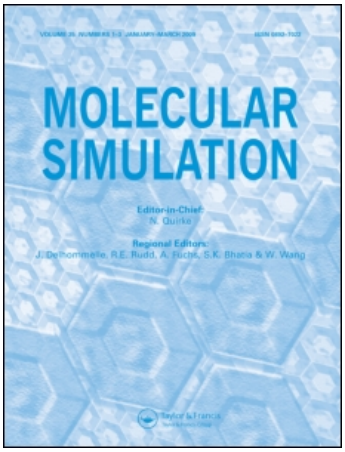

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A generalized Hamiltonian-based algorithm for rigorous equilibrium molecular dynamics simulation in the isobaric-isothermal ensemble

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A generalized Hamiltonian-based algorithm for rigorous equilibrium molecular dynamics simulation in the isobaric–isothermal ensemble

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In this work, we employ a Hamiltonian-based procedure to derive a generalized Nosé barostat, which generates trajectories that rigorously satisfy the statistical mechanical isobaric–isothermal (NpT) ensemble. This generalized algorithm, unlike Nosé's original NpT algorithm, maintains rigor in the presence of (i) a non-zero system momentum and (ii) non-negligible external forces. The generalized algorithm reduces to the conventional Nosé NpT algorithm when neither condition is satisfied. The key element of the generalized algorithm is that the thermostat and barostat are applied only to those degrees of freedom that contribute to the temperature and pressure, which excludes, e.g. the total system momentum. We show that the generalized algorithm satisfies the two criteria for rigor (Hamiltonian and non-Hamiltonian) that exist in the literature. Finally, we provide some numerical examples demonstrating the success of the generalized algorithm.

Keywords: Molecular dynamics; NpT; Isobaric–isothermal ensemble; Hamiltonian

1. Introduction

One of the most common algorithms for equilibrium molecular dynamics (EMD) simulation in the canonical (NVT) ensemble is known as the Nosé-Hoover thermostat, which introduces a time-dilation variable in an extended system [1,2]. This thermostat has been successfully used in thousands of published reports of EMD and non-equilibrium molecular dynamics (NEMD) simulations. It is also known that the Nosé-Hoover thermostat does not rigorously generate trajectories in the NVT ensemble in the presence of either (i) a non-zero total system momentum or (ii) non-negligible external forces [3]. Recently, Keffer *et al.* have presented a generalized NVT algorithm, which maintains rigor if either or both of these constraints is violated [4,5]. This generalized NVT algorithm is very practical since, in many modern simulations, a material is simulated in the presence of an external force. For example, the simulation of a fluid adsorbed in a nanoporous material typically involves dynamic fluid molecules in the presence of a static adsorbent framework, which imposes an external force on the fluid—see, e.g. [6].

Nosé also derived an NpT algorithm, in which he introduced a space dilation variable. This new variable acts as a barostat [7]. This algorithm again rigorously generates trajectories in the NpT ensemble only if the two conditions above are met. In this work, we generalize Nosé's NpT algorithm to maintain rigor in the presence of either or both (i) a non-zero total system momentum or (ii) non-negligible external forces.

We are aided in this derivation by the development of a Hamiltonian-based procedure for generating EMD and NEMD algorithms. Many MD algorithms exist today, which do not have a Hamiltonian. Certainly, it is possible to generate a rigorous algorithm without a Hamiltonian. One of the historical examples is the SLLOD algorithm of Evans and Morris, which has been rigorously shown to model shear flow in NEMD systems, but which does not have a Hamiltonian in the general case [8,9]. However, we

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feel that there is an advantage in a procedure that does begin with a Hamiltonian because it provides a direct link between well-known continuum mechanics and the molecular-level mechanics of the simulation. An example of the value of this Hamiltonian-based procedure already exists: the development of proper-SLLOD, which extends the rigor of the SLLOD algorithm from shear flows to arbitrary, homogeneous flows [10,11]. This work demonstrates that the existence of a methodical procedure can be useful in generating a rigorous NpT algorithm.

The remainder of the paper is organized as follows. In Section 2, we apply our procedure to develop a generalized NpT algorithm. We prove that this algorithm is rigorous in a statistical mechanical sense using the two criteria that exist in the literature, namely the Hamiltonian-based criterion of Nosé [1] and the non-Hamiltonian criterion of Tuckerman *et al.* [12,13]. In Section 3, we present a numerical example that clearly demonstrates the rigor of the new algorithm. In Section 4, we provide a brief discussion of the relationship of this NpT algorithm to other NpT algorithms in the literature. In Section 5, we present our conclusions.

