v)]$$

such that when one takes derivatives w.r.t. v , $c(\epsilon)$ will appear to cancel $1/\epsilon, 1/\epsilon^2$.

Secondly, notice that the limiting dynamics (33) tells us that

$$v + \nabla U = \sqrt{2}\xi,$$

which implies that v will more likely be equal to $-\nabla U$ ¹. To certain degree the function $Q(x, t, \epsilon)$ should be averaged with more weights near $-\nabla U$ and less weights far away from $-\nabla U$. If that is the case, we can pick

$$F(x, v, \epsilon) = \exp[c(\epsilon)(v + \nabla U)^2].$$

In particular, we choose the special potential field $U = x^2/2$, then

$$F(x, v, \epsilon) = \exp[c(\epsilon)(v + x)^2]. \quad (37)$$

One more thing we should keep in mind is that the stationary solution of the Kramers equation (34) is given by the Boltzmann distribution

$$W_{\text{st}}(x, v) = \frac{1}{Z} \exp\left(-\frac{1}{2}\epsilon v^2 - U(x)\right)$$

¹Intuitively, we can think that $v \approx \nabla U$, then in the Kramers equation (34), we can roughly do the following substitutions

$$\begin{aligned} -vW &\rightarrow \nabla U P, \\ v + \nabla U &\rightarrow 0, \\ \frac{1}{\epsilon^2} \frac{\partial^2}{\partial v^2} W &\rightarrow \frac{\partial^2}{\partial x^2} P \end{aligned}$$

and recover the Smoluchowski equation.

and the stationary solution of the Smoluchowski equation (35) is given by

$$P_{\text{st}}(x) = \frac{1}{Z} \exp(-U(x)).$$

Now let us take derivative on both sides of (36) w.r.t. t , then

$$\begin{aligned} \frac{\partial Q}{\partial t} &= \int_{-\infty}^{+\infty} F(x, v, \epsilon) \frac{\partial W}{\partial t} dv \\ &= \int_{-\infty}^{+\infty} -F \frac{\partial}{\partial x}(vW) + \frac{1}{\epsilon} F \frac{\partial}{\partial v}(v+x)W + \frac{1}{\epsilon^2} F \frac{\partial^2}{\partial v^2} W dv \end{aligned}$$

consider the special form (37) of F , we have

$$\begin{aligned} \frac{\partial Q}{\partial t} &= - \int_{-\infty}^{+\infty} v \frac{\partial W}{\partial x} F dv - \int_{-\infty}^{+\infty} \frac{2c}{\epsilon} (v+x)^2 W F dv \\ &\quad + \int_{-\infty}^{+\infty} \frac{1}{\epsilon^2} [4c^2(v+x)^2 + 2c] W F dv \end{aligned}$$

A possible way to handle the above equality is to represent the right hand side by Q , namely, find out a differential equation Q is satisfied. Then consider the limiting behavior of that equation and check the convergence to Smoluchowski equation.

References

- [1] H.C. Anderson, *Molecular dynamics simulations at constant pressure and/or temperature*, J. Chem. Phys, 72(4), 15 Feb. 1980.
- [2] H.J.C. Berendsen, J.P.M. Postma, W.F. van Gunsterne, A. DiNola, J.R.Haak, *Molecular dynamics with coupling to an external bath*, Computer Physics Communications, 2008.01.006
- [3] G. Bussi, M. Parrinello, *Stochastic thermostats: comparison of local and global schemes*, J. Chem. Phys., 81: 3684, 1984.
- [4] D.J.Evans, *Computer experiment for nonlinear thermodynamics of Couette flow*, J. Chem. Phys., 78: 3298-3302, 1983.
- [5] D.J.Evans, *Nonequilibrium molecular dynamics via Gauss's principle of least constraint*, Physical review A, Vol 28, No 2, August 1983.
- [6] D.J.Evans, W.G. Hoover, B.H. Failor, B. Moran, A.J.C. Ladd, *Nonequilibrium molecular dynamics via Gauss's principle of least constraint*, Phys. Rev. A, 28: 1016-1021, 1983.
- [7] Dann Frenkel, Berend Smit *Understanding Molecular Simulation: From Algorithms to Application*, Academic Press, 2002. 1992.

- [8] [http://en.wikipedia.org/wiki/Gauss% 27_principle_of_least_constraint](http://en.wikipedia.org/wiki/Gauss%27_principle_of_least_constraint)
- [9] T.Morishita, *Fluctuation formulas in molucular dynamics simulations with the weak coupling heat bath*, J. Chem. Phy. 113:2976-2982, 2000.
- [10] W. G. Hoover, *Canonical dynamics: Equilibrium phase-space distributions*, Physical Review A, Vol 31, No. 3, 1695-1697 1985.
- [11] W.G. Hoover, A.J.C.Ladd, B. Moran, *High strain rate plastic flow studied via nonequilibrium molecular dynamics*, Phys. Rev. Lett., 48:1818-1820, 1982.
- [12] S. Nosé, *A molecular dynamics for simulations in canonical ensemble*, Molecular Physics, Vol 52, No. 2, 255-268 1984.
- [13] S. Nosé, *A unified formulation of the constant temperature molecular dynamics methods*, J. Chem. Phy. 81(1), 1 July. 1984.
- [14] L.V.Woodcock, *Isothermal molecular dynamics calculations for liquid salt*, Chem. Phys. Letter., 10: 257-261, 1971.
- [15] <http://wiki.gromacs.org/index.php/Thermostats>