

Chem 860. Lecture 12

Canonical MD with extended Lagrangian

March 4, 2009

1 Ensemble in Molecular Dynamics

What we talked about so far is microcanonical molecular dynamics in which the total energy is conserved. Although at the thermodynamic limit different ensembles should give you the same answer, it is useful to do simulations with the desired thermodynamic condition - such as constant temperature and pressure. For interfacial systems, controlling the proper condition is even more relevant.

1.1 Canonical is NOT isokinetic

It's important to know that canonical ensemble does not imply that kinetic energy (i.e., an *instantaneous temperature*) does not fluctuate. It is only a thermodynamical variable that characterizes the energy distribution of the system. At equilibrium, we know:

$$P(p) = \left(\frac{\beta}{2\pi m}\right)^{3/2} \exp[-\beta p^2/2m]$$

and

$$3k_B T = \langle p^2/m \rangle$$

To compute the variance of the temperature, we need the second and fourth moment of the Maxwell distribution:

$$\begin{aligned}\langle p^2 \rangle &= \int d\mathbf{p} p^2 P(p) = 3m/\beta \\ \langle p^4 \rangle &= \int d\mathbf{p} p^4 P(p) = 15(m/\beta)^2\end{aligned}$$

Thus (T_k is the total kinetic energy of the system),

$$\frac{\sigma_{T_k}^2}{\langle T_k \rangle_{NVT}^2} = \frac{\langle T_k^2 \rangle_{NVT} - \langle T_k \rangle_{NVT}^2}{\langle T_k \rangle_{NVT}^2} = \frac{N \langle p^4 \rangle + N(N-1) \langle p^2 \rangle^2 - N^2 \langle p^2 \rangle^2}{N^2 \langle p^2 \rangle^2}$$

$$= \frac{\langle p^4 \rangle - \langle p^2 \rangle^2}{N \langle p^2 \rangle^2} = \frac{2}{3N}$$

So the relative fluctuations in the *instantaneous* temperature decreases as the number of particles increases.

1.2 The Anderson model

Intuitive: the effect of the heat bath is to exchange energy with the system. So we occasionally pick a set of particles in random to re-assign its velocity based on the Maxwell distribution at temperature T . Apparently, this is most straightforward to implement in a Velocity-Verlet algorithm.

Pseudo-code:

... after velocity update

```
do i=1, N_particle
if (rand() < nu * dt) then
v(i)=Gaussian(T)
endif
enddo
```

...

It can be shown that the Anderson model does produce a canonical distribution (e.g., one can monitor the velocity distribution), and static properties such as pressure are independent of the collision frequency (ν). However, the stochastic “kicks” perturbs the dynamics of the system, which makes dynamical properties sensitive to the value of the collision frequency (e.g., the kicks would artificially decorrelate the velocities, which modifies the velocity autocorrelation function, which in turn modifies the diffusion constant).

1.3 Nosé-Hoover dynamics

The extended Lagrangian approach is widely used - for constant temperature, pressure simulations, as well as in simulations in which expensive optimizations have to be done (e.g., relaxing the electronic degrees of freedom in polarizable models or electronic structure theory).

For constant-temperature simulations, the basic idea is that canonical trajectories in the real molecular systems are generated by sampling microcanonical ensemble for an extended system (i.e., with extra degrees of freedom that represent “thermostat”).

The Lagrangian of this system is given as,

$$\mathcal{L}_{Nose} = \sum_{i=1}^N \frac{m_i \dot{\mathbf{r}}_i^2}{2} - U(\mathbf{r}^N) + \frac{Q}{2} \dot{s}^2 - \frac{L}{\beta} \ln s$$

where Q is an effective mass associated with the extended degree of freedom (s). L is a variable to be determined later. The magic of ln will become clear soon.