2. The generalized NpT EMD algorithm

In discussing NpT algorithms, it is important to recognize that there are several applicable manners of classification. First, there are algorithms that allow isotropic fluctuations of the system volume [7], which are appropriate for equilibrium MD simulations of fluids, and there are "fully flexible" algorithms that allow for arbitrary changes in the size and shape of the simulation volume [14], which are appropriate for simulation of solid materials. However, in general, any approach can be modified to work for either isotropic or fully flexible systems—see, e.g. [15,16]. Second, NpT algorithms can be categorized based on whether they use the atomic [2,7,15,16] or molecular [17] formulation of the virial contribution to the pressure. Third, NpT algorithms can be categorized as to whether they account for holonomic constraints [17] or not [7] (e.g. whether bonds are fixed or flexible). Again, any given algorithm can, in general, be modified to simulate properly rigid or flexible molecules—see, e.g. [15]. In this paper, we focus on an NpT algorithm allowing isotropic fluctuations of flexible molecules using the atomic virial.

To derive the rigorous and generalized NpT algorithm, we follow the same 6-step procedure that was used to generalize the NVT algorithm [4,5]. The steps are as follows:

1. Define the Hamiltonian in terms of the peculiar and Center-of-Mass (COM) coordinates in the time- and space-dilated frame of reference.
2. Express the Hamiltonian in terms of the laboratory coordinates in the time- and space-dilated frame of reference.
3. Derive the equations of motion in terms of the laboratory coordinates in the time- and space-dilated frame of reference, relying on the symplectic relationship between the Hamiltonian and the equations of motion in the frame of reference.
4. Identify a non-symplectic transformation from the peculiar and COM coordinates in the time-dilated frame of reference to the peculiar and COM coordinates in the physical frame of reference.
5. Express the equations of motion for the peculiar and COM coordinates in the physical frame of reference.
6. Prove that the resulting equations of motion rigorously generate trajectories in the appropriate ensemble.

To begin, we label the laboratory position and momentum of particle i in dimension α, respectively, as $r'_{i,\alpha}$ and $p'_{i.\alpha}$. The prime indicates that these variables refer to the dilated frame of reference. The mass of particle i is labeled m'_i. The peculiar position, $\rho'_{i,\alpha}$ and momentum, $\pi'_{i,\alpha}$, are defined with respect to the COM position and COM momentum,

$$\rho'_{i,\alpha} \equiv r'_{i,\alpha} - R'_\alpha \tag{2.1a}$$

$$\frac{\pi'_{i,\alpha}}{m'_i} \equiv \frac{p'_{i,\alpha}}{m'_i} - \frac{P'_\alpha}{M'} \tag{2.1b}$$

where the COM momentum, P'_α, is

$$P'_\alpha \equiv \sum_{i=1}^{N} p'_{i,\alpha} \tag{2.2a}$$

the COM position, $1R'_\alpha$, is

$$R'_\alpha \equiv \frac{\sum_{i=1}^{N} m'_i r'_{i,\alpha}}{M'} \tag{2.2b}$$

and the total mass of the system, M', is

$$M' \equiv \sum_{i=1}^{N} m'_i \tag{2.2c}$$

As a result of the definitions in equations (2.1) and (2.2), it is clear that the following constraints apply to the peculiar position and momentum:

$$\sum_{i=1}^{N} \pi'_{i,\alpha} = 0 \tag{2.3a}$$

$$\sum_{i=1}^{N} m'_i \rho'_{i,\alpha} = 0 \tag{2.3b}$$

In other words, only $N-1$ of the particles have independent degrees of freedom.

The first step of the procedure is to write the Hamiltonian in terms of the peculiar and COM coordinates. This is useful because, in the these coordinates, it becomes clear where the time- and space-dilation variables should appear. We then insert the time- and space-dilation variables only in the peculiar

coordinates. The Hamiltonian is

$$H'_{\mathrm{NpT}} = \frac{1}{2}\sum_{i=1}^{N}\sum_{\alpha=1}^{3}\frac{\pi'^2_{i,\alpha}}{s^2\ell_\alpha^2 m'_i} + \frac{1}{2}\sum_{\alpha=1}^{3}\frac{P'^2_\alpha}{M'} + U_{\mathrm{int}}(\rho'_{i,\alpha}\ell_\alpha - \rho'_{j,\alpha}\ell_\alpha) + U_{\mathrm{ext}}(\rho'_{i,\alpha}\ell_\alpha, R'_\alpha) + \frac{1}{2Q_s}p_s^2 + fk_{\mathrm{B}}T_{\mathrm{set}}\ln(s) + \sum_{\alpha=1}^{3}\frac{p^2_{\ell,\alpha}}{2Q_{\ell,\alpha}} + p_{\mathrm{set}}V_{\mathrm{o}}\prod_{\alpha=1}^{3}\ell_\alpha \tag{2.4}$$

