A Few Notes on the Implementation of r-RESPA
Directed Toward a MTS Novice

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Contents

The key published references here are

Tuckerman, M.E., Berne, B. J., Martyna, G. J., "Reversible multiple time scale molecular dynamics", *J. Chem. Phys.* **97**(3) 1992 p. 1990-2001.

Martyna, G. J., Tuckerman, M. E., Tobias, D. J., Klein, M. L., "Explicit reversible integrators for extended system dynamics", *Mol. Phys.* **87**(5) 1996 p. 1117-1157.

Case 0. Some Initial Information

The content of these notes is going to assume two things. First, we will assume that such a thing as the Liouville operator, *L*, exists and that it has the following following properties. It gives the time evolution of any property.

$$A(t) = \exp(iLt)A(0) \tag{0.1}$$

If A(t) were the position or the momentum, then the Liouville operator provides an equivalent way of expressing the equations of motion. Second, for the purposes of this work the Liouville operator is defined as the sum of the time deriviative of all the independent variables in the system multiplied by the differentiation operator with respect to that variable.

$$iL = \sum_{i=1}^{N_v} \frac{dx_i}{dt}\frac{\partial}{\partial x_i} \tag{0.2}$$

In the microcanonical ensemble of *N* particles, the independent variables are 3N positions and momenta. In this case, the Liouville operator becomes

$$iL = \sum_{i=1}^{N}\sum_{\alpha=1}^{3}\left(\frac{dr_{i,\alpha}}{dt}\frac{\partial}{\partial r_{i,\alpha}} + \frac{dp_{i,\alpha}}{dt}\frac{\partial}{\partial p_{i,\alpha}} \right) \tag{0.3}$$

In the NVT and NPT ensembles, we will have additional independent variables associated with the thermostat and the barostat. In the rest of these notes, we drop but assume the summation.

The second thing you need to know for these notes is the general mathematical relation.

$$\exp\left(c\frac{\partial}{\partial g(q)} \right) f(q) = \exp\left(c\frac{\partial}{\partial g(q)} \right) f\left(g^{-1}(g(q)) \right) = f\left(g^{-1}(g(q) + c) \right) \tag{0.4}$$

where c is independent of q. We will use three specific cases of this relation

$$\exp\left(c\frac{\partial}{\partial q} \right) f(q) = f(q + c) \tag{0.5}$$

$$\exp\left(cq\frac{\partial}{\partial q} \right) f(q) = f(q\exp(c)) \tag{0.6}$$

$$\exp\left(cq^2\frac{\partial}{\partial q} \right) f(q) = \frac{q}{1 - cq} \tag{0.7}$$

Case I. NVE – one time scale

The equations of motion are

$$\frac{dr_{i,\alpha}}{dt} = \frac{p_{i,\alpha}}{m_i} \tag{I.1}$$

$$\frac{dp_{i,\alpha}}{dt} = -\frac{\partial E}{\partial r_{i,\alpha}} = F \tag{I.2}$$

The Liouville operator, L, provides an equivalent way of expressing the equations of motion.

$$A(t) = \exp(iLt)A(0) \tag{I.3}$$

where

$$iL = \frac{dr_{i,\alpha}}{dt}\frac{\partial}{\partial r_{i,\alpha}} + \frac{dp_{i,\alpha}}{dt}\frac{\partial}{\partial p_{i,\alpha}} \tag{I.4}$$

We substitute equations (1) and (2) into equation (4).

$$iL = \frac{p_{i,\alpha}}{m_i}\frac{\partial}{\partial r_{i,\alpha}} + F\frac{\partial}{\partial p_{i,\alpha}} \tag{I.5}$$

This Liouville operator must be symmetric in order to generate a reversible numerical integration algorithm. In order to make it symmetric, consider splitting up the two terms as

$$iL = iL_1 + iL_2 \tag{I.6}$$

where

$$iL_1 = \frac{p_{i,\alpha}}{m_i}\frac{\partial}{\partial r_{i,\alpha}} \tag{I.7}$$

$$iL_2 = F\frac{\partial}{\partial p_{i,\alpha}} \tag{I.8}$$

We then split the long time Liouville operator into a symmetric form.

$$iL = \frac{iL_2}{2} + iL_1 + \frac{iL_2}{2} \tag{I.9}$$

This symmetric form of the Liouville operator is essential to generate a reversible integration algorithm.

Next we consider performing the operator on a discrete step size, Δt. For the discrete time propagator, we use the notation,

$$G(\Delta t) = \exp(iL\Delta t) = \exp\left(\frac{iL_2\Delta t}{2}\right)\exp(iL_1\Delta t)\exp\left(\frac{iL_2\Delta t}{2}\right) = U_3U_2U_1 \tag{I.10}$$

We then perform the Liouville operation on system of interest. At time t, we have $r_{i,\alpha}(t), p_{i,\alpha}(t)$. We are going to indicate the variables as $\Gamma(0) = \left[r_{i,\alpha}(t), p_{i,\alpha}(t)\right] = \left[r_{i,\alpha}{}^{(0)}, p_{i,\alpha}{}^{(0)}\right]$. Carefully, understand that this superscript does not indicate time; it indicates progress within the algorithm for a single time step. We have to apply each of the three operations in equation (10) on the position and the momentum, since those are our independent variables.

$$\Gamma(1) = U_1\Gamma(0) \tag{I.11.a}$$

$$\Gamma(2) = U_2\Gamma(1) \tag{I.11.b}$$

$$\Gamma(\Delta t) = \Gamma(3) = U_3\Gamma(2) \tag{I.11.c}$$

We apply the first operation to the position, where we invoke equation (0.5)

$$r_{i,\alpha}{}^{(1)} = \exp\left(i\frac{\Delta t}{2}F\frac{\partial}{\partial p_{i,\alpha}}\right)r_{i,\alpha}{}^{(0)} = r_{i,\alpha}(t) + \frac{\Delta t}{2}F(t)\frac{\partial r_{i,\alpha}}{\partial p_{i,\alpha}} = r_{i,\alpha}{}^{(0)} \tag{I.12}$$

In other words, the first operator doesn't change the position. We apply the first operation to the momentum

$$p_{i,\alpha}{}^{(1)} = \exp\left(i\frac{\Delta t}{2}F\frac{\partial}{\partial p_{i,\alpha}}\right)p_{i,\alpha}{}^{(0)} = p_{i,\alpha}{}^{(0)} + \frac{\Delta t}{2}F(r_{i,\alpha}{}^{(0)}) \tag{I.13}$$

$$\Gamma(1) = \left[r_{i,\alpha}{}^{(1)}, p_{i,\alpha}{}^{(1)}\right] = \left[r_{i,\alpha}{}^{(0)}, p_{i,\alpha}{}^{(0)} + \frac{\Delta t}{2}F(r_{i,\alpha}{}^{(0)})\right] \tag{I.14}$$

So we have position and momentum after the first operation. We now apply the second operation to the position and momentum output from the first operation, $\Gamma(1)$.

$$r_{i,\alpha}{}^{(2)} = \exp\left(i\Delta t\frac{p_{i,\alpha}}{m_i}\frac{\partial}{\partial r_{i,\alpha}}\right)r_{i,\alpha}{}^{(1)} = r_{i,\alpha}{}^{(1)} + \Delta t\frac{p_{i,\alpha}{}^{(1)}}{m_i} \tag{I.15}$$

$$p_{i,\alpha}{}^{(2)} = \exp\left(i\Delta t \frac{p_{i,\alpha}}{m_i} \frac{\partial}{\partial r_{i,\alpha}} \right) p_{i,\alpha}{}^{(1)} = p_{i,\alpha}{}^{(1)} \tag{I.16}$$

$$\Gamma(2) = \left[r_{i,\alpha}{}^{(2)}, p_{i,\alpha}{}^{(2)} \right] = \left[r_{i,\alpha}{}^{(1)} + \Delta t \frac{p_{i,\alpha}{}^{(1)}}{m_i}, p_{i,\alpha}{}^{(1)} \right] \tag{I.17}$$

So we have position and momentum after the second operation. We now apply the third operation to the position and momentum output from the first operation, $\Gamma(2)$.

$$r_{i,\alpha}{}^{(3)} = \exp\left(i \frac{\Delta t}{2} F \frac{\partial}{\partial p_{i,\alpha}} \right) r_{i,\alpha}{}^{(2)} = r_{i,\alpha}{}^{(2)} + \frac{\Delta t}{2} F(t) \frac{\partial r_{i,\alpha}}{\partial p_{i,\alpha}} = r_{i,\alpha}{}^{(2)} \tag{I.18}$$

$$p_{i,\alpha}{}^{(3)} = \exp\left(i \frac{\Delta t}{2} F \frac{\partial}{\partial p_{i,\alpha}} \right) p_{i,\alpha}{}^{(2)} = p_{i,\alpha}{}^{(2)} + \frac{\Delta t}{2} F(r_{i,\alpha}{}^{(2)}) \tag{I.19}$$

$$\Gamma(3) = \left[r_{i,\alpha}{}^{(3)}, p_{i,\alpha}{}^{(3)} \right] = \left[r_{i,\alpha}{}^{(2)}, p_{i,\alpha}{}^{(2)} + \frac{\Delta t}{2} F(r_{i,\alpha}{}^{(2)}) \right] \tag{I.20}$$

The efficient algorithm to implement this algorithm is simply

$$p_{i,\alpha}\left(t + \frac{\Delta t}{2} \right) = p_{i,\alpha}(t) + \frac{\Delta t}{2} F(r_{i,\alpha}(t)) \tag{I.21}$$

$$r_{i,\alpha}(t + \Delta t) = r_{i,\alpha}(t) + \Delta t p_{i,\alpha}\left(t + \frac{\Delta t}{2} \right) \tag{I.22}$$

$$p_{i,\alpha}\left(t + \Delta t\right) = p_{i,\alpha}\left(t + \frac{\Delta t}{2} \right) + \frac{\Delta t}{2} F(r_{i,\alpha}(t + \Delta t)) \tag{I.23}$$

This algorithm requires one force evaluation per time step.

An optional aside.