The corresponding Hamiltonian is then

$$\mathcal{H}_{Nose} = \sum_{i=1}^N \mathbf{q}_i \mathbf{p}_i - \mathcal{L}_{Nose}$$

where $\mathbf{q}_i = \{\mathbf{r}_i, s\}$ and

$$\mathbf{p}_i = \frac{\partial \mathcal{L}_{Nose}}{\partial \dot{\mathbf{r}}_i} = m_i s^2 \dot{\mathbf{r}}_i$$

$$p_s = \frac{\partial \mathcal{L}_{Nose}}{\partial \dot{s}} = Q \dot{s}$$

Substituting those in, we get the Nosé Hamiltonian,

$$\mathcal{H}_{Nose} = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i s^2} + U(\mathbf{r}^N) + \frac{p_s^2}{2Q} + L \frac{\ln s}{\beta}$$

Thus, the microcanonical partition function associated with the Nosé Hamiltonian is given by,

$$Q_{Nose} = \frac{1}{N!} \int dp_s ds d\mathbf{p}^N d\mathbf{r}^N \delta(E - \mathcal{H}_{Nose})$$

Substituting in the Nosé Hamiltonian, and using the property,

$$\delta f(s) = \delta(s - s_0) / |f'(s_0)|$$

(s_0 being the root of function $f(s)$), with straightforward algebra, we get

$$Q_{Nose} = C \frac{1}{N!} \int d\mathbf{p}'^N d\mathbf{r}^N \exp[-\beta \frac{3N+1}{L} \mathcal{H}(\mathbf{p}', \mathbf{r})]$$

where $\mathbf{p}' = \mathbf{p}/s$ and $\mathcal{H}(\mathbf{p}', \mathbf{r}) = \sum_{i=1}^N \frac{\mathbf{p}'_i^2}{2m_i} + U(\mathbf{r}^N)$.

The “*exp*” comes about due to the “magic” choice of “*ln*” in the original Nosé Lagrangian. We see that if we choose $L = 3N + 1$, the Q_{Nose} is essentially the canonical partition function of the system characterized by $\mathbf{r}^N, \mathbf{p}'^N$. In other words,

$$\langle A(\mathbf{p}/s, \mathbf{r}) \rangle_{Nose} = \langle A(\mathbf{p}', \mathbf{r}) \rangle_{NVT}$$

A technical point is that we distinguish “real” variables (physical system) and “virtual” variables (extended system):

$$\begin{aligned}\mathbf{r}' &= \mathbf{r} \\ \mathbf{p}' &= \mathbf{p}/s; \text{Note : } \mathbf{p} = ms^2\dot{\mathbf{r}} \\ s' &= s \\ t' &= t/s\end{aligned}$$

So the extended variable s can be thought as adjusting the integration time step of the system. One may choose to propagate the equation of motion in terms of the “physical” variables or “virtual” variables. To ensure correct canonical distribution for the “physical” system, different L values need to be adapted (see Frenkel and Smit).

Another tricky point we want to mention without deep explanation is that the correct distribution is generated if there is a *single* constant of motion; for isolated systems (without external force), this means that the correct distribution is obtained only if the center of mass is fixed. For some (seemingly trivial) systems (e.g., a harmonic oscillator), there can be non-trivial conservation laws, which prevents the Nose-Hoover algorithm to generate a canonical distribution; see Tuckerman et al., J. Chem. Phys. 116, 1678, 2001). A useful alternative is to use the so-called Nosé-Hoover chain, in which a set of thermostats are associated with each other (G. J. Martyna, et al. J. Chem. Phys. 97, 2635, 1992); qualitatively speaking, this is meant to provide extra “kicks” to the momentum associated with the thermostat, which ultimately helps sampling the phase space of the real system.

A key parameter in the Nosé-Hoover MD is the effective mass “ Q ”. A small Q corresponds to a low inertia of the heat bath and leads to rapid T fluctuations while a large Q gives slow response to the T change. The magnitude of Q has only a minor influence on the dynamical quantities such as diffusion constant.

For the application of Nosé-Hoover (chain) MD to protein systems, see two “benchmark studies”: Merz et al., J. Phys. Chem. 100, 1927 (1996); Tobias et al., J. Phys. Chem. 97, 12959 (1993), where they showed that NHC can be very effective in terms of achieving equilibrium (i.e., reaching canonical distribution). One interesting metric, which we will also see later, was introduced by Thirumalai et al. (J. Phys. Chem. 93, 6975, 1989). Take any single particle property, say, kinetic energy: $F_i(t)$, one can define the time-average, $\bar{f}_i(t) = (1/t) \int_0^t F_i(s) ds$, and then the average/fluctuation of f_i :

$$\bar{f}(t) = (1/N) \sum_{i=1}^N f_i(t) \tag{1}$$

$$\Omega(t) = (1/N) \sum_{i=1}^N [f_i(t) - \bar{f}(t)]^2 \tag{2}$$

For an ergodic system, time average approaches system average, so $\Omega(t)$ should approach 0 at long time t . Thirumalai et al. found that the behavior of $\Omega(t)$ is diffusive, i.e., $\Omega(0)/\Omega(t) \approx$

$D_F t$. Thus the magnitude of D_F can be used to measure the rate that the system approaches ergodicity - which serves as a metric for measuring the efficiency of sampling.

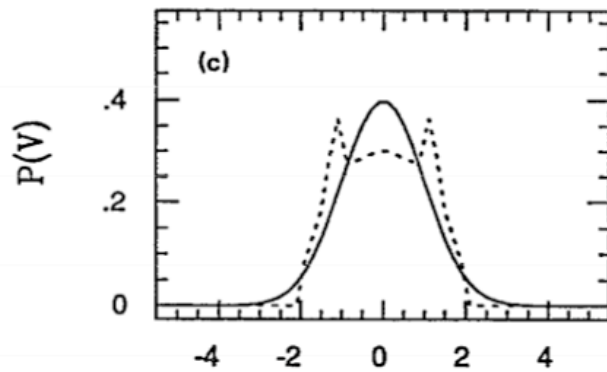
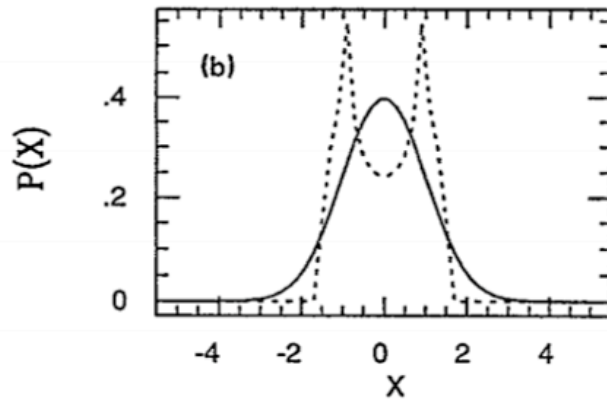
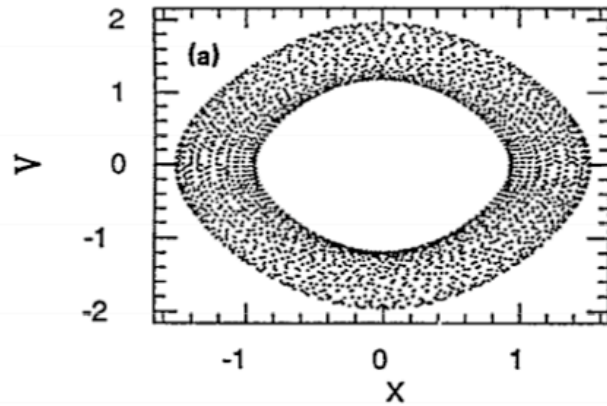
Tobias/Merz et al. found that NHC can be much more effective than microcanonical or Langevin dynamics for protein systems. Interestingly, both studies seem to show that even dynamics - e.g., reflected by velocity ACF - can be quite insensitive to parameters in NHC. Thus NHC can be very useful in practice to extract even approximate dynamical properties.