where s is the time-dilation variable, ℓ *or* ℓ_α is space-dilation variable in direction α, p_s is the momentum of the time-dilation variable, $p_{\ell,\alpha}$ is the momentum of the space-dilation variable in the α direction, Q_s is the inertial mass of the time-dilation variable, $Q_{\ell,\alpha}$ is the inertial mass of the space-dilation variable in the α direction, f is the number of degrees of freedom in the system, k_{B} is Boltzmann's constant, T_{set} is the set temperature and p_{set} is the set pressure. The potential energy due to internal interactions, U_{int}, is typically only a function of the peculiar positions. The potential energy due to external interactions, U_{ext}, is typically a function of both the peculiar and COM positions. The variable, V_{o}, is an arbitrary reference volume, which will not appear in the equations of motion, but relates the volume in the laboratory frame of reference to the volume in the time- and space-dilated frame of reference through

$$V(t) = V_{\mathrm{o}}\prod_{\alpha=1}^{3}\ell_\alpha. \tag{2.5}$$

The Hamiltonian has eight terms that represent, from left to right, the peculiar kinetic energy, the COM kinetic energy, the internal potential energy, the external potential energy, the kinetic energy of the time-dilation variable, the potential energy of the time-dilation variable, the kinetic energy of the space-dilation variable and the potential energy of the space-dilation variable. Also note that the intermolecular/intramolecular potential energy is not assumed to have an explicit volume dependence to account for the fact that commonly employed long-range mean-field corrections to the potential energy are functions of density, which changes with time in the NpT ensemble. This approximation can be applied at any point in the derivation, so we can wait to apply it until after the equations of motion have been derived. We also note that we have chosen to work in terms of three space-dilation variables, instead of one volume-dilation variable, so that we recognize the analogy between the space- and time-dilation variables.

It is again crucial to note that only the peculiar coordinates are scaled by the time- and space-dilation variables. The temperature of this system will be defined using the equipartition theorem. The velocity that appears in the equipartition theorem must be the peculiar velocity. In other words, the time-dilation variable is our thermostat and must act on the kinetic energy that corresponds to the temperature of the system. Since COM kinetic energy does not change the temperature of the system, it should not be thermostatted. Similarly, when we impose the space-dilation variable, it must act solely on the peculiar position and momentum, because it is the peculiar properties that are used to define the pressure. Since the COM coordinates should not change the pressure of our system, they should not be influenced by the barostat. This is the fundamental difference between Nosé's original NpT algorithm and this generalized algorithm. In Nosé's original algorithm, the laboratory positions and momenta were thermostatted and barostatted. As a result, the original algorithm is only valid in the absence of any COM motion or any external forces that might cause COM motion.

The second step of the procedure is to rewrite the Hamiltonian in terms of the laboratory coordinates. This is necessary because the symplectic relationship between the Hamiltonian and the equations of motion exists in the laboratory coordinates. Thus, we can write the Hamiltonian as

$$H'_{\mathrm{NpT}} = \frac{1}{2}\sum_{i=1}^{N}\sum_{\alpha=1}^{3}\frac{p'^2_{i,\alpha}}{s^2\ell_\alpha^2 m'_i} + \frac{1}{2}\sum_{\alpha=1}^{3}\left(1 - \frac{1}{s^2\ell_\alpha^2}\right)\times\frac{P'^2_\alpha}{M'} + U_{\mathrm{int}}(\rho'_{i,\alpha}\ell_\alpha - \rho'_{j,\alpha}\ell_\alpha) + U_{\mathrm{ext}}(r'_{i,\alpha}\ell_\alpha - R'_\alpha\ell_\alpha, R'_\alpha) + \frac{1}{2Q_s}p_s^2 + fk_{\mathrm{B}}T_{\mathrm{set}}\ln(s) + \sum_{\alpha=1}^{3}\frac{p^2_{\ell,\alpha}}{2Q_{\ell,\alpha}} + p_{\mathrm{set}}V_{\mathrm{o}}\prod_{\alpha=1}^{3}\ell_\alpha \tag{2.6}$$

In this equation, we understand that the COM properties are explicit functions of the laboratory coordinates, as given in equation (2.2).