It has been pointed out that this derivation contains an arbitrary element in that we chose to split the term in the Liouville operator that contained the momentum derivative and placed it around the term that contained the position derivative. We could imagine a reversible algorithm, where we switched the definitions of L_1 and L_2 in equations (I.7) and (I.8). Then we have

$$iL_1 = F \frac{\partial}{\partial p_{i,\alpha}} \tag{I.24}$$

$$iL_2 = \frac{p_{i,\alpha}}{m_i}\frac{\partial}{\partial r_{i,\alpha}} \tag{I.25}$$

We split the second operator into symmetric halves as shown in equation (I.9). The first operator doesn't change the momentum, only the position.

$$r_{i,\alpha}{}^{(1)} = \exp\left(i\frac{\Delta t}{2}\frac{p_{i,\alpha}}{m_i}\frac{\partial}{\partial r_{i,\alpha}} \right) r_{i,\alpha}{}^{(0)} = r_{i,\alpha}{}^{(0)} + \frac{\Delta t}{2}\frac{p_{i,\alpha}{}^{(0)}}{m_i} \tag{I.26}$$

$$\Gamma(1) = \left[r_{i,\alpha}{}^{(1)}, p_{i,\alpha}{}^{(1)} \right] = \left[r_{i,\alpha}{}^{(0)} + \frac{\Delta t}{2}\frac{p_{i,\alpha}{}^{(0)}}{m_i}, p_{i,\alpha}{}^{(0)} \right] \tag{I.27}$$

The second operator changes only the momentum.

$$p_{i,\alpha}{}^{(2)} = \exp\left(i\Delta t F \frac{\partial}{\partial p_{i,\alpha}} \right) p_{i,\alpha}{}^{(1)} = p_{i,\alpha}{}^{(1)} + \Delta t F(r_{i,\alpha}{}^{(1)}) \tag{I.28}$$

$$\Gamma(2) = \left[r_{i,\alpha}{}^{(2)}, p_{i,\alpha}{}^{(2)} \right] = \left[r_{i,\alpha}{}^{(0)} + \frac{\Delta t}{2}\frac{p_{i,\alpha}{}^{(0)}}{m_i}, p_{i,\alpha}{}^{(1)} + \Delta t F(r_{i,\alpha}{}^{(1)}) \right] \tag{I.29}$$

The third operator doesn't change the momentum, only the position.

$$r_{i,\alpha}{}^{(3)} = \exp\left(i\frac{\Delta t}{2}\frac{p_{i,\alpha}}{m_i}\frac{\partial}{\partial r_{i,\alpha}} \right) r_{i,\alpha}{}^{(2)} = r_{i,\alpha}{}^{(2)} + \frac{\Delta t}{2}\frac{p_{i,\alpha}{}^{(2)}}{m_i} \tag{I.30}$$

$$\Gamma(3) = \left[r_{i,\alpha}{}^{(3)}, p_{i,\alpha}{}^{(3)} \right] = \left[r_{i,\alpha}{}^{(0)} + \Delta t\frac{p_{i,\alpha}{}^{(0)}}{m_i} + \frac{\Delta t^2}{2}\frac{F(r_{i,\alpha}{}^{(1)})}{m_i}, p_{i,\alpha}{}^{(0)} + \Delta t F(r_{i,\alpha}{}^{(1)}) \right] \tag{I.31}$$

This algorithm is perfectly acceptable. It requires only one force evaluation per step so it is no more computationally intensive than the first version. However, this method has one drawback that makes this method less desirable than the first version, namely that the force is only evaluated at the half-step. Therefore, we cannot for example calculate the pressure with this algorithm. The pressure has a kinetic and potential component. The kinetic contribution to the pressure requires the momentum. The potential contribution to the pressure requires the positions and the forces. Therefore, in order to calculate the pressure at time *t* we need the momenta, positions, and forces at time *t*. This second version of the algorithm does not provide us with all three quantities at the same time. Therefore, we prefer the first version.

This example brings up an important point. In Tuckerman's papers on the RESPA algorithm, there are a lot of seemingly arbitrary choices that are made without justification, as illustrated here. However, there may be practical reasons for making the choices that Tuckerman

made that he did not choose to present in his published work. Therefore, we must understand that what Tuckerman does present is only one of the possible implementations of r-RESPA. If we only want a method that has been demonstrated to work then we should follow Tuckerman's lead closely, making the same seemingly arbitrary decisions that he has made. If, on the other hand, our purpose is to explore and refine the r-RESPA algorithm, then we are not limited to his choices, but will have to verify the consequences of our alternate choices ourselves.

Case II. NVE – two time scales

In the microcanonical ensemble, when we have forces that act on two different time scales, the equations of motion are

$$\frac{dr_{i,\alpha}}{dt} = \frac{p_{i,\alpha}}{m_i} \tag{II.1}$$

$$\frac{dp_{i,\alpha}}{dt} = -\frac{\partial E_L}{\partial r_{i,\alpha}} - \frac{\partial E_S}{\partial r_{i,\alpha}} = F_L + F_S \tag{II.2}$$

where the subscripts S and L indicate forces that need to be updated on **S**hort and **L**ong time scales respectively. In Tuckerman's terminology the "reference system" includes all motion updated on the short time scale. The Liouville operator, L, provides an equivalent way of expressing the equations of motion.

$$A(t) = \exp(iLt)A(0) \tag{II.3}$$

where

$$iL = \frac{dr_{i,\alpha}}{dt}\frac{\partial}{\partial r_{i,\alpha}} + \frac{dp_{i,\alpha}}{dt}\frac{\partial}{\partial p_{i,\alpha}} \tag{II.4}$$

We substitute equations (1) and (2) into equation (4).

$$iL = \frac{p_{i,\alpha}}{m_i}\frac{\partial}{\partial r_{i,\alpha}} + F_L\frac{\partial}{\partial p_{i,\alpha}} + F_S\frac{\partial}{\partial p_{i,\alpha}} \tag{II.5}$$

We group everything that is going to be solved in the short time scale together in the Liouville operator for the reference system.

$$iL = iL_L + iL_S \tag{II.6}$$

where

$$iL_L = F_L\frac{\partial}{\partial p_{i,\alpha}} \tag{II.7}$$

$$iL_S = \frac{p_{i,\alpha}}{m_i}\frac{\partial}{\partial r_{i,\alpha}} + F_S\frac{\partial}{\partial p_{i,\alpha}} \tag{II.8}$$

We then split the long time Liouville operator into a symmetric distribution about the short time Liouville operator.

$$iL = \frac{iL_L}{2} + iL_S + \frac{iL_L}{2} \tag{II.9}$$

Note that the short time Liouville operator must also be split in the way outlined in Case I above. Since we have already performed this split, we will not repeat it here. This symmetric form of the Liouville operator is essential to generate a reversible integration algorithm.

Next we consider performing the operator on a discrete step size, Δt. For the discrete time propagator, we use the notation,

$$G(\Delta t) = \exp(iL\Delta t) = \exp\left(\frac{iL_L\Delta t}{2}\right)\exp\left(iL_S\Delta t\right)\exp\left(\frac{iL_L\Delta t}{2}\right) \tag{II.10}$$

The forces involved in the long operator, L_L are such that they can be integrated with long time steps, Δt. The forces involved in the short operator, L_S are such that they can be integrated with short time steps, $\Delta t/n$. If we divide these steps into n smaller steps, we have

$$G(\Delta t) = \exp\left(\frac{iL_L\Delta t}{2}\right)\left[\exp\left(iL_S\frac{\Delta t}{n}\right)\right]^n \exp\left(\frac{iL_L\Delta t}{2}\right) \tag{II.11}$$

We can write this as

$$G(\Delta t) = U_{n+2}U_{n+1}U_n \ldots U_2U_1 \tag{II.12}$$

where the first and last operations correspond to the long time steps and the n operations in the middle correspond to n small time steps, which taken together equal one long time step.

We then perform the Liouville operation on system of interest. At time t, we have $r_{i,\alpha}(t), p_{i,\alpha}(t)$. We are going to indicate the variables as $\Gamma(0) = \left[r_{i,\alpha}(t), p_{i,\alpha}(t)\right] = \left[r_{i,\alpha}{}^{(0)}, p_{i,\alpha}{}^{(0)}\right]$. Carefully, understand that this superscript does not indicate time; it indicates progress within the algorithm for a single time step. We have to apply each of the n+2 operations in equation (12) on the position and the momentum, since those are our independent variables.

$$\Gamma(1) = U_1\Gamma(0) \tag{II.13.a}$$

$$\Gamma(2) = U_2\Gamma(1) \tag{II.13.b}$$

$$\Gamma(\Delta t) = \Gamma(n+2) = U_{n+2}\Gamma(n+1) \tag{II.13.c}$$

We then perform the Liouville operation on system of interest. We perform each of the n+2 operations on the RHS of equation (12) starting with the term on the far right.

The first operation does not change the position. The first operation does change the momentum.

$$p_{i,\alpha}{}^{(1)} = \exp\left(i\frac{\Delta t}{2} F_L \frac{\partial}{\partial p_{i,\alpha}} \right) p_{i,\alpha}{}^{(0)} = p_{i,\alpha}{}^{(0)} + \frac{\Delta t}{2} F_L(r_{i,\alpha}{}^{(0)}) \tag{II.14}$$

$$\Gamma(1) = \left[r_{i,\alpha}{}^{(1)}, p_{i,\alpha}{}^{(1)} \right] = \left[r_{i,\alpha}{}^{(0)}, p_{i,\alpha}{}^{(0)} + \frac{\Delta t}{2} F_L(r_{i,\alpha}{}^{(0)}) \right] \tag{II.15}$$

So we have position and momentum after the first operation. We now apply the second operation to the position and momentum output from the first operation, $\Gamma(1)$, n times. We have already done this in Case I. The only difference is that here our time step is $\Delta t/n$. This gives us $\Gamma(n+1) = \left[r_{i,\alpha}{}^{(n+1)}, p_{i,\alpha}{}^{(n+1)} \right]$. So we have position and momentum after the n short-time operation. We now apply the third operation to the position and momentum output, $\Gamma(n+1)$. The long-range operator does not change the position.

$$p_{i,\alpha}{}^{(n+2)} = \exp\left(i\frac{\Delta t}{2} F_L \frac{\partial}{\partial p_{i,\alpha}} \right) p_{i,\alpha}{}^{(n+1)} = p_{i,\alpha}{}^{(n+1)} + \frac{\Delta t}{2} F_L(r_{i,\alpha}{}^{(n+1)}) \tag{II.16}$$

The long range forces never change positions. This algorithm requires one evaluation of the long-time forces per long-time step.

The efficient algorithm to implement this algorithm is simply to update the momenta with the long-range force contribution every n steps.

Case III. NVT – two time scales

The equations of motion in the canonical ensemble using the Nosé-Hoover thermostat are

$$\frac{dr_{i,\alpha}}{dt} = \frac{p_{i,\alpha}}{m_i} \tag{III.1}$$

$$\frac{dp_{i,\alpha}}{dt} = -\frac{\partial E_L}{\partial r_{i,\alpha}} - \frac{\partial E_S}{\partial r_{i,\alpha}} - \frac{p_\eta}{Q} p_{i,\alpha} \tag{III.2}$$

$$\frac{d\eta}{dt} = \frac{p_\eta}{Q} \tag{III.3}$$

$$\frac{dp_\eta}{dt} = \left(\sum_{\alpha=1}^{3} \sum_{j=1}^{N} \frac{{p_{j,\alpha}}^2}{m_j} - 3Nk_B T_{set} \right) = 3Nk_B \left(T(t) - T_{set} \right) \tag{III.4}$$

For this system, the Liouville operator is unambiguously,

$$iL = \frac{dr_{i,\alpha}}{dt}\frac{\partial}{\partial r_{i,\alpha}} + \frac{dp_{i,\alpha}}{dt}\frac{\partial}{\partial p_{i,\alpha}} + \frac{d\eta}{dt}\frac{\partial}{\partial \eta} + \frac{dp_\eta}{dt}\frac{\partial}{\partial p_\eta} \tag{III.5}$$

However, this isn't the most convenient way to express the equations of motion for several reasons. First, the inertia mass of the thermostat, Q, is system size dependent, meaning you have to change it for different numbers of molecules. Also η doesn't appear in the equations of motion. It serves no purpose and can be ignored. However, if you want to calculate the Hamiltonian to make sure that your code is conserving the Hamiltonian then you need η. But there is a more important reason to thoroughly investigate this system. It is because when we come to the NPT system, there is Hamiltonian. So, the questions arises, can we use the Liouville form in the absence of a Hamiltonian. In this case, where we do have a Hamiltonian we can check our result. We will obtain the Liouville operator for an alternate formulation of the NVT system, using equation (III.5), which we know to be rigourous, as our starting point. We will also obtain the Liouville operator by modifying the equations of motion in (III.1) through (III.4).