2 Homework

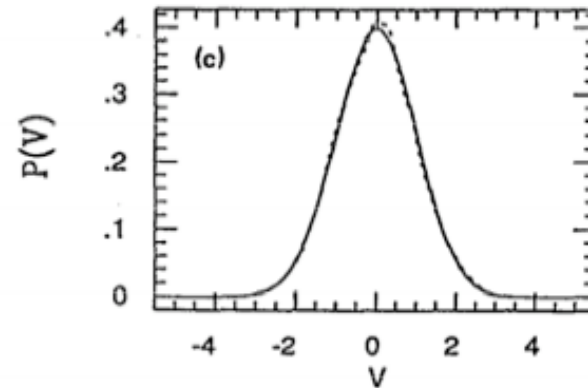
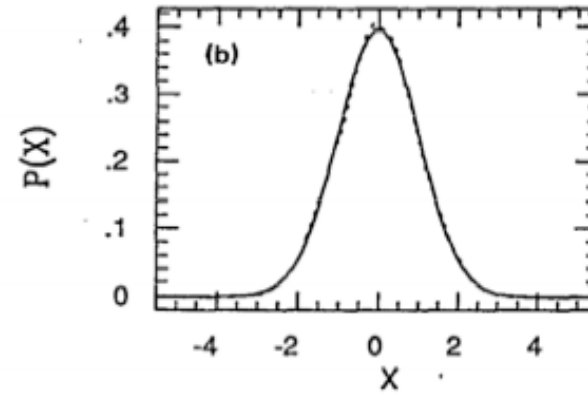
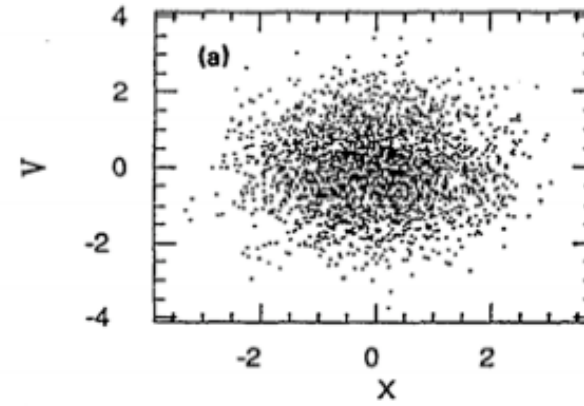
2.1 Pencil exercises: extended Lagrangian

Show explicitly that the microcanonical partition function associated with the Nosé Hamiltonian gives the canonical partition function for the physical system with specific choice of L .

Nose-Hoover



Nose-Hoover Chain (M=2)



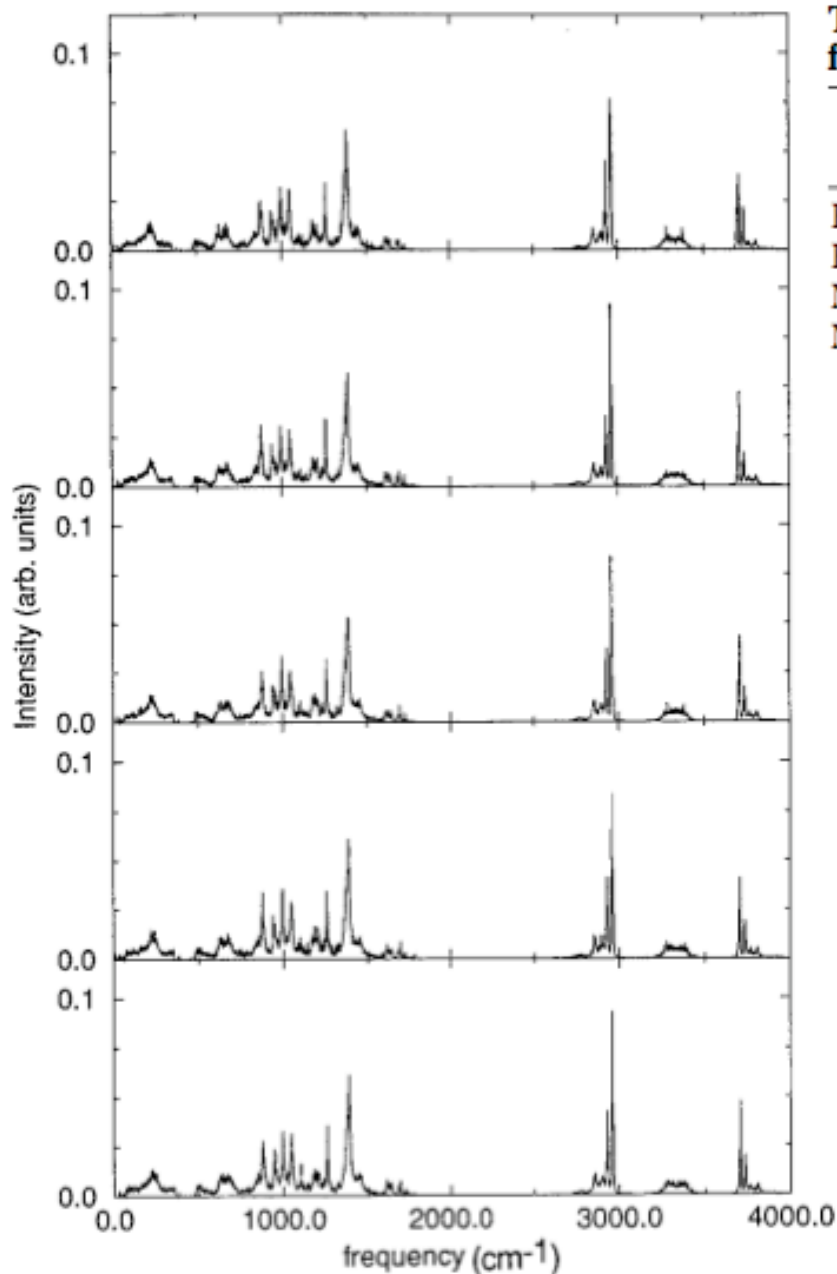


TABLE 2: Average Temperature and Configuration Energy for AFP Solvated by Water at 300 K

simulation	T (K)	T_{solute} (K)	T_{solvent} (K)	U_{conf} (kcal/mol)	D_{KE}
Berendsen 1 scaling factor	306.1	254.0	314.8	-12 492	5.0
Berendsen 2 scaling factors	306.0	300.2	307.0	-12 538	6.2
NHC 1 chain	297.4	249.1	305.4	-12 601	5.2
NHC 2 chain	296.6	299.9	296.1	-12 668	6.2

TABLE I: Kinetic Energy Diffusion Constants (D_{KE})

simulation method	τ (ps)	D_{KE} (ps ⁻¹) ^a	simulation method	τ (ps)	D_{KE} (ps ⁻¹) ^a
NVE		2.57 ± 0.40	MNHC	0.5	7.25 ± 1.2
Langevin	0.5	7.15 ± 0.80	Langevin	0.05	17.8 ± 2.4
NH	0.5	2.86 ± 0.62	MNHC	0.05	31.6 ± 4.7
NHC	0.5	2.41 ± 0.42	Langevin	0.02	30.0 ± 3.5

^a Averages of slopes obtained by least-squares fitting $\Omega_{\text{KE}}(0)/\Omega_{\text{KE}}(t)$ vs t data in 5-ps blocks between $t = 2-5$ ps. Tabulated uncertainties are the standard deviations of the block averages.

$$Q \sim kT/\tau^2$$