The third step of the procedure is to derive the equations of motion for the laboratory coordinates and dilation variables in the dilated frame of reference. This is straightforward due to the symplectic nature of the Hamiltonian for these variables in this frame of reference:

$$\frac{\mathrm{d}r'_{i,\alpha}}{\mathrm{d}t'} = \frac{\partial H'_{\mathrm{NpT}}}{\partial p'_{i,\alpha}} = \frac{p'_{i,\alpha}}{s^2\ell_\alpha^2 m'_i} + \left(1 - \frac{1}{s^2\ell_\alpha^2}\right)\frac{P'_\alpha}{M'} \tag{2.7a}$$

$$\frac{\mathrm{d}p'_{i,\alpha}}{\mathrm{d}t'} = -\frac{\partial H'_{\mathrm{NpT}}}{\partial r'_{i,\gamma}}$$

$$= -\sum_{\substack{j=1\\ j\neq i}}^{N}\left[\frac{\partial U_{\mathrm{int}}}{\partial(\rho'_{i,\alpha}\ell_\alpha - \rho'_{j,\alpha}\ell_\alpha)}\frac{\partial(\rho'_{i,\alpha}\ell_\alpha - \rho'_{j,\alpha}\ell_\alpha)}{\partial r'_{i,\alpha}}\right]$$

$$- \sum_{j=1}^{N}\frac{\partial U_{\mathrm{ext}}}{\partial(\rho'_{j,\alpha}\ell_\alpha)}\frac{\partial(\rho'_{j,\alpha}\ell_\alpha)}{\partial r'_{i,\alpha}} - \frac{\partial U_{\mathrm{ext}}}{\partial R'_{i,\alpha}}\frac{\partial R'_{i,\alpha}}{\partial r'_{i,\alpha}}$$

$$= \ell_\alpha F^{\mathrm{int}}_{i,\alpha} + \ell_\alpha F^{\mathrm{ext,pec}}_{i,\alpha} - \ell_\alpha\frac{m'_i}{M'}\sum_{j=1}^{N}F^{\mathrm{ext,pec}}_{j,\alpha}$$

$$+ \frac{m'_i}{M'}F^{\mathrm{ext,COM}}_{\alpha} \tag{2.7b}$$

$$\frac{\mathrm{d}s}{\mathrm{d}t'} = \frac{\partial H'_{\mathrm{NpT}}}{\partial p_s} = \frac{p_s}{Q_s} \tag{2.7c}$$

$$\frac{\mathrm{d}p_s}{\mathrm{d}t'} = -\frac{\partial H'_{\mathrm{NpT}}}{\partial s}$$

$$= \sum_{i=1}^{N}\sum_{\alpha=1}^{3}\frac{p'^2_{i,\alpha}}{s^3\ell^2_\alpha m'_i} - \frac{1}{s^3\ell^2_\alpha}\sum_{\alpha=1}^{3}\frac{P'^2_\alpha}{M} - \frac{f k_{\mathrm{B}}T_{\mathrm{set}}}{s} \tag{2.7d}$$

$$\frac{\mathrm{d}\ell_\alpha}{\mathrm{d}t'} = \frac{\partial H'_{\mathrm{NpT}}}{\partial p_{\ell,\alpha}} = \frac{p_{\ell,\alpha}}{Q_{\ell,\alpha}} \tag{2.7e}$$

$$\frac{\mathrm{d}p_{l,\alpha}}{\mathrm{d}t'} = -\frac{\partial H'_{\mathrm{NpT}}}{\partial \ell_\alpha}$$

$$= \sum_{i=1}^{N}\sum_{\alpha=1}^{3}\frac{p'^2_{i,\alpha}}{s^2\ell^3_\alpha m'_i} - \sum_{\alpha=1}^{3}\frac{1}{s^2\ell^3_\alpha}\frac{P'^2_\alpha}{M'}$$

$$- \sum_{i=1}^{N}\frac{\partial U_{\mathrm{int}}}{\partial(r'_{i,\alpha}\ell_\alpha)}\frac{\partial(r'_{i,\alpha}\ell_\alpha)}{\partial\ell_\alpha}$$

$$- \sum_{i=1}^{N}\frac{\partial U_{\mathrm{ext}}}{\partial(\rho'_{i\alpha}\ell_\alpha)}\frac{\partial(\rho'_{i\alpha}\ell_\alpha)}{\partial\ell_\alpha} - p_{\mathrm{set}}V_{\mathrm{o}}\prod_{\substack{\beta=1\\ \alpha\neq\beta}}^{3}\ell_\beta$$