First, let's introduce our new variables,

$$\zeta_T = \frac{p_\eta}{Q} \tag{III.6}$$

$$\nu_T \equiv \sqrt{\frac{3Nk_B T_{set}}{Q}} \tag{III.7}$$

Our equations of motion become

$$\frac{dr_{i,\alpha}}{dt} = \frac{p_{i,\alpha}}{m_i} \tag{III.8}$$

$$\frac{dp_{i,\alpha}}{dt} = -\frac{\partial E_L}{\partial r_{i,\alpha}} - \frac{\partial E_S}{\partial r_{i,\alpha}} - \zeta_T p_{i,\alpha} = F_L + F_S - \zeta_T p_{i,\alpha} \tag{III.9}$$

$$\frac{d\eta}{dt} = \zeta_T \tag{III.10}$$

$$\frac{d\zeta_T}{dt} = \upsilon_T^2 \left(\frac{T(t)}{T_{set}} - 1 \right) \tag{III.11}$$

We have retained equation (III.10) strictly for the calculation of the Hamiltonian. For this system, the Liouville operator is

$$iL = \frac{dr_{i,\alpha}}{dt}\frac{\partial}{\partial r_{i,\alpha}} + \frac{dp_{i,\alpha}}{dt}\frac{\partial}{\partial p_{i,\alpha}} + \frac{d\eta}{dt}\frac{\partial}{\partial \eta} + \frac{d\zeta_T}{dt}\frac{\partial}{\partial \zeta_T} \tag{III.12}$$

Now, if we take (III.5) as our starting point, and make the substitutions of (III.6) and (III.7) directly into the Liouville operator, we will obtain the same result. If we are not interested in calculating the Hamiltonian, then we can drop (III.10) altogether and our Liouville operator becomes

$$iL = \frac{dr_{i,\alpha}}{dt}\frac{\partial}{\partial r_{i,\alpha}} + \frac{dp_{i,\alpha}}{dt}\frac{\partial}{\partial p_{i,\alpha}} + \frac{d\zeta_T}{dt}\frac{\partial}{\partial \zeta_T} \tag{III.13}$$

It wasn't obvious to me initially that we could simply start with equation (III.13), but after this analysis, it is clear that equation (III.13) is valid. When we move to NPT and do not have a Hamiltonian and thus cannot rely on the symplectic nature of the equations of motion, we will still be able to write the Liouville operator. For the time being, we will proceed with equation (III.12). We like the alternate form of the thermostat variable and we want to be able to calculate the Hamiltonian.

We substitute equations (8) through (11) into equation (12).

$$iL = \frac{p_{i,\alpha}}{m_i}\frac{\partial}{\partial r_{i,\alpha}} + F_L \frac{\partial}{\partial p_{i,\alpha}} + F_S \frac{\partial}{\partial p_{i,\alpha}} - \zeta_T p_{i,\alpha}\frac{\partial}{\partial p_{i,\alpha}} + \zeta_T \frac{\partial}{\partial \eta} + \nu_T^2 \left(\frac{T(t)}{T_{set}} - 1 \right)\frac{\partial}{\partial \zeta_T} \tag{III.14}$$

We group everything that is going to be solved in the short time scale together in the Liouville operator for the reference system.

$$iL = iL_L + iL_S \tag{III.15}$$

where

$$iL_L = F_L \frac{\partial}{\partial p_{i,\alpha}} - \zeta_T p_{i,\alpha} \frac{\partial}{\partial p_{i,\alpha}} + \zeta_T \frac{\partial}{\partial \eta} + \nu_T^2 \left(\frac{T(t)}{T_{set}} - 1 \right) \frac{\partial}{\partial \zeta_T} \tag{III.16}$$

$$iL_S = \frac{p_{i,\alpha}}{m_i} \frac{\partial}{\partial r_{i,\alpha}} + F_S \frac{\partial}{\partial p_{i,\alpha}} \tag{III.17}$$

The long time Liouville operator has four terms. We split these up so that they can be applied in one order at the beginning and in the reverse order at the end so that we have a symmetric total Liouville operator. There are an infinity of choices as to how to split this thing up and order the terms. For example,

$$\begin{aligned} iL = & \frac{1}{2} \left[\nu_T^2 \left(\frac{T(t)}{T_{set}} - 1 \right) \frac{\partial}{\partial \zeta_T} + \zeta_T \frac{\partial}{\partial \eta} - \zeta_T p_{i,\alpha} \frac{\partial}{\partial p_{i,\alpha}} F_L \frac{\partial}{\partial p_{i,\alpha}} \right] \\ & + iL_S + \frac{1}{2} \left[F_L \frac{\partial}{\partial p_{i,\alpha}} - \zeta_T p_{i,\alpha} \frac{\partial}{\partial p_{i,\alpha}} + \zeta_T \frac{\partial}{\partial \eta} + \nu_T^2 \left(\frac{T(t)}{T_{set}} - 1 \right) \frac{\partial}{\partial \zeta_T} \right] \end{aligned} \tag{III.18}$$

This satisfies the symmetry criterion. However, this is not what has been used by Tuckerman. Following Tuckerman, we define a different symmetric distribution. Before we present Tuckerman's choice of ordering, let us briefly investigate some of the consequences of ordering these terms.

First we must remind ourselves that we are using the Liouville operator to generate a numerical algorithm. The Liouville operator has much more general utility, which we ignore here. In the interest of generating a numerical algorithm, we will only operate on the independent variables, $r_{i,\alpha}$, $p_{i,\alpha}$, η, and ζ_T, never on any other functions of them. As a result, each individual term in the operator will only change the variable, with respect to which we are differentiating. We have already seen this in the previous two cases. The term that differentiates with respect to position changes the position but not the momentum. This has various implications.

For example, the term which contains η will only change η. Since η does not appear on the RHS of any equations of motion, it's value won't change anything. ζ_T does appear on the RHS of the equation of motion for η, so the relative positions of the terms that differentiate with respect to η and ζ_T will matter, at least to the value of η. But, the relative positions of the terms that contain that differentiate with respect to η and $p_{i,\alpha}$ will not matter to anything involved in the generation of a numerical algorithm.

Let's take a simple example, where we examine the effect of the order of the two terms in equation (III.16), which include differentiation with respect to $p_{i,\alpha}$. The question we ask is, "Does their relative order matter?" For case A, we have

$$iL_A = \frac{1}{2} \left[-\zeta_T p_{i,\alpha} \frac{\partial}{\partial p_{i,\alpha}} + F_L \frac{\partial}{\partial p_{i,\alpha}} \right] + iL_S + \frac{1}{2} \left[F_L \frac{\partial}{\partial p_{i,\alpha}} - \zeta_T p_{i,\alpha} \frac{\partial}{\partial p_{i,\alpha}} \right] \tag{III.19}$$

For case B, we switch the order of the operators and we have

$$iL_B = \frac{1}{2}\left[F_L \frac{\partial}{\partial p_{i,\alpha}} - \zeta_T p_{i,\alpha} \frac{\partial}{\partial p_{i,\alpha}} \right] + iL_S + \frac{1}{2}\left[-\zeta_T p_{i,\alpha} \frac{\partial}{\partial p_{i,\alpha}} + F_L \frac{\partial}{\partial p_{i,\alpha}} \right] \tag{III.20}$$

We only examine their effect on the momentum since the other variables will be unchanged by the operations outside of L_s. In case A, we have (invoking equation (0.6) for the first time)

$$p_{i,\alpha}{}^{(A.1)} = \exp\left(-i\frac{\Delta t}{2}\zeta_T p_{i,\alpha} \frac{\partial}{\partial p_{i,\alpha}} \right) p_{i,\alpha}{}^{(0)} = p_{i,\alpha}{}^{(0)} \exp\left(-\frac{\Delta t}{2}\zeta_T{}^{(0)} \right) \tag{III.21}$$

$$\begin{aligned} p_{i,\alpha}{}^{(A.2)} &= \exp\left(i\frac{\Delta t}{2} F_L \frac{\partial}{\partial p_{i,\alpha}} \right) p_{i,\alpha}{}^{(A.1)} = p_{i,\alpha}{}^{(A.1)} + \frac{\Delta t}{2} F_L\left(r_{i,\alpha}{}^{(A.1)} \right) \\ &= p_{i,\alpha}{}^{(0)} \exp\left(-\frac{\Delta t}{2}\zeta_T{}^{(0)} \right) + \frac{\Delta t}{2} F_L\left(r_{i,\alpha}{}^{(0)} \right) \end{aligned} \tag{III.22}$$

In case B, we have

$$p_{i,\alpha}{}^{(B.1)} = \exp\left(i\frac{\Delta t}{2} F_L \frac{\partial}{\partial p_{i,\alpha}} \right) p_{i,\alpha}{}^{(0)} = p_{i,\alpha}{}^{(0)} + \frac{\Delta t}{2} F_L\left(r_{i,\alpha}{}^{(0)} \right) \tag{III.23}$$

$$\begin{aligned} p_{i,\alpha}{}^{(B.2)} &= \exp\left(-i\frac{\Delta t}{2}\zeta_T p_{i,\alpha} \frac{\partial}{\partial p_{i,\alpha}} \right) p_{i,\alpha}{}^{(B.1)} = p_{i,\alpha}{}^{(B.1)} \exp\left(-\frac{\Delta t}{2}\zeta_T{}^{(0)} \right) \\ &= \left[p_{i,\alpha}{}^{(0)} + \frac{\Delta t}{2} F_L\left(r_{i,\alpha}{}^{(0)} \right) \right] \exp\left(-\frac{\Delta t}{2}\zeta_T{}^{(0)} \right) \end{aligned} \tag{III.24}$$

Clearly, the equation (III.22) and (III.24) are not the same. As a result, we see that the order of terms that include differentiation with respect to the same variable are important. Which of these algorithms in this example is superior? We don't know. Both are reversible. In order to reach a conclusion about the optimal algorithm, we would have to conduct a comparative evaluation, which is beyond the scope of these introductory notes.

This brings up another interesting point. The last term in equation (III.16) actually contains two terms. Do the order of these two terms matter. Again, let us investigate by comparing the two options.

$$iL_A = \frac{1}{2}\nu_T^2\left(-1 + \frac{T(t)}{T_{set}} \right)\frac{\partial}{\partial \zeta_T} + iL_S + \frac{1}{2}\nu_T^2\left(\frac{T(t)}{T_{set}} - 1 \right)\frac{\partial}{\partial \zeta_T} \tag{III.25}$$

For case B, we switch the order of the operators and we have

$$iL_A = \frac{1}{2}\nu_T^2\left(\frac{T(t)}{T_{set}} - 1\right)\frac{\partial}{\partial\zeta_T} + iL_S + \frac{1}{2}\nu_T^2\left(-1 + \frac{T(t)}{T_{set}}\right)\frac{\partial}{\partial\zeta_T} \tag{III.26}$$

We only examine their effect on ζ_T since the other variables will be unchanged by the operations outside of L_s. In case A, we have

$$\zeta_T^{(A.1)} = \exp\left(-i\frac{\Delta t}{2}\nu_T^2\frac{\partial}{\partial\zeta_T}\right)\zeta_T^{(0)} = \zeta_T^{(0)} - \frac{\Delta t}{2}\nu_T^2 \tag{III.27}$$

$$\begin{aligned}\zeta_T^{(A.2)} &= \exp\left(i\frac{\Delta t}{2}\nu_T^2\frac{T(t)}{T_{set}}\frac{\partial}{\partial\zeta_T}\right)\zeta_T^{(A.1)} = \zeta_T^{(A.1)} + \frac{\Delta t}{2}\nu_T^2\frac{T^{(A.1)}}{T_{set}} \\ &\zeta_T^{(0)} + \frac{\Delta t}{2}\nu_T^2\left(\frac{T^{(0)}}{T_{set}} - 1\right)\end{aligned} \tag{III.28}$$

In case B, we have

$$\zeta_T^{(B.1)} = \exp\left(i\frac{\Delta t}{2}\nu_T^2\frac{T(t)}{T_{set}}\frac{\partial}{\partial\zeta_T}\right)\zeta_T^{(0)} = \zeta_T^{(0)} + \frac{\Delta t}{2}\nu_T^2\frac{T(t)}{T_{set}} \tag{III.29}$$

$$\begin{aligned}\zeta_T^{(B.2)} &= \exp\left(-i\frac{\Delta t}{2}\nu_T^2\frac{\partial}{\partial\zeta_T}\right)\zeta_T^{(B.1)} = \zeta_T^{(B.1)} - \frac{\Delta t}{2}\nu_T^2 \\ &\zeta_T^{(0)} + \frac{\Delta t}{2}\nu_T^2\left(\frac{T^{(0)}}{T_{set}} - 1\right)\end{aligned} \tag{III.30}$$

Equation (III.28) and (III.30) yield the same result so it it okay to lump them together as one term as has been done. What is the difference, in which order mattered for the momentum but not for the thermostat? The difference in these two examples is that the momentum appears in the prefactor in front of the differentiation with respect to momentum. So in fact, the two terms were nonlinear in the momentum. Since ζ_T appears in a linear manner in the terms which differentiate with respect to ζ_T, that order doesn't matter.

Having explored the effect of order, we now provide Tuckerman's choice of ordering.

$$\begin{aligned}iL = &\frac{1}{2}\left[\nu_T^2\left(\frac{T(t)}{T_{set}} - 1\right)\frac{\partial}{\partial\zeta_T} + \frac{F_L}{2}\frac{\partial}{\partial p_{i,\alpha}} - \zeta_T p_{i,\alpha}\frac{\partial}{\partial p_{i,\alpha}} + \frac{F_L}{2}\frac{\partial}{\partial p_{i,\alpha}} + \zeta_T\frac{\partial}{\partial\eta}\right] \\ &+ iL_S + \frac{1}{2}\left[\zeta_T\frac{\partial}{\partial\eta} + \frac{F_L}{2}\frac{\partial}{\partial p_{i,\alpha}} - \zeta_T p_{i,\alpha}\frac{\partial}{\partial p_{i,\alpha}} + \frac{F_L}{2}\frac{\partial}{\partial p_{i,\alpha}} + \nu_T^2\left(\frac{T(t)}{T_{set}} - 1\right)\frac{\partial}{\partial\zeta_T}\right]\end{aligned} \tag{III.31}$$

This choice is presented without justification and we assume that Tuckerman has shown that this particular choice of ordering of the terms provides a stable numerical algorithm. From our first example, we saw that the order of the two terms that contained differentiation with respect to the momentum mattered. We see that Tuckerman has addressed this issue by splitting the force term into halves again. Presumably, this choice was arrived at after the comparison of a set of different alternatives. Anyway, for our purposes, we continue with this choice. This division contains n+10 operations, since the small Liouville operator is being split into n smaller time steps.

The first operator will change only ζ_T.

$$\zeta_T{}^{(1)} = \exp\left(i\frac{\Delta t}{2}\nu_T^2\left(\frac{T^{(0)}}{T_{set}} - 1\right)\frac{\partial}{\partial \zeta_T}\right)\zeta_T{}^{(0)} = \zeta_T{}^{(0)} + \frac{\Delta t}{2}\nu_T^2\left(\frac{T^{(0)}}{T_{set}} - 1\right) \tag{III.32}$$

$$\Gamma(1) = \left[r_{i,\alpha}{}^{(1)}, p_{i,\alpha}{}^{(1)}, \eta^{(1)}, \zeta_T{}^{(1)}\right] = \left[r_{i,\alpha}{}^{(0)}, p_{i,\alpha}{}^{(0)}, \eta^{(0)}, \zeta_T{}^{(1)}\right] \tag{III.33}$$

The second, third, and fourth operators will change only momentum.

$$p_{i,\alpha}{}^{(2)} = \exp\left(i\frac{\Delta t}{2}\frac{F_L}{2}\frac{\partial}{\partial p_{i,\alpha}}\right)p_{i,\alpha}{}^{(1)} = p_{i,\alpha}{}^{(1)} + \frac{\Delta t}{4}F_L\left(r_{i,\alpha}{}^{(1)}\right) = p_{i,\alpha}{}^{(0)} + \frac{\Delta t}{4}F_L\left(r_{i,\alpha}{}^{(0)}\right) \tag{III.34}$$

$$\Gamma(2) = \left[r_{i,\alpha}{}^{(2)}, p_{i,\alpha}{}^{(2)}, \eta^{(2)}, \zeta_T{}^{(2)}\right] = \left[r_{i,\alpha}{}^{(0)}, p_{i,\alpha}{}^{(2)}, \eta^{(0)}, \zeta_T{}^{(1)}\right] \tag{III.35}$$

$$p_{i,\alpha}{}^{(3)} = \exp\left(-i\frac{\Delta t}{2}\zeta_T p_{i,\alpha}\frac{\partial}{\partial p_{i,\alpha}}\right)p_{i,\alpha}{}^{(2)} = p_{i,\alpha}{}^{(2)}\exp\left(-\frac{\Delta t}{2}\zeta_T{}^{(2)}\right) = p_{i,\alpha}{}^{(2)}\exp\left(-\frac{\Delta t}{2}\zeta_T{}^{(1)}\right) \tag{III.36}$$

$$\Gamma(3) = \left[r_{i,\alpha}{}^{(3)}, p_{i,\alpha}{}^{(3)}, \eta^{(3)}, \zeta_T{}^{(3)}\right] = \left[r_{i,\alpha}{}^{(0)}, p_{i,\alpha}{}^{(3)}, \eta^{(0)}, \zeta_T{}^{(1)}\right] \tag{III.37}$$

$$p_{i,\alpha}{}^{(4)} = \exp\left(i\frac{\Delta t}{2}\frac{F_L}{2}\frac{\partial}{\partial p_{i,\alpha}}\right)p_{i,\alpha}{}^{(3)} = p_{i,\alpha}{}^{(3)} + \frac{\Delta t}{4}F_L\left(r_{i,\alpha}{}^{(3)}\right) = p_{i,\alpha}{}^{(3)} + \frac{\Delta t}{4}F_L\left(r_{i,\alpha}{}^{(0)}\right) \tag{III.38}$$

$$\Gamma(4) = \left[r_{i,\alpha}{}^{(4)}, p_{i,\alpha}{}^{(4)}, \eta^{(4)}, \zeta_T{}^{(4)}\right] = \left[r_{i,\alpha}{}^{(0)}, p_{i,\alpha}{}^{(4)}, \eta^{(0)}, \zeta_T{}^{(1)}\right] \tag{III.39}$$

The fifth operator will change only η.

$$\eta^{(5)} = \exp\left(i\frac{\Delta t}{2}\zeta_T\frac{\partial}{\partial \eta}\right)\eta^{(4)} = \eta^{(4)} + \frac{\Delta t}{2}\zeta_T{}^{(4)} = \eta^{(0)} + \frac{\Delta t}{2}\zeta_T{}^{(1)} \tag{III.40}$$

$$\Gamma(5) = \left[r_{i,\alpha}{}^{(5)}, p_{i,\alpha}{}^{(5)}, \eta^{(5)}, \zeta_T{}^{(5)}\right] = \left[r_{i,\alpha}{}^{(0)}, p_{i,\alpha}{}^{(4)}, \eta^{(5)}, \zeta_T{}^{(1)}\right] \tag{III.41}$$

We then apply the short time operator given in Case I n times.

$$\Gamma(n+5)=\left[r_{i,\alpha}{}^{(n+5)},p_{i,\alpha}{}^{(n+5)},\eta^{(n+5)},\zeta_T{}^{(n+5)}\right]=\left[r_{i,\alpha}{}^{(n+5)},p_{i,\alpha}{}^{(n+5)},\eta^{(5)},\zeta_T{}^{(1)}\right] \tag{III.42}$$

We then go through the long time operators in the reverse order.

$$\eta^{(n+6)}=\exp\left(i\frac{\Delta t}{2}\zeta_T\frac{\partial}{\partial\eta}\right)\eta^{(n+5)}=\eta^{(n+5)}+\frac{\Delta t}{2}\zeta_T{}^{(n+5)}=\eta^{(5)}+\frac{\Delta t}{2}\zeta_T{}^{(1)} \tag{III.43}$$

$$\Gamma(n+6)=\left[r_{i,\alpha}{}^{(n+6)},p_{i,\alpha}{}^{(n+6)},\eta^{(n+6)},\zeta_T{}^{(n+6)}\right]=\left[r_{i,\alpha}{}^{(n+5)},p_{i,\alpha}{}^{(n+5)},\eta^{(n+6)},\zeta_T{}^{(1)}\right] \tag{III.44}$$

$$p_{i,\alpha}{}^{(n+7)}=\exp\left(i\frac{\Delta t}{2}\frac{F_L}{2}\frac{\partial}{\partial p_{i,\alpha}}\right)p_{i,\alpha}{}^{(n+6)}=p_{i,\alpha}{}^{(n+6)}+\frac{\Delta t}{4}F_L\left(r_{i,\alpha}{}^{(n+6)}\right)=p_{i,\alpha}{}^{(n+5)}+\frac{\Delta t}{4}F_L\left(r_{i,\alpha}{}^{(n+5)}\right) \tag{III.45}$$

$$\Gamma(n+7)=\left[r_{i,\alpha}{}^{(n+7)},p_{i,\alpha}{}^{(n+7)},\eta^{(n+7)},\zeta_T{}^{(n+7)}\right]=\left[r_{i,\alpha}{}^{(n+5)},p_{i,\alpha}{}^{(n+7)},\eta^{(n+6)},\zeta_T{}^{(1)}\right] \tag{III.46}$$

$$\begin{aligned}p_{i,\alpha}{}^{(n+8)}&=\exp\left(-i\frac{\Delta t}{2}\zeta_T p_{i,\alpha}\frac{\partial}{\partial p_{i,\alpha}}\right)p_{i,\alpha}{}^{(n+7)}=p_{i,\alpha}{}^{(n+7)}\exp\left(-\frac{\Delta t}{2}\zeta_T{}^{(n+7)}\right)\\&=p_{i,\alpha}{}^{(n+7)}\exp\left(-\frac{\Delta t}{2}\zeta_T{}^{(1)}\right)\end{aligned} \tag{III.47}$$

$$\Gamma(n+8)=\left[r_{i,\alpha}{}^{(n+8)},p_{i,\alpha}{}^{(n+8)},\eta^{(n+8)},\zeta_T{}^{(n+8)}\right]=\left[r_{i,\alpha}{}^{(n+5)},p_{i,\alpha}{}^{(n+8)},\eta^{(n+6)},\zeta_T{}^{(1)}\right] \tag{III.48}$$

$$p_{i,\alpha}{}^{(n+9)}=\exp\left(i\frac{\Delta t}{2}\frac{F_L}{2}\frac{\partial}{\partial p_{i,\alpha}}\right)p_{i,\alpha}{}^{(n+8)}=p_{i,\alpha}{}^{(n+8)}+\frac{\Delta t}{4}F_L\left(r_{i,\alpha}{}^{(n+8)}\right)=p_{i,\alpha}{}^{(n+8)}+\frac{\Delta t}{4}F_L\left(r_{i,\alpha}{}^{(n+5)}\right) \tag{III.49}$$

$$\Gamma(n+9)=\left[r_{i,\alpha}{}^{(n+9)},p_{i,\alpha}{}^{(n+9)},\eta^{(n+9)},\zeta_T{}^{(n+9)}\right]=\left[r_{i,\alpha}{}^{(n+5)},p_{i,\alpha}{}^{(n+9)},\eta^{(n+6)},\zeta_T{}^{(1)}\right] \tag{III.50}$$

$$\begin{aligned}\zeta_T{}^{(n+10)}&=\exp\left(i\frac{\Delta t}{2}\nu_T^2\left(\frac{T^{(0)}}{T_{set}}-1\right)\frac{\partial}{\partial\zeta_T}\right)\zeta_T{}^{(n+9)}=\zeta_T{}^{(n+9)}+\frac{\Delta t}{2}\nu_T^2\left(\frac{T^{(n+9)}}{T_{set}}-1\right)\\&=\zeta_T{}^{(1)}+\frac{\Delta t}{2}\nu_T^2\left(\frac{T^{(n+9)}}{T_{set}}-1\right)\end{aligned} \tag{III.51}$$

$$\Gamma(n+10)=\left[r_{i,\alpha}{}^{(n+10)},p_{i,\alpha}{}^{(n+10)},\eta^{(n+10)},\zeta_T{}^{(n+10)}\right]=\left[r_{i,\alpha}{}^{(n+5)},p_{i,\alpha}{}^{(n+9)},\eta^{(n+6)},\zeta_T{}^{(n+10)}\right] \tag{III.52}$$

So we can express this as the following algorithm. First, we compute the forces and the temperature at time 0.

$$\zeta_T^{(1)} = \zeta_T^{(0)} + \frac{\Delta t}{2}\nu_T^2\left(\frac{T^{(0)}}{T_{set}} - 1\right) \tag{III.53}$$

$$p_{i,\alpha}^{(2)} = p_{i,\alpha}^{(0)} + \frac{\Delta t}{4}F_L\left(r_{i,\alpha}^{(0)}\right) \tag{III.54}$$

$$p_{i,\alpha}^{(3)} = p_{i,\alpha}^{(2)}\exp\left(-\frac{\Delta t}{2}\zeta_T^{(1)}\right) \tag{III.55}$$

$$p_{i,\alpha}^{(4)} = p_{i,\alpha}^{(3)} + \frac{\Delta t}{4}F_L\left(r_{i,\alpha}^{(0)}\right) \tag{III.56}$$

$$\eta^{(5)} = \eta^{(0)} + \frac{\Delta t}{2}\zeta_T^{(1)} \tag{III.57}$$

We then apply the short time operator given in Case I n times. We calculate the forces at positions, $r_{i,\alpha}^{(n+5)}$, available at the end of the short time loop.

$$\eta^{(n+6)} = \eta^{(5)} + \frac{\Delta t}{2}\zeta_T^{(1)} \tag{III.58}$$

$$p_{i,\alpha}^{(n+7)} = p_{i,\alpha}^{(n+5)} + \frac{\Delta t}{4}F_L\left(r_{i,\alpha}^{(n+5)}\right) \tag{III.59}$$

$$p_{i,\alpha}^{(n+8)} = p_{i,\alpha}^{(n+7)}\exp\left(-\frac{\Delta t}{2}\zeta_T^{(1)}\right) \tag{III.60}$$

$$p_{i,\alpha}^{(n+9)} = p_{i,\alpha}^{(n+8)} + \frac{\Delta t}{4}F_L\left(r_{i,\alpha}^{(n+5)}\right) \tag{III.61}$$

We calculate the temperature.

$$\zeta_T^{(n+10)} = \zeta_T^{(1)} + \frac{\Delta t}{2}\nu_T^2\left(\frac{T^{(n+9)}}{T_{set}} - 1\right) \tag{III.62}$$

If we choose, we can combine equations (III.54) through (III.56) to yield

$$p_{i,\alpha}^{(4)} = \left[p_{i,\alpha}^{(0)} + \frac{\Delta t}{4}F_L\left(r_{i,\alpha}^{(0)}\right)\right]\exp\left(-\frac{\Delta t}{2}\zeta_T^{(1)}\right) + \frac{\Delta t}{4}F_L\left(r_{i,\alpha}^{(0)}\right) \tag{III.63}$$

Similarly, we can combine equations (III.59) through (III.61) to yield

$$p_{i,\alpha}{}^{(n+9)} = \left[p_{i,\alpha}{}^{(n+5)} + \frac{\Delta t}{4} F_L\left(r_{i,\alpha}{}^{(n+5)}\right)\right] \exp\left(-\frac{\Delta t}{2}\zeta_T{}^{(1)}\right) + \frac{\Delta t}{4} F_L\left(r_{i,\alpha}{}^{(n+5)}\right) \tag{III.64}$$

When we set $\zeta_T{}^{(1)}$ to be a constant value of zero, we obtain

$$p_{i,\alpha}{}^{(n+9)} = p_{i,\alpha}{}^{(n+5)} + \frac{\Delta t}{2} F_L\left(r_{i,\alpha}{}^{(n+5)}\right) \tag{III.65}$$

which is consistent with the result for the NVE ensemble of case II. This is useful. We only have to code up the NVT result. If we set ζ_T to zero, we have the NVE ensemble.

Case IV. NPT – two time scales – XO-RESPA

In terms of developing the reversible RESPA numerial integration algorithm, there doesn't need to be much that is different between the NVT and the NPT ensembles. However, empirically, one finds that putting all of the barostat operations in the long time step, in an analogous manner to what was done with the thermostat only works for some systems. When one generates an NPT algorithm analogous to our NVT algorithm, it has been labeled eXtended variables Outside RESPA (XO-RESPA). Martyna et al. have shown that this won't work well for NPT simulation of systems with stiff vibrating bonds, which is one of the things we are interested in. However, XO-RESPA NPT is easy to understand because it is directly analogous to the NVT case.

Regardless of our choice of RESPA technique, tor the isobaric-isothermal ensemble, the equations of motions are

$$\frac{dr_{i,\alpha}}{dt} = \frac{p_{i,\alpha}}{m_i} + \zeta_P\left(r_{i,\alpha} - R_{0,\alpha}\right) \tag{IV.1}$$

$$\frac{dp_{i,\alpha}}{dt} = F_L + F_S - \left(\zeta_T + \zeta_P\right)p_{i,\alpha} \tag{IV.2}$$

$$\frac{ds}{dt} = s\zeta_T \tag{IV.3}$$

$$\frac{d\zeta_T}{dt} = \upsilon_T^2\left(\frac{T(t)}{T_{set}} - 1\right) \tag{IV.4}$$

$$\frac{d\ell}{dt'} = \ell\zeta_P \tag{IV.5}$$

$$\frac{d\zeta_P}{dt'} = \frac{s^2}{\ell^2}\nu_P^2\frac{V(t)}{fk_BT_{set}}\left[p(t) - p_{set}\right] + \zeta_P\left(\zeta_T - \zeta_P\right) \tag{IV.6}$$

where R_0 is the center of mass of the system, defined as

$$R_{0,\alpha} = \frac{\sum_{i=1}^{N} m_i r_{i,\alpha}}{\sum_{i=1}^{N} m_i} \tag{IV.7}$$

and the system volume, V, is given by

$$V = \ell^3 V_o \tag{IV.8}$$

where V_o is an arbitrary reference volume and can be equated to the initial value of the volume, when the ℓ was initialized to unity. Also, ν_P is the controller frequency of the barostat and p is the hydrostatic pressure.

The NPT Liouville operator is

$$iL = \frac{dr_{i,\alpha}}{dt}\frac{\partial}{\partial r_{i,\alpha}} + \frac{dp_{i,\alpha}}{dt}\frac{\partial}{\partial p_{i,\alpha}} + \frac{ds}{dt}\frac{\partial}{\partial s} + \frac{d\zeta_T}{dt}\frac{\partial}{\partial \zeta_T} + \frac{d\ell}{dt}\frac{\partial}{\partial \ell} + \frac{d\zeta_P}{dt}\frac{\partial}{\partial \zeta_P} \tag{IV.9}$$

If you substitute equations (IV.1) through (IV.6) into equation (IV.9).

$$\begin{aligned} iL = &\left[\frac{p_{i,\alpha}}{m_i} + \zeta_P\left(r_{i,\alpha} - R_{0,\alpha}\right)\right]\frac{\partial}{\partial r_{i,\alpha}} + \left[F_L + F_S - \left(\zeta_T + \zeta_P\right)p_{i,\alpha}\right]\frac{\partial}{\partial p_{i,\alpha}} \\ &+ s\zeta_T\frac{\partial}{\partial s} + \upsilon_T^2\left(\frac{T(t)}{T_{set}} - 1\right)\frac{\partial}{\partial \zeta_T} + \ell\zeta_P\frac{\partial}{\partial \ell} + \left[\frac{s^2}{\ell^2}\nu_P^2\frac{V(t)}{fk_BT_{set}}\left[p(t) - p_{set}\right] + \zeta_P\left(\zeta_T - \zeta_P\right)\right]\frac{\partial}{\partial \zeta_P} \end{aligned} \tag{IV.10}$$

We will again break this Liouville operator into a short time and long time operator.

$$iL = i\frac{1}{2}L_L + iL_S + i\frac{1}{2}L_L \tag{IV.11}$$

where the symmetric short term Liouville operator is the same as has been defined before,

$$iL_S = \frac{1}{2}F_S\frac{\partial}{\partial p_{i,\alpha}} + \frac{p_{i,\alpha}}{m_i}\frac{\partial}{\partial r_{i,\alpha}} + \frac{1}{2}F_S\frac{\partial}{\partial p_{i,\alpha}} \tag{IV.12}$$

The long term Liouville operator contains everything else. All that remains to be determined is the order and splitting of terms. We take as our starting point the form that was given for the NVT case. THe key point to take from the canonical example is the way to split multiple terms in front of the same differential operator. In the NVT case, we used

$$\left(\frac{F_L}{2} - \left(\zeta_T + \zeta_P\right)p_{i,\alpha}\right)\frac{\partial}{\partial p_{i,\alpha}} = \frac{F_L}{2}\frac{\partial}{\partial p_{i,\alpha}} - \left(\zeta_T + \zeta_P\right)p_{i,\alpha}\frac{\partial}{\partial p_{i,\alpha}} + \frac{F_L}{2}\frac{\partial}{\partial p_{i,\alpha}} \tag{IV.13}$$

where the term that was of the form $q\frac{\partial}{\partial q}$ is placed in the middle and the term of the form $\frac{\partial}{\partial q}$ was split and placed on the outside. Following this model, we split the NPT terms as

$$\zeta_P\left(r_{i,\alpha} - R_{0,\alpha}\right)\frac{\partial}{\partial r_{i,\alpha}} = -\frac{\zeta_P R_{0,\alpha}}{2}\frac{\partial}{\partial r_{i,\alpha}} + \zeta_P r_{i,\alpha}\frac{\partial}{\partial r_{i,\alpha}} - \frac{\zeta_P R_{0,\alpha}}{2}\frac{\partial}{\partial r_{i,\alpha}} \tag{IV.14}$$

and

$$\left[\frac{s^2}{\ell^2}\nu_P^2\frac{V(t)}{fk_BT_{set}}\left[p(t)-p_{set}\right]+\zeta_P(\zeta_T-\zeta_P)\right]\frac{\partial}{\partial\zeta_P}=\frac{1}{2}\frac{s^2}{\ell^2}\nu_P^2\frac{V(t)}{fk_BT_{set}}\left[p(t)-p_{set}\right]\frac{\partial}{\partial\zeta_P}$$
$$+\frac{\zeta_P\zeta_T}{2}\frac{\partial}{\partial\zeta_P}-\zeta_P^2\frac{\partial}{\partial\zeta_P}+\frac{\zeta_P\zeta_T}{2}\frac{\partial}{\partial\zeta_P}+\frac{1}{2}\frac{s^2}{\ell^2}\nu_P^2\frac{V(t)}{fk_BT_{set}}\left[p(t)-p_{set}\right]\frac{\partial}{\partial\zeta_P} \qquad \text{(IV.15)}$$

where we had 3 terms of the form $q^2\frac{\partial}{\partial q}$, $q\frac{\partial}{\partial q}$ and $\frac{\partial}{\partial q}$. Following our pattern, we placed the term of the highest order in the interior of the sequence of operations.

Now we must determine where to place equation (IV.14) and (IV.15) within the total operator. Following the NVT logic, we place the operator for ζ_T first and we place the operator for ζ_P immediately after that. (The choice of which to place first was arbitrary.) This tells us where to place (IV.15). Next we place (IV.14). Because (IV.14) contains only ζ_P, it's value will only be effected by the placement relative to the operator taking the derivative with respect to ζ_P. Since that operator has been placed second, we can equivalently place (IV.14) anywhere after that. However, equation (IV.14) changes the positions and changes in position will change the forces. Since we only want to calculate forces once per time step, we need to operate on the momentum before we operate on the positions. These considerations lead to

$$iL_L=\ell\zeta_P\frac{\partial}{\partial\ell}+s\zeta_T\frac{\partial}{\partial s}-\frac{\zeta_PR_{0,\alpha}}{2}\frac{\partial}{\partial r_{i,\alpha}}+\zeta_Pr_{i,\alpha}\frac{\partial}{\partial r_{i,\alpha}}-\frac{\zeta_PR_{0,\alpha}}{2}\frac{\partial}{\partial r_{i,\alpha}}$$
$$+\frac{F_L}{2}\frac{\partial}{\partial p_{i,\alpha}}-(\zeta_T+\zeta_P)p_{i,\alpha}\frac{\partial}{\partial p_{i,\alpha}}+\frac{F_L}{2}\frac{\partial}{\partial p_{i,\alpha}}+$$
$$\frac{1}{2}\frac{s^2}{\ell^2}\nu_P^2\frac{V(t)}{fk_BT_{set}}\left[p(t)-p_{set}\right]\frac{\partial}{\partial\zeta_P}+\frac{\zeta_P\zeta_T}{2}\frac{\partial}{\partial\zeta_P}-\zeta_P^2\frac{\partial}{\partial\zeta_P}+\frac{\zeta_P\zeta_T}{2}\frac{\partial}{\partial\zeta_P} \qquad \text{(IV.16)}$$
$$+\frac{1}{2}\frac{s^2}{\ell^2}\nu_P^2\frac{V(t)}{fk_BT_{set}}\left[p(t)-p_{set}\right]\frac{\partial}{\partial\zeta_P}+\nu_T^2\left(\frac{T(t)}{T_{set}}-1\right)\frac{\partial}{\partial\zeta_T}$$

This is the form that we will use for the term on the far-right of equation (IV.11). We will use the reverse order of terms in equation (IV.16) for the first term on the RHS of equation (IV.11).

Equation (IV.16) contains 14 operations. (Thus equation (IV.11) contains n+28 operations. We now apply them in sequence to the initial state,
$\Gamma(0)=\left[r_{i,\alpha}{}^{(0)},p_{i,\alpha}{}^{(0)},s^{(0)},\zeta_T{}^{(0)},\ell^{(0)},\zeta_P{}^{(0)}\right]$.

First we calculate $V\left(\ell^{(0)}\right)$, $T\left(p_{i,\alpha}{}^{(0)}\right)$, $F\left(r_{i,\alpha}{}^{(0)}\right)$, $p\left(r_{i,\alpha}{}^{(0)},p_{i,\alpha}{}^{(0)},F_L\left(r_{i,\alpha}{}^{(0)}\right)\right)$, and $R_{0,\alpha}{}^{(0)}$.

$$\zeta_T{}^{(1)}=\zeta_T{}^{(0)}+\frac{\Delta t}{2}\nu_T^2\left(\frac{T^{(0)}}{T_{set}}-1\right) \qquad \text{(IV.17)}$$

$$\zeta_P^{(2)} = \zeta_P^{(0)} + \frac{\Delta t}{4}\frac{s^2}{\ell^2}\nu_P^2 \frac{V^{(0)}}{fk_B T_{set}}\left[p^{(0)} - p_{set}\right] \tag{IV.18}$$

$$\zeta_P^{(3)} = \zeta_P^{(2)} \exp\left(\frac{\Delta t}{4}\zeta_T^{(1)}\right) \tag{IV.19}$$

$$\zeta_P^{(4)} = \frac{\zeta_P^{(3)}}{1 + \frac{\Delta t}{2}\zeta_P^{(3)}} \tag{IV.20}$$

$$\zeta_P^{(5)} = \zeta_P^{(4)} \exp\left(\frac{\Delta t}{4}\zeta_T^{(1)}\right) \tag{IV.21}$$

$$\zeta_P^{(6)} = \zeta_P^{(5)} + \frac{\Delta t}{4}\frac{s^2}{\ell^2}\nu_P^2 \frac{V^{(0)}}{fk_B T_{set}}\left[p^{(0)} - p_{set}\right] \tag{IV.22}$$

$$p_{i,\alpha}^{(7)} = p_{i,\alpha}^{(0)} + \frac{\Delta t}{4}F_L\left(r_{i,\alpha}^{(0)}\right) \tag{IV.23}$$

$$p_{i,\alpha}^{(8)} = p_{i,\alpha}^{(7)} \exp\left(-\frac{\Delta t}{2}\left(\zeta_T^{(1)} + \zeta_P^{(6)}\right)\right) \tag{IV.24}$$

$$p_{i,\alpha}^{(9)} = p_{i,\alpha}^{(8)} + \frac{\Delta t}{4}F_L\left(r_{i,\alpha}^{(0)}\right) \tag{IV.25}$$

$$r_{i,\alpha}^{(10)} = r_{i,\alpha}^{(0)} - \frac{\Delta t}{4}\zeta_P^{(6)} R_{0,\alpha}^{(0)} \tag{IV.26}$$

$$r_{i,\alpha}^{(11)} = r_{i,\alpha}^{(10)} \exp\left(\frac{\Delta t}{2}\zeta_P^{(6)}\right) \tag{IV.27}$$

Calculate new $R_{0,\alpha}^{(11)}$.

$$r_{i,\alpha}^{(12)} = r_{i,\alpha}^{(11)} - \frac{\Delta t}{4}\zeta_P^{(6)} R_{0,\alpha}^{(11)} \tag{IV.28}$$

$$s^{(13)} = s^{(0)} \exp\left(\frac{\Delta t}{2}\zeta_T^{(1)}\right) \tag{IV.29}$$

$$\ell^{(14)} = \ell^{(0)} \exp\left(\frac{\Delta t}{2} \zeta_P{}^{(6)} \right) \tag{IV.30}$$

We then apply the short time operator given in Case I n times. We have the positions and momenta, $r_{i,\alpha}{}^{(n+14)}$ and $p_{i,\alpha}{}^{(n+14)}$ available at the end of the short time loop.

$$\ell^{(n+15)} = \ell^{(14)} \exp\left(\frac{\Delta t}{2} \zeta_P{}^{(6)} \right) \tag{IV.31}$$

$$s^{(n+16)} = s^{(13)} \exp\left(\frac{\Delta t}{2} \zeta_T{}^{(1)} \right) \tag{IV.32}$$

Calculate new $R_{0,\alpha}{}^{(n+14)}$.

$$r_{i,\alpha}{}^{(n+17)} = r_{i,\alpha}{}^{(n+14)} - \frac{\Delta t}{4} \zeta_P{}^{(6)} R_{0,\alpha}{}^{(n+14)} \tag{IV.33}$$

$$r_{i,\alpha}{}^{(n+18)} = r_{i,\alpha}{}^{(n+17)} \exp\left(\frac{\Delta t}{2} \zeta_P{}^{(6)} \right) \tag{IV.34}$$

Calculate new $R_{0,\alpha}{}^{(n+18)}$.

$$r_{i,\alpha}{}^{(n+19)} = r_{i,\alpha}{}^{(n+18)} - \frac{\Delta t}{4} \zeta_P{}^{(6)} R_{0,\alpha}{}^{n+(18)} \tag{IV.35}$$

Calculate $F_L\left(r_{i,\alpha}{}^{(n+19)}\right)$.

$$p_{i,\alpha}{}^{(n+20)} = p_{i,\alpha}{}^{(n+14)} + \frac{\Delta t}{4} F_L\left(r_{i,\alpha}{}^{(n+19)}\right) \tag{IV.36}$$

$$p_{i,\alpha}{}^{(n+21)} = p_{i,\alpha}{}^{(n+20)} \exp\left(-\frac{\Delta t}{2} \left(\zeta_T{}^{(1)} + \zeta_P{}^{(6)} \right) \right) \tag{IV.37}$$

$$p_{i,\alpha}{}^{(n+22)} = p_{i,\alpha}{}^{(n+21)} + \frac{\Delta t}{4} F_L\left(r_{i,\alpha}{}^{(n+19)}\right) \tag{IV.38}$$

Calculate $V\left(\ell^{(14)}\right)$ and $p\left(r_{i,\alpha}{}^{(n+19)}, p_{i,\alpha}{}^{(n+22)}, F_L\left(r_{i,\alpha}{}^{(n+19)}\right)\right)$.

$$\zeta_P{}^{(n+23)} = \zeta_P{}^{(6)} + \frac{\Delta t}{4} \frac{s^2}{\ell^2} \nu_P^2 \frac{V\left(\ell^{(14)}\right)}{f k_B T_{set}} \left[p^{(n+22)} - p_{set} \right] \tag{IV.39}$$

$$\zeta_P^{(n+24)} = \zeta_P^{(n+23)} \exp\left(\frac{\Delta t}{4} \zeta_T^{(1)} \right) \tag{IV.40}$$

$$\zeta_P^{(n+25)} = \frac{\zeta_P^{(n+24)}}{1 + \frac{\Delta t}{2} \zeta_P^{(n+24)}} \tag{IV.41}$$

$$\zeta_P^{(n+26)} = \zeta_P^{(n+25)} \exp\left(\frac{\Delta t}{4} \zeta_T^{(1)} \right) \tag{IV.42}$$

$$\zeta_P^{(n+27)} = \zeta_P^{(n+26)} + \frac{\Delta t}{4} \frac{s^2}{\ell^2} \nu_P^2 \frac{V\left(\ell^{(14)}\right)}{f k_B T_{set}} \left[p^{(n+22)} - p_{set} \right] \tag{IV.43}$$

$$\zeta_T^{(n+28)} = \zeta_T^{(1)} + \frac{\Delta t}{2} \nu_T^2 \left(\frac{T^{(n+22)}}{T_{set}} - 1 \right) \tag{IV.44}$$

So this algorithm requires that we evaluate the volume, temperature, forces and pressure only once per time step, at the final values of position and momentum. It does require us to evaluate the center of mass of the system four times per long time step, which is not computationally expensive, but does require that we use an MPI_ALLREDUCE communication subroutine to perform the interprocessor summation.

Case V. NPT – two time scales - XI-RESPA

Martyna et al. have shown that for NPT simulation of systems with stiff vibrating bonds, one needs to put part of the barostat operation in the reference (short time scale) system. This division of operations has been labeled eXtended variables Inside RESPA (XI-RESPA). Martyna et al. have shown that this works well for NPT simulation of systems with stiff vibrating bonds, which is one of the things we are interested in. Regardless of our choice of RESPA technique, tor the isobaric-isothermal ensemble, the equations of motions and Liouville operator are the same as that given in Case IV, up through equations (IV.11). Therefore, we start our analysis here with equation (V.12), assuming equations (V.1) through (V.11) are identical to equations (IV.1) through (IV.11).

In a system with stiff vibrating bonds the pressure is a strong function of the position of atoms comprising the bond. Since these positions change rapidly in the short time step, it would be unwise to use a long time step for the barostat based on the instantaneous positions. As a result, we have to move some portion of the barostat inside the reference (short time) system. Another way to state the same thing is that changing the space dilation variable changes the separation between atoms. In a stiff vibrator, the energy is very sensitive to changes in position, therefore, the space dilation variable must be integrated on the short time step. What has been done in the past by Martyna *et al.* is to move the space-dilation term inside the short time system and leave the space dilation momentum term in the long time step. The justification for this is unknown. Perhaps there is empirical evidence that this method suffices. Owing to time constraints that prevent us from doing a full blown study of the algorithmic alternatives, we obediently follow their example here.

We begin our discussion with the molecular-level definition of pressure,

$$p = \frac{1}{3}\sum_{\alpha=1}^{3} p_{\alpha\alpha} \tag{V.12}$$

Each diagonal component of the pressure tensor is defined in terms of a kinetic contribution and a potential contribution

$$p_{\alpha\alpha} = \frac{1}{V}\left[\sum_{i=1}^{N}\frac{p_{i,\alpha}^2}{m_i} + \sum_{i=1}^{N} r_{i,\alpha}F_{i,\alpha}\right] \tag{V.13}$$

In a two time step algorithm, the pressure can be written as

$$p_{\alpha\alpha} = \frac{1}{V}\left[\sum_{i=1}^{N}\frac{p_{i,\alpha}^2}{m_i} + \sum_{i=1}^{N} r_{i,\alpha}F_{i,\alpha}^{S} + \sum_{i=1}^{N} r_{i,\alpha}F_{i,\alpha}^{L}\right] \tag{V.14}$$

where we have explicitly separated out the forces associated with the short and long time scales. It will pe instructive to write the pressure as

$$p_{\alpha\alpha} = p_{\alpha\alpha}^{S} + p_{\alpha\alpha}^{L} \tag{V.15}$$

where

$$p_{\alpha\alpha}^{S} = \frac{1}{V}\left[\sum_{i=1}^{N}\frac{p_{i,\alpha}^{2}}{m_i} + \sum_{i=1}^{N} r_{i,\alpha}F_{i,\alpha}^{S}\right] \tag{V.16}$$

$$p_{\alpha\alpha}^{L} = \frac{1}{V}\left[\sum_{i=1}^{N} r_{i,\alpha}F_{i,\alpha}^{L}\right] \tag{V.17}$$

We have enough terms now that we are going to break the short time Liouville operator into terms.

$$iL_S = \frac{1}{2}iL_S^{ext} + iL_S^{\text{int}} + \frac{1}{2}iL_S^{ext} \tag{V.18}$$

Following what was done in the NVT case, the interior portion of the short time operator has the form

$$iL_S^{\text{int}} = \frac{1}{2}\frac{p_{i,\alpha}}{m_i}\frac{\partial}{\partial r_{i,\alpha}} + \zeta_P r_{i,\alpha}\frac{\partial}{\partial r_{i,\alpha}} + \frac{1}{2}\frac{p_{i,\alpha}}{m_i}\frac{\partial}{\partial r_{i,\alpha}} \tag{V.19}$$

Here we are going to leave the center of mass contribution to the time derivative of the position in the long time loop since the center of mass term is not expected to change during the short time steps. (It only changes during the application of periodic boundary conditions in the long time step.) We complete the short time operator by surrounding the interior terms with the short time momentum, space dilation, and short time pressure momentum terms.

$$iL_S^{ext} = F_S\frac{\partial}{\partial p_{i,\alpha}} + \ell\zeta_P\frac{\partial}{\partial \ell} + \frac{s^2}{\ell^2}\nu_P^2\frac{V(t)}{fk_BT_{set}}p^S(t)\frac{\partial}{\partial \zeta_P} \tag{V.20}$$

We now look to the long-time operator. The long term Liouville operator contains everything else. All that remains to be determined is the order and splitting of terms. We take as our starting point the form that was given for the NPT XO RESPA case, which will be the same here except for the fact that some of the terms are now located in the short time operator. We have

$$\begin{aligned} iL_L = {} & s\zeta_T\frac{\partial}{\partial s} - \zeta_P R_{0,\alpha}\frac{\partial}{\partial r_{i,\alpha}} + \frac{F_L}{2}\frac{\partial}{\partial p_{i,\alpha}} - (\zeta_T + \zeta_P)p_{i,\alpha}\frac{\partial}{\partial p_{i,\alpha}} + \frac{F_L}{2}\frac{\partial}{\partial p_{i,\alpha}} + \\ & \frac{1}{2}\frac{s^2}{\ell^2}\nu_P^2\frac{V(t)}{fk_BT_{set}}\left[p^L(t) - p_{set}\right]\frac{\partial}{\partial \zeta_P} + \frac{\zeta_P\zeta_T}{2}\frac{\partial}{\partial \zeta_P} - \zeta_P^2\frac{\partial}{\partial \zeta_P} + \frac{\zeta_P\zeta_T}{2}\frac{\partial}{\partial \zeta_P} \\ & + \frac{1}{2}\frac{s^2}{\ell^2}\nu_P^2\frac{V(t)}{fk_BT_{set}}\left[p^L(t) - p_{set}\right]\frac{\partial}{\partial \zeta_P} + \nu_T^2\left(\frac{T(t)}{T_{set}} - 1\right)\frac{\partial}{\partial \zeta_T} \end{aligned} \tag{V.21}$$

This is the form that we will use for the term on the far-right of equation (IV.11). We will use the reverse order of terms in equation (V.21) for the first term on the RHS of equation (IV.21).

There are eleven operations in (V.21). We now apply the operations in sequence to the initial state, $\Gamma(0) = \left[r_{i,\alpha}{}^{(0)}, p_{i,\alpha}{}^{(0)}, s^{(0)}, \zeta_T{}^{(0)}, \ell^{(0)}, \zeta_P{}^{(0)} \right]$.

First we calculate $V\left(\ell^{(0)}\right)$, $T\left(p_{i,\alpha}{}^{(0)}\right)$, $F\left(r_{i,\alpha}{}^{(0)}\right)$, $p\left(r_{i,\alpha}{}^{(0)}, p_{i,\alpha}{}^{(0)}, F_L\left(r_{i,\alpha}{}^{(0)}\right)\right)$, and $R_{0,\alpha}{}^{(0)}$.

$$\zeta_T{}^{(1)} = \zeta_T{}^{(0)} + \frac{\Delta t}{2} \nu_T^2 \left(\frac{T^{(0)}}{T_{set}} - 1 \right) \tag{V.22}$$

$$\zeta_P{}^{(2)} = \zeta_P{}^{(0)} + \frac{\Delta t}{4} \frac{s^2}{\ell^2} \nu_P^2 \frac{V^{(0)}}{f k_B T_{set}} \left[p^{L(0)} - p_{set} \right] \tag{V.23}$$

$$\zeta_P{}^{(3)} = \zeta_P{}^{(2)} \exp\left(\frac{\Delta t}{4} \zeta_T{}^{(1)} \right) \tag{V.24}$$

$$\zeta_P{}^{(4)} = \frac{\zeta_P{}^{(3)}}{1 + \frac{\Delta t}{2} \zeta_P{}^{(3)}} \tag{V.25}$$

$$\zeta_P{}^{(5)} = \zeta_P{}^{(4)} \exp\left(\frac{\Delta t}{4} \zeta_T{}^{(1)} \right) \tag{V.26}$$

$$\zeta_P{}^{(6)} = \zeta_P{}^{(5)} + \frac{\Delta t}{4} \frac{s^2}{\ell^2} \nu_P^2 \frac{V^{(0)}}{f k_B T_{set}} \left[p^{L(0)} - p_{set} \right] \tag{V.27}$$

$$p_{i,\alpha}{}^{(7)} = p_{i,\alpha}{}^{(0)} + \frac{\Delta t}{4} F_L\left(r_{i,\alpha}{}^{(0)} \right) \tag{V.28}$$

$$p_{i,\alpha}{}^{(8)} = p_{i,\alpha}{}^{(7)} \exp\left(-\frac{\Delta t}{2} \left(\zeta_T{}^{(1)} + \zeta_P{}^{(6)} \right) \right) \tag{V.29}$$

$$p_{i,\alpha}{}^{(9)} = p_{i,\alpha}{}^{(8)} + \frac{\Delta t}{4} F_L\left(r_{i,\alpha}{}^{(0)} \right) \tag{V.30}$$

$$r_{i,\alpha}{}^{(10)} = r_{i,\alpha}{}^{(0)} - \frac{\Delta t}{2} \zeta_P{}^{(6)} R_{0,\alpha}{}^{(0)} \tag{V.31}$$

$$s^{(11)} = s^{(0)} \exp\left(\frac{\Delta t}{2} \zeta_T{}^{(1)} \right) \tag{V.32}$$

We then apply the short time operator given in equation (V.18) *n* times. We are renumbering the superscripts for the interior loop. There are nine operations in the short time operator.

$$\zeta_P{}^{(1)} = \zeta_P{}^{(0)} + \frac{\Delta t}{2}\frac{s^2}{\ell^2}\nu_P^2\frac{V^{(0)}}{fk_BT_{set}}p^{S(0)} \tag{V.33}$$

$$\ell^{(2)} = \ell^{(0)}\exp\left(\frac{\Delta t}{2}\zeta_P{}^{(1)}\right) \tag{V.34}$$

$$p_{i,\alpha}{}^{(3)} = \exp\left(i\frac{\Delta t}{2}F_S\frac{\partial}{\partial p_{i,\alpha}}\right)p_{i,\alpha}{}^{(0)} = p_{i,\alpha}{}^{(0)} + \frac{\Delta t}{2}F_S(r_{i,\alpha}{}^{(0)}) \tag{V.35}$$

$$r_{i,\alpha}{}^{(4)} = \exp\left(i\frac{\Delta t}{2}\frac{p_{i,\alpha}}{m_i}\frac{\partial}{\partial r_{i,\alpha}}\right)r_{i,\alpha}{}^{(0)} = r_{i,\alpha}{}^{(0)} + \frac{\Delta t}{2}\frac{p_{i,\alpha}{}^{(3)}}{m_i} \tag{V.36}$$

$$r_{i,\alpha}{}^{(5)} = \exp\left(i\Delta t\zeta_P r_{i,\alpha}\frac{\partial}{\partial r_{i,\alpha}}\right)r_{i,\alpha}{}^{(4)} = r_{i,\alpha}{}^{(4)}\exp\left(\Delta t\zeta_P{}^{(1)}\right) \tag{V.37}$$

$$r_{i,\alpha}{}^{(6)} = \exp\left(i\frac{\Delta t}{2}\frac{p_{i,\alpha}}{m_i}\frac{\partial}{\partial r_{i,\alpha}}\right)r_{i,\alpha}{}^{(5)} = r_{i,\alpha}{}^{(5)} + \frac{\Delta t}{2}\frac{p_{i,\alpha}{}^{(3)}}{m_i} \tag{V.38}$$

Calculate short range forces.

$$p_{i,\alpha}{}^{(7)} = \exp\left(i\frac{\Delta t}{2}F_S\frac{\partial}{\partial p_{i,\alpha}}\right)p_{i,\alpha}{}^{(3)} = p_{i,\alpha}{}^{(3)} + \frac{\Delta t}{2}F_S(r_{i,\alpha}{}^{(6)}) \tag{V.39}$$

$$\ell^{(8)} = \ell^{(2)}\exp\left(\frac{\Delta t}{2}\zeta_P{}^{(1)}\right) \tag{V.40}$$

Calculate short range pressure and new volume.

$$\zeta_P{}^{(9)} = \zeta_P{}^{(1)} + \frac{\Delta t}{2}\frac{s^2}{\ell^2}\nu_P^2\frac{V^{(8)}}{fk_BT_{set}}p^{S(6)} \tag{V.41}$$

At the end of the internal loop, we have the positions and momenta, $r_{i,\alpha}{}^{(9n+11)}$, $p_{i,\alpha}{}^{(9n+11)}$, $\ell^{(9n+11)}$ and $\zeta_P{}^{(9n+11)}$ available. We finish the long-time loop in reverse order.

$$s^{(9n+12)} = s^{(11)} \exp\left(\frac{\Delta t}{2} \zeta_T{}^{(1)} \right) \tag{V.42}$$

Calculate new $R_{0,\alpha}{}^{(9n+11)}$. This won't have changed since the system conserves mass until the application of PBCs, but check this in the code.

$$r_{i,\alpha}{}^{(9n+13)} = r_{i,\alpha}{}^{(9n+11)} - \frac{\Delta t}{2} \zeta_P{}^{(6)} R_{0,\alpha}{}^{(9n+11)} \tag{V.43}$$

Calculate $F_L\left(r_{i,\alpha}{}^{(9n+13)}\right)$.

$$p_{i,\alpha}{}^{(9n+14)} = p_{i,\alpha}{}^{(9n+11)} + \frac{\Delta t}{4} F_L\left(r_{i,\alpha}{}^{(9n+13)}\right) \tag{V.44}$$

$$p_{i,\alpha}{}^{(9n+15)} = p_{i,\alpha}{}^{(9n+14)} \exp\left(-\frac{\Delta t}{2} \left(\zeta_T{}^{(1)} + \zeta_P{}^{(9n+11)} \right) \right) \tag{V.45}$$

$$p_{i,\alpha}{}^{(9n+16)} = p_{i,\alpha}{}^{(9n+15)} + \frac{\Delta t}{4} F_L\left(r_{i,\alpha}{}^{(9n+13)}\right) \tag{V.46}$$

Calculate $V\left(\ell^{(9n+11)}\right)$ and $p^L\left(r_{i,\alpha}{}^{(9n+13)}, p_{i,\alpha}{}^{(9n+16)}, F_L\left(r_{i,\alpha}{}^{(9n+13)}\right)\right)$ and $T\left(p_{i,\alpha}{}^{(9n+16)}\right)$.

$$\zeta_P{}^{(9n+17)} = \zeta_P{}^{(6)} + \frac{\Delta t}{4} \frac{s^2}{\ell^2} \nu_P^2 \frac{V\left(\ell^{(9n+11)}\right)}{f k_B T_{set}} \left[p^{L(9n+16)} - p_{set} \right] \tag{V.47}$$

$$\zeta_P{}^{(9n+18)} = \zeta_P{}^{(9n+17)} \exp\left(\frac{\Delta t}{4} \zeta_T{}^{(1)} \right) \tag{V.48}$$

$$\zeta_P{}^{(9n+19)} = \frac{\zeta_P{}^{(9n+18)}}{1 + \frac{\Delta t}{2} \zeta_P{}^{(9n+18)}} \tag{V.49}$$

$$\zeta_P{}^{(9n+20)} = \zeta_P{}^{(9n+19)} \exp\left(\frac{\Delta t}{4} \zeta_T{}^{(1)} \right) \tag{V.50}$$

$$\zeta_P{}^{(9n+21)} = \zeta_P{}^{(9n+20)} + \frac{\Delta t}{4} \frac{s^2}{\ell^2} \nu_P^2 \frac{V\left(\ell^{(9n+11)}\right)}{f k_B T_{set}} \left[p^{L(9n+16)} - p_{set} \right] \tag{V.51}$$

$$\zeta_T{}^{(9n+22)} = \zeta_T{}^{(1)} + \frac{\Delta t}{2} \nu_T^2 \left(\frac{T^{(9n+16)}}{T_{set}} - 1 \right) \tag{V.52}$$

So this algorithm requires that we evaluate the volume, temperature, forces and pressure only once per time step, at the final values of position and momentum. It may require us to evaluate the center of mass of the system twice per long time step, which is not computationally expensive, but does require that we use an MPI_ALLREDUCE communication subroutine to perform the interprocessor summation. It also requires calculation of the pressure in the short time loop which requires a call to MPI_ALLREDUCE.

Case VI. NVE – three time scales

The extension to three time scales, the so-called "double r-RESPA" method is straightforward. The equations of motion are

$$\frac{dr_{i,\alpha}}{dt} = \frac{p_{i,\alpha}}{m_i} \tag{VI.1}$$

$$\frac{dp_{i,\alpha}}{dt} = -\frac{\partial E_L}{\partial r_{i,\alpha}} - \frac{\partial E_M}{\partial r_{i,\alpha}} - \frac{\partial E_S}{\partial r_{i,\alpha}} = F_L + F_M + F_S \tag{VI.2}$$

where the subscripts S, M and L indicate forces that need to be updated on **S**hort, **M**edium and **L**ong time scales respectively. The Liouville operator is

$$iL = \frac{p_{i,\alpha}}{m_i}\frac{\partial}{\partial r_{i,\alpha}} + F_L\frac{\partial}{\partial p_{i,\alpha}} + F_M\frac{\partial}{\partial p_{i,\alpha}} + F_S\frac{\partial}{\partial p_{i,\alpha}} \tag{VI.3}$$

We group everything that is going to be solved in the short time scale together in the Liouville operator for the reference system.

$$iL = iL_L + iL_M + iL_S \tag{VI.4}$$

where

$$iL_L = F_L\frac{\partial}{\partial p_{i,\alpha}} \tag{VI.5}$$

$$iL_M = F_M\frac{\partial}{\partial p_{i,\alpha}} \tag{VI.6}$$

$$iL_S = \frac{p_{i,\alpha}}{m_i}\frac{\partial}{\partial r_{i,\alpha}} + F_S\frac{\partial}{\partial p_{i,\alpha}} \tag{VI.7}$$

We then split the long time and medium time Liouville operator into a symmetric distribution about the short time Liouville operator.

$$iL = \frac{iL_L}{2} + \frac{iL_M}{2} + iL_S + \frac{iL_M}{2} + \frac{iL_L}{2} \tag{VI.8}$$

The discrete time operator is then

$$G(\Delta t) = \exp\left(\frac{iL_L \Delta t}{2}\right)\left\{\exp\left(\frac{iL_M}{2}\frac{\Delta t}{m}\right)\left[\exp\left(iL_S \frac{\Delta t}{nm}\right)\right]^n \exp\left(\frac{iL_M}{2}\frac{\Delta t}{m}\right)\right\}^m \exp\left(\frac{iL_L \Delta t}{2}\right) \qquad \text{(VI.9)}$$

The procedure is then analogous to what was done in the two-time-scale r-RESPA. We have a loop over m steps in which the medium-time operations are performed. Inside that we have a loop over n steps in which the short-time operations are performed.

Case VII. NVT – three time scales

The equations of motion are

$$\frac{dr_{i,\alpha}}{dt} = \frac{p_{i,\alpha}}{m_i} \tag{VII.1}$$

$$\frac{dp_{i,\alpha}}{dt} = F_L + F_M + F_S - \zeta_T p_{i,\alpha} \tag{VII.2}$$

$$\frac{d\eta}{dt} = \zeta_T \tag{VII.3}$$

$$\frac{d\zeta_T}{dt} = \upsilon_T^2 \left(\frac{T(t)}{T_{set}} - 1 \right) \tag{VII.4}$$

The Liouville operator is split as

$$iL = iL_L + iL_M + iL_S \tag{VII.5}$$

where all the thermostating is done in the long-time scale so that

$$iL_L = \zeta_T \frac{\partial}{\partial \eta} + \frac{F_L}{2} \frac{\partial}{\partial p_{i,\alpha}} - \zeta_T p_{i,\alpha} \frac{\partial}{\partial p_{i,\alpha}} + \frac{F_L}{2} \frac{\partial}{\partial p_{i,\alpha}} + \nu_T^2 \left(\frac{T(t)}{T_{set}} - 1 \right) \frac{\partial}{\partial \zeta_T} \tag{VII.6}$$

$$iL_M = F_M \frac{\partial}{\partial p_{i,\alpha}} \tag{VII.7}$$

$$iL_S = \frac{p_{i,\alpha}}{m_i} \frac{\partial}{\partial r_{i,\alpha}} + F_S \frac{\partial}{\partial p_{i,\alpha}} \tag{VII.8}$$

The order of operations in equation (VI.2) is given for the first application of the long-time operator. The second application of the long-time operator will of course have the terms in the reverse order.

The procedure is a straightforward integration of Case III (NVT two-time scales) and Case V (NVE three-time scales).

Case VIII. NPT – three time scales

The equations of motion are the same as in the two time scale case except that the force is now split into three terms.

$$\frac{dp_{i,\alpha}}{dt} = F_L + F_M + F_S - \left(\zeta_T + \zeta_P\right) p_{i,\alpha} \tag{VIII.1}$$

and the pressure is split into three terms

$$p_{\alpha\alpha} = \frac{1}{V}\left[\sum_{i=1}^{N}\frac{p_{i,\alpha}^2}{m_i} + \sum_{i=1}^{N} r_{i,\alpha} F_{i,\alpha}^S + \sum_{i=1}^{N} r_{i,\alpha} F_{i,\alpha}^M + \sum_{i=1}^{N} r_{i,\alpha} F_{i,\alpha}^L\right] \tag{VIII.2}$$

The Liouville operator is split as

$$iL = iL_L + iL_M + iL_S \tag{VIII.3}$$

The short time operator and the long time operator are the same as that given in the NPT-XO-RESPA or NPT-XI-RESPA sections. Additionally, we now have an middle time scale operator. In the case of NPT-XO-RESPA, the middle time scale operator has the form

$$iL_M = F_M \frac{\partial}{\partial p_{i,\alpha}} \tag{VIII.4}$$

In the case of NPT-XI-RESPA, the middle time scale operator has the form

$$iL_M = F_M \frac{\partial}{\partial p_{i,\alpha}} + \frac{s^2}{\ell^2}\nu_P^2 \frac{V(t)}{f k_B T_{set}} p^M(t) \frac{\partial}{\partial \zeta_P} \tag{VIII.5}$$

The procedure is a straightforward integration of Case IV or V (NPT two-time scales) and Case VI (NVE three-time scales).

Case IX. NPH – three time scales

The NPH ensemble can be simulated by using the NPT algorithm and setting the thermostat frequency to zero.

The NVT ensemble can be simulated by using the NPT algorithm and setting the barostat frequency to zero.

The NVE ensemble can be simulated by using the NPT algorithm and setting both the thermostat and the barostat frequency to zero.

As a result, we only need to code up the NPT algorithm.