Brief notes on Non-Hamiltonean Molecular Dynamics Techniques

Simon Poblete

1 Introduction

This session is about some techniques for the generation of trajectories that produce non-microcanonical averages on a molecular-dynamics scheme. The "extended molecular dynamics" approach consists in **the extension of the phase space of the system of interest**. Then, by solving the equations of motion in this space, generated by an "extended hamiltonian", one can obtain averages that in the original(and physical) space correspond to the desired ensemble. In this spirit, I am just going to talk briefly about the firsts attempts to generate such equations of motion for different ensembles, disregarding any possible physical interpretation of the additional degrees of freedom. Then, present the general formalism developed by Tuckerman et al. for the construction of such systems, considering the non-hamiltoninan structure of the equations if needed. Finally, equations of motion designed by the same authors for NPT ensembles are shown.

2 Andersen barostat + Nosé-Hoover thermostat revisited

- Andersen

  I start just showing briefly the equations of motion of the Andersen's barostat, an isotropic way of generating an isobaric-isoenthalpic ensemble. Defining

$$\vec{\rho}_i = \frac{\vec{r}_i}{V^{1/3}} \tag{1}$$

  we can write the Lagrangian

$$\mathcal{L} = \frac{1}{2}V^{2/3}\sum_i \dot{\rho}_i^2 - \sum_{i<j} u(V^{1/3}\rho_{ij}) + \frac{1}{2}M\dot{V}^2 - \alpha V \tag{2}$$

  where the additional terms don't have necessarily a physical meaning. In this scheme, a Hamiltonean and its equation of motion can be obtained to finally demonstrate that the partition function is the corresponding to a NPH ensemble. Thus, any average of a quantity that depends on the physical variables, would correspond to the average over this ensemble with corrections of order N^{-2}. Note that we have an additional parameter M and also, a conjutgated momenta associated to V, that can be eliminated from the equations of motion. Let's not forget then, that what we have done here is extend the phase space to more variables in such a way that our averages will correspond to the desired ensemble averages.

- Nosé thermostat

  In this case, we consider the following hamiltonian

$$\mathcal{H} = \mathcal{H}_0 + \frac{p_\eta^2}{2Q} + \frac{L}{dN\beta}\log\eta \tag{3}$$

  where $\mathcal{H}_0$ contains the dependence of the physical positions and momenta, Q is the mass associated with the additional degree of freedom η and L, a constant.

  From here it is possible to obtain the equations of motion and also to calculate the partition function considering that the hamiltonian is a constant of motion K,

$$\Omega = \int\int\int\int d^{3N}r d^{3N}p d\eta dp_\eta \delta(\mathcal{H}_0 + \frac{p_\eta^2}{2Q} + \frac{L}{dN\beta}\log\eta - K) \tag{4}$$

  that, after some minimal work can be written as

$$\Omega\alpha\int\int d^{3N}r d^{3N}p e^{-\beta\mathcal{H}_0} \tag{5}$$

  under the right choice of L.

3 Non Hamiltonean Molecular Dynamics

So far, Tuckerman et al. have developed a "systematic way" of designing equations of motion of extended molecular dynamics. Basically, it consists on identifying all the conserved quantities in order to define correctly the hypersurface of the phase space that is covered by the equations of motion (in the case of ergodic systems, of course) and to determine the compressibility of this space. This point states that, most of the time, the equations of motion are non-Hamiltonean in the sense that they do not conserve the metric of the phase space. Then, an invariant volume element has to be found in order to define correctly the volume integrals that define the averages and the partition function.

For this, let's consider a general dynamical system

$$\dot{\mathbf{x}} = F(\mathbf{x}, t) \tag{6}$$

so, let's consider the evolution of the system as a coordinate transformation from $\mathbf{x}_0$ to $\mathbf{x}_t$. Then, the volume element changes according to

$$d\mathbf{x}_t = J(\mathbf{x}_t, \mathbf{x}_0) d\mathbf{x}_0 \tag{7}$$

where $J(\mathbf{x}_t, \mathbf{x}_0)$ is the jacobian of the transformation, that satisfies the equation

$$\frac{dJ}{dt} = K\kappa(\mathbf{x}_t) \tag{8}$$

with $\kappa(\mathbf{x}_t) = \sum_i \frac{\partial \cdot x_t^i}{\partial x_t^i}$.

Also the jacobian is the ratio between the volume elements in terms of the determinants of the metric tensor g

$$\sqrt{g_0} = \sqrt{g_t} J(\mathbf{x}_t, \mathbf{x}_0) \tag{9}$$

and we can solve the equation for $J(\mathbf{x}_t, \mathbf{x}_0)$ and find a solution of the form

$$J(\mathbf{x}_t, \mathbf{x}_0) = e^{\int_0^t \kappa(\tau) d\tau} = e^{w(t)-w(0)} \tag{10}$$

writing $\int^t \kappa(\tau) d\tau = w(t)$. So we finally conclude that

$$\sqrt{g} = e^{-w(t)} \tag{11}$$

so...ACHTUNG!!! Every time that you design equations of motion in an extended system, you have to check your metric and the conserved quantities in order to generate the proper distribution!!!

So here is the deal. First we have our equations. Then, find the metric. Later, eliminate all the possible trivial variables. And finally, calculate our precious partition function.

4 Examples

- Nosé-Hoover chains

  Just as an example of how to calculate such things, let's see the Nosé-Hoover chain algorithm, given by the equations

$$
\begin{aligned}
\dot{\mathbf{r}_\mathbf{i}} &= \frac{\mathbf{p_i}}{m_i} && (12)\\
\dot{\mathbf{p}_\mathbf{i}} &= \mathbf{F_i} - \frac{p_{\eta_1}}{Q_1}\mathbf{p_i} && (13)\\
\dot{\eta}_k &= \frac{p_{\eta_k}}{Q_k}, k = 1, ..., M && (14)\\
\dot{p}_{\eta_1} &= \left[\sum \frac{\mathbf{p_i}^2}{m_i} - LkT\right] && (15)\\
\dot{p}_{\eta_k} &= \left[\frac{p^2_{\eta_{k-1}}}{Q_{k-1}} - kT\right] - \frac{p_{\eta_{k+1}}}{Q_{k+1}} p_{\eta_k}, k = 2, ..., M-1 && (16)\\
\dot{p}_{eta_M} &= \left[\frac{p^2_{\eta_{M-1}}}{Q_{M-1}} - kT\right] && (17)\\
& && (18)
\end{aligned}
$$

with

$$
H' = H(p, r) + \sum_{k=1}^{M} \frac{p^2_{\eta_k}}{2Q_k} + LkT\eta_1 + kT \sum_{k=2}^{M} \eta_k \tag{19}
$$

so, the metric is

$$
\sqrt{g} e^{N d\eta_1 + \sum_{k=2}^{M} \eta_k} \tag{20}
$$

that produces the desired NVT partition function when the total force is null.

- Hoover barostat Hoover thermostat fails at generating the volume distribution. As can be seen by the same formalism, with the equations of motion

$$
\begin{aligned}
\dot{\mathbf{r}_\mathbf{i}} &= \frac{\mathbf{p_i}}{m_i} + \frac{p_\epsilon}{W}\mathbf{r_i} && (21)\\
\dot{\mathbf{p}_\mathbf{i}} &= \mathbf{F_i} - \frac{p_\eta}{Q}\mathbf{p_i} - \frac{p_\epsilon}{W}\mathbf{p_i} && (22)\\
\dot{V} &= \frac{dV p_\epsilon}{W} && (23)\\
\dot{p}_\epsilon &= dV(P_{int} - P_{ext}) - \frac{p_\eta}{Q} p_\epsilon && (24)\\
\dot{\eta} &= \frac{p_\eta}{Q} && (25)\\
\dot{p}_{\eta_1} &= \sum \frac{\mathbf{p_i}^2}{m_i} - LkT + \frac{p^2_\epsilon}{W} && (26)\\
& && (27)
\end{aligned}
$$

the Hamiltonian

$$
H' = H(p, r) + \frac{p^2_\epsilon}{2W} + \frac{p^2_\eta}{2Q} + LkT\eta + P_{ext}V \tag{28}
$$

and the metric

$$\sqrt{g} = \frac{1}{V} e^{-d\epsilon + (Nd+1)\eta} \tag{29}$$

where $\epsilon = \frac{1}{d} \log V/V_0$, V_0 a reference volume, we obtain as a partition function

$$\Omega \alpha \int dV \frac{1}{V} e^{-\beta P_{ext} V \int d^N \mathbf{p} \int d^N \mathbf{r} e^{-\beta H}} \tag{30}$$

Clearly, the extra V^{-1} factor does not correspond to the desired case.

In this case, the pressure is obtained as

$$P_{int} = \frac{1}{dV} \left[\sum_{i=1}^{N} \frac{\mathbf{p_i}^2}{m_i} + \sum_{i=1}^{N} \mathbf{r_i} \cdot \mathbf{F_i} - (dV) \frac{\partial \phi}{\partial V} \right] \tag{31}$$

- NPT algorithms - Martyna-Tobias-Klein hybrid scheme Finally, skiping a lot of schemes, I show briefly the equations of the hybrid scheme of MTK. Here the shape of the simulation cell can change and also the volume. The temperature is kept constant, at the same time. The equations are

$$\begin{aligned}
\dot{\mathbf{r}}_i &= \frac{\mathbf{p_i}}{m_i} + \frac{\overleftrightarrow{\mathbf{p}}_{g_0}}{W_{g_0}} \mathbf{r_i} + \frac{p_\epsilon}{W} \mathbf{r_i} \\
\dot{\mathbf{p}}_i &= \mathbf{F_i} - \frac{\overleftrightarrow{\mathbf{p}}_{g_0}}{W_{g_0}} \mathbf{p_i} - \left(1 + \frac{D}{DN}\right) \frac{p_\epsilon}{W} \mathbf{p_i} - \frac{p_\xi}{Q} \mathbf{p_i} \\
\dot{V} &= \frac{DV p_\epsilon}{W} \\
\dot{p}_\epsilon &= DV(P_{int} - P_{ext}) + \frac{D}{DN} \sum_{i=1}^{N} \frac{\mathbf{p_i}^2}{m_i} - \frac{p_\xi}{Q} p_\epsilon \\
\dot{\overleftrightarrow{\mathbf{h}}}_0 &= \frac{\overleftrightarrow{\mathbf{p}}_{g_0} \overleftrightarrow{\mathbf{h}}_0}{W_{g_0}} \\
\dot{\overleftrightarrow{\mathbf{p}}}_{g_0} &= V(\overleftrightarrow{\mathbf{P}}_{int} - \overleftrightarrow{\mathbf{I}} P_{ext}) - \frac{V}{D} Tr \left[\overleftrightarrow{\mathbf{P}}_{int} - \overleftrightarrow{\mathbf{I}} P_{ext} \right] \overleftrightarrow{\mathbf{I}} - \frac{p_\xi}{Q} \overleftrightarrow{\mathbf{p}}_{g_0} \\
\dot{\xi} &= \frac{p_\xi}{Q} \\
\dot{p}_\xi &= \sum_{i=1}^{N} \frac{\mathbf{p}^2}{m_i} + \frac{p_\epsilon^2}{W} + \frac{1}{W_{g_0}} Tr \left[\overleftrightarrow{\mathbf{p}}_{g_0}{}^t \overleftrightarrow{\mathbf{p}}_{g_0} \right] - (ND + D^2) k_b T
\end{aligned}$$

with the pressures given by

$$(P_{int})_{\alpha\beta} = \frac{1}{V} \left[\sum_{i=1}^{N} \frac{(\mathbf{p}_i)_\alpha (\mathbf{p}_i)_\beta}{m_i} + (\mathbf{F_i})_\alpha (\mathbf{F_i})_\beta - (\overleftrightarrow{\phi'} \overleftrightarrow{\mathbf{h}}^t)_{\alpha\beta} \right] \tag{32}$$

$$(\phi')_{\alpha\beta} = \frac{\partial \phi(\mathbf{r}, \overleftrightarrow{h})}{\partial (h)_{\alpha\beta}} \tag{33}$$

and the Hamiltonian

$$H = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} + \frac{1}{2W_{g_0}} Tr[\overleftrightarrow{\mathbf{p}}^t_{g_0} \overleftrightarrow{\mathbf{p}}_{g_0}] + \frac{P-\epsilon^2}{2W} + \frac{p_\xi^2}{2Q} + \phi(R, v, H_0) P_{ext} V + (N_f + d^2) k_B T \xi \tag{34}$$

and the metric

$$\sqrt{g} = e^{-(Nd+d^2)\xi} \tag{35}$$

that resemble the NPT partition function.

5 References

1. Tuckerman, Mundy and Martyna, Europhys. Let **45**, 149 (1999)
2. Tuckerman, Martyna, J. Phys. Chem. B **104**, 159 (2000)
3. Martyna, Tobias and Klein, J. Chem. Phys. **101**, 4177 (1994)
4. Tuckerman, Liu, Ciccotti and Martyna, J. Chem. Phys. **115**, 1678(2001)