$$= \sum_{i=1}^{N}\sum_{\alpha=1}^{3}\frac{p'^2_{i,\alpha}}{s^2\ell^3_\alpha m'_i} - \sum_{\alpha=1}^{3}\frac{1}{s^2\ell^3_\alpha}\frac{P'^2_\alpha}{M'}$$

$$+ \sum_{i=1}^{N}F^{\mathrm{int}}_{i,\alpha}r'_{i,\alpha} + \sum_{i=1}^{N}F^{\mathrm{ext,pec}}_{i,\alpha}\rho'_{i\alpha}$$

$$- p_{\mathrm{set}}V_{\mathrm{o}}\prod_{\substack{\beta=1\\ \alpha\neq\beta}}^{3}\ell_\beta \tag{2.7f}$$

where we have used the chain rule for differentiation and the facts that the peculiar and COM positions are functions of all of the laboratory positions,

$$\frac{\partial\rho'_{i,\alpha}}{\partial r'_{j,\beta}} = \delta_{ij}\delta_{\alpha\beta} - \frac{m'_j}{M'}\delta_{\alpha\beta} \tag{2.8a}$$

$$\frac{\partial R'_\alpha}{\partial r'_{i,\beta}} = \frac{m'_i}{M'}\delta_{\alpha\beta} \tag{2.8b}$$

$$\frac{\partial\left(\rho'_{i,\alpha} - \rho'_{j,\alpha}\right)}{\partial r'_{k,\beta}} = \delta_{ik}\delta_{\alpha\beta} - \frac{m'_k}{M'}\delta_{\alpha\beta} - \delta_{jk}\delta_{\alpha\beta}$$

$$+ \frac{m'_k}{M'}\delta_{\alpha\beta} = \left(\delta_{ik} - \delta_{jk}\right)\delta_{\alpha\beta} \tag{2.8c}$$

We have also defined new forces to simplify the notation,

$$F'^{\mathrm{int}}_{i,\alpha} = -\sum_{\substack{j=1\\ j\neq i}}^{N}\frac{\partial U_{\mathrm{int}}\left(\rho'_{i,\alpha} - \rho'_{j,\alpha}\right)}{\partial\left(\rho'_{i,\alpha} - \rho'_{j,\alpha}\right)} \tag{2.9a}$$

$$F'^{\mathrm{ext,pec}}_{i,\alpha} = -\frac{\partial U_{\mathrm{ext}}\left(\rho'_{i,\alpha}, R'_\alpha\right)}{\partial\rho'_{i,\alpha}} \tag{2.9b}$$

$$F'^{\mathrm{ext,COM}}_{\alpha} = -\frac{\partial U_{\mathrm{ext}}\left(\rho'_{i,\alpha}, R'_\alpha\right)}{\partial R'_\alpha} \tag{2.9c}$$

The fourth step of the procedure is to identify the transformation from the peculiar and COM coordinates in the mathematical frame of reference to the peculiar and COM coordinates in the physical frame of reference. The change of variables for the dilation variables is one of convenience:

$$\mathrm{d}t = \frac{1}{s}\mathrm{d}t' \tag{2.10a}$$

$$m_i = m'_i \tag{2.10b}$$

$$\rho_{i,\alpha} = \ell_\alpha\rho'_{i,\alpha} \tag{2.10c}$$

$$\pi_{i,\alpha} = \frac{\pi'_{i,\alpha}}{s\ell_\alpha} \tag{2.10d}$$

$$R_\alpha = R'_\alpha \tag{2.10e}$$

$$P_\alpha = P'_\alpha \tag{2.10f}$$

$$\eta_T = s \tag{2.10g}$$

$$\zeta_T = \frac{p_s}{Q_s} \tag{2.10h}$$

$$\eta_{P,\alpha} = \ell_\alpha \tag{2.10i}$$

$$\zeta_{P,\alpha} = \frac{s}{\ell_\alpha}\frac{p_{\ell,\alpha}}{Q_{\ell,\alpha}} \tag{2.10j}$$

The Hamiltonian in terms of the peculiar and COM coordinates in the physical frame of reference is

$$H_{\mathrm{NpT}} = \frac{1}{2}\sum_{i=1}^{N}\sum_{\alpha=1}^{3}\frac{\pi_{i,\alpha}^2}{m_i} + \frac{1}{2}\sum_{\alpha=1}^{3}\frac{P_\alpha^2}{M} + U_{\mathrm{int}}\left(\rho_{i,\alpha}-\rho_{j,\alpha}\right) + U_{\mathrm{ext}}\left(\rho_{i,\alpha},R_\alpha\right) + \frac{fk_{\mathrm{B}}T_{\mathrm{set}}}{2\nu_T^2}\zeta_T^2 + fk_{\mathrm{B}}T_{\mathrm{set}}\ln\left(\eta_T\right) + \sum_{\alpha=1}^{3}\frac{\eta_{P,\alpha}^2}{\eta_T^2}\frac{fk_{\mathrm{B}}T_{\mathrm{set}}}{2\nu_{P,\alpha}^2}\zeta_{P,\alpha}^2 + p_{\mathrm{set}}V_{\mathrm{o}}\prod_{\alpha=1}^{3}\eta_{P,\alpha} \quad (2.11)$$

where we have replaced the inertial masses of the thermostat and barostat with controller frequencies (units of Hz) that have the advantage of being system size independent:

$$\nu_T \equiv \sqrt{\frac{fk_{\mathrm{B}}T_{\mathrm{set}}}{Q_s}} \quad (2.12a)$$

$$\upsilon_{P,\alpha} = \sqrt{\frac{fk_{\mathrm{B}}T_{\mathrm{set}}}{Q_{\ell,\alpha}}} \quad (2.12b)$$

The fifth step of the procedure is to write the equations of motion in terms of the peculiar and COM coordinates in the physical frame of reference. The derivation is given in Appendix A. The resulting equations of motion are

$$\frac{\mathrm{d}\rho_{i,\alpha}}{\mathrm{d}t} = \frac{\pi_{i,\alpha}}{m_i} + \rho_{i,\alpha}\zeta_{P,\alpha} \quad (2.13a)$$

$$\frac{\mathrm{d}\pi_{i,\alpha}}{\mathrm{d}t} = F_{i,\alpha}^{\mathrm{int}} + F_{i,\alpha}^{\mathrm{ext,pec}} - \frac{m_i'}{M'}\sum_{j=1}^{N}F_{j,\alpha}^{\mathrm{ext,pec}} - \pi_{i,\alpha}(\zeta_T+\zeta_{P,\alpha}) \quad (2.13b)$$

$$\frac{\mathrm{d}R_\alpha}{\mathrm{d}t} = \eta_T\frac{P_\alpha}{M} \quad (2.13c)$$

$$\frac{\mathrm{d}P_\alpha}{\mathrm{d}t} = \eta_T F_\alpha^{\mathrm{ext,COM}} \quad (2.13d)$$

$$\frac{\mathrm{d}\eta_T}{\mathrm{d}t} = \eta_T\zeta_T \quad (2.13e)$$

$$\frac{\mathrm{d}\zeta_T}{\mathrm{d}t} = \nu_T^2\left(\frac{T(t)}{T_{\mathrm{set}}}-1\right) \quad (2.13f)$$

$$\frac{\mathrm{d}\eta_{P,\alpha}}{\mathrm{d}t} = \eta_{P,\alpha}\zeta_{P,\alpha} \quad (2.13g)$$

$$\frac{\mathrm{d}\zeta_{P,\alpha}}{\mathrm{d}t} = \frac{\eta_T^2}{\eta_{P,\alpha}^2}\frac{\nu_{P,\alpha}^2V(t)}{fk_{\mathrm{B}}T_{\mathrm{set}}}(p_{\alpha\alpha}(t)-p_{\mathrm{set}}) + \zeta_{P,\alpha}\zeta_T - \zeta_{P,\alpha}^2 \quad (2.13h)$$

where the temperature and the $\alpha\alpha$ component of the pressure tensor, $p_{\alpha\alpha}$, are defined through generalized equipartition theorems [18] as

$$T(t) = \frac{1}{fk_{\mathrm{B}}}\sum_{i=1}^{N}\frac{\pi_{i,\alpha}^2}{m_i} \quad (2.14a)$$

$$p_{\alpha\alpha}(t) = \frac{1}{V(t)}\left[\sum_{i=1}^{N}\frac{\pi_{i,\alpha}^2}{m_i} + \sum_{i=1}^{N}(F_{i,\alpha}^{in}+F_{i,\alpha}^{\mathrm{ext,pec}})\rho_{i,\alpha}\right] \quad (2.14b)$$

The sixth and final step of the procedure is to prove that the equations of motion generate trajectories in the isobaric–isothermal (NpT) ensemble. We provide the analytical details of the proof in Appendix B using both Nosé's Hamiltonian method [3] and the non-Hamiltonian method of Tuckerman *et al.* [11,12]. Note again that the $N-1$ independent peculiar coordinates will never be conserved, thus, preventing any deviation due to an additional constraint.

To conclude our derivation of the NpT equations of motion, we present the equations when all three of the space-dilation variables are the same. (This does not mean that we have a cubic simulation volume, only that the relative volume changes are the same in each dimension of the unit cell.) In order to derive these equations, we can repeat the six-step procedure outlined above. When the derivation is complete, we have the following equations of motion:

$$\frac{\mathrm{d}\rho_{i,\alpha}}{\mathrm{d}t} = \frac{\pi_{i,\alpha}}{m_i} + \rho_{i,\alpha}\zeta_P \quad (2.15a)$$

$$\frac{\mathrm{d}\pi_{i,\alpha}}{\mathrm{d}t} = F_{i,\alpha}^{\mathrm{int}} + F_{i,\alpha}^{\mathrm{ext,pec}} - \frac{m_i'}{M'}\sum_{j=1}^{N}F_{j,\alpha}^{\mathrm{ext,pec}} - \pi_{i,\alpha}(\zeta_T+\zeta_P) \quad (2.15b)$$

$$\frac{\mathrm{d}R_\alpha}{\mathrm{d}t} = \eta_T\frac{P_\alpha}{M} \quad (2.15c)$$

$$\frac{\mathrm{d}P_\alpha}{\mathrm{d}t} = \eta_T F_\alpha^{\mathrm{ext,COM}} \quad (2.15d)$$

$$\frac{\mathrm{d}\eta_T}{\mathrm{d}t} = \eta_T\zeta_T \quad (2.15e)$$

$$\frac{\mathrm{d}\zeta_T}{\mathrm{d}t} = \nu_T^2\left(\frac{T(t)}{T_{\mathrm{set}}}-1\right) \quad (2.15f)$$

$$\frac{\mathrm{d}\eta_P}{\mathrm{d}t} = \eta_P\zeta_P \quad (2.15g)$$

$$\frac{\mathrm{d}\zeta_P}{\mathrm{d}t} = \frac{\eta_T^2}{\eta_P^2}\frac{\nu_P^2V(t)}{fk_{\mathrm{B}}T_{\mathrm{set}}}(p(t)-p_{\mathrm{set}}) + \zeta_p\zeta_T - \zeta_P^2 \quad (2.15h)$$

where

$$p(t) = \frac{1}{3}\sum_{\alpha=1}^{3}p_{\alpha\alpha}(t) \quad (2.16)$$

At this point, it is appropriate to point out several features of this generalized NpT algorithm. It reduces to our previous generalized NVT algorithm in the absence of a barostat, i.e. when ($\eta_p = 1$ and when $\zeta_p = 0$ [4,5]. It is

equivalent to Nosé's NpT algorithm [7] when there is no COM momentum and no external forces. It is equivalent to the Nosé–Hoover NVT algorithm when there is no barostat, no COM momentum, and no external forces [1,2]. However, in its most general form, the algorithm is new and different from any existing NpT algorithm. To our knowledge, it is the only MD NpT algorithm that has been proven to generate rigorous trajectories in the NpT ensemble in the presence of (i) non-zero COM momentum and (ii) non-negligible external forces. The only way for the thermostat to become active is if the instantaneous temperature is not equal to the set temperature. Likewise, the only way for the barostat to become active is if the instantaneous pressure is not equal to the set pressure. The additional terms in the barostat account for the fact that once active (i.e. $\zeta_p \neq 0$), there are additional contributions to the barostat momentum evolution necessary to maintain a consistent connection to Hamiltonian mechanics.

3. Numerical examples

In this section, we present the results of six simulations. In the first three, we used the equations of motion given by the conventional Nosé NpT algorithm [7]. In the second three simulations, we used the equations of motion given by the generalized algorithm, as presented in equation (2.15). For each algorithm, we explore three cases: (i) zero total linear momentum and no external forces, (ii) non-zero total linear momentum and no external forces, (iii) zero initial total linear momentum and an external force. Our results show that both the original and generalized algorithm generate the same results for case (i), in which both algorithms are equivalent. However, only the generalized algorithm generates the same results for cases (ii) and (iii).

We performed EMD simulations of 1000 Lennard–Jones particles ($\sigma = 3.822$ Å, $\varepsilon/k_B = 137.0$ K, molecular weight = 16.042) at a molar volume of 392.62 Å^3/molecule and a temperature of 350 K. The timestep was 2 fs and, after equilibration, data was collected for 0.2 ns. The thermostat frequency was 10^{-5} fs^{-1}. A r-RESPA scheme was implemented using the Liouville operator formalism as described by Tuckerman *et al.* [19] For case (ii), in which we had a non-zero total linear momentum, the system translated at a uniform velocity of 10 Å fs^{-1}. For case (iii), we inserted a "super gravity" external force, of the form $-m_i g*$, with acceleration 9.81×10^{-8} Å fs^{-2}. We used a large value of $g*$ to demonstrate clearly the effect of an external force on the simulation trajectory.

In figure 1, we present the average temperature, pressure and self-diffusivity of the six simulations. The temperature is normalized by the set temperature, 350 K. The pressure is normalized by the value taken from the Lennard–Jones equation of state [20], which should describe this state point accurately. The self-diffusivity is normalized by the average of the self-diffusivity calculated from case (i) for both the original and generalized algorithms.

First, from figure 1, we see that both the original and the generalized algorithms yield reasonable results for case (i), as they should. We also see that the presence of a uniform translation (case (ii)) or a uniform acceleration (case (iii)) does not affect the thermodynamic state of the simulated system, when one uses the generalized algorithm, as indicated by the fact that we obtain the same thermodynamic and transport properties in all three cases. The conventional algorithm fails in cases (ii) and (iii). In case (ii), the conventional algorithm defines a temperature based on the kinetic energy. Since, this kinetic energy contains uniform translation, the actual "true" temperature of the simulation is something else. As a result, all of the other calculated properties are incorrect. In case (iii), the thermostat tries to slow the effect of the uniform acceleration of the system, resulting in clearly aphysical behavior.

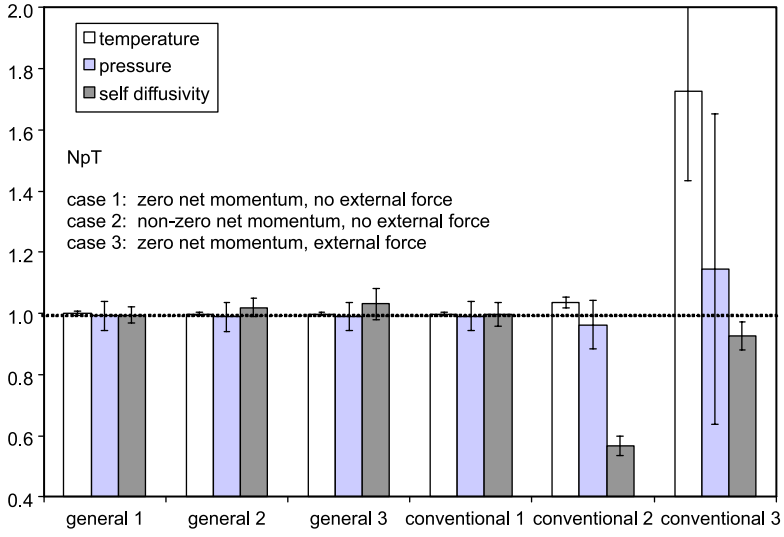

Figure 1. Comparison of conventional and generalized NpT algorithms for three cases.

4. Discussion

It is useful at this point to provide a brief discussion of the relationship between this new NpT algorithm and other NpT algorithms in the literature. There are numerous NpT algorithms, including that of Hoover [2], Melchionna *et al.* [15] and Martyna *et al.* [16]. In 2001, Tuckerman *et al.* published a comparison of these three NpT algorithms [12] using non-Hamiltonian criteria for rigor. They conclude that only the algorithm of Martyna *et al.* the so-called MTK NpT algorithm, rigorously generates trajectories in the NpT ensemble in either the presence or absence of external forces. The MTK algorithm as originally derived and presented in reference [16] is not necessarily rigorous in the presence of non-zero system momentum or external forces. The MTK with a single Nosé–Hoover thermostat reduces to the Nosé–Hoover NVT algorithm in the absence of the barostat. Since it is well established, that the Nosé–Hoover NVT is not rigorous in the presence of non-zero total momentum or external forces [3], the MTK algorithm with a single thermostat is likewise not rigorous under those conditions. In the original MTK NpT paper, they do suggest that a chain of Nosé–Hoover thermostats [21] be used to overcome problems associated with a non-zero total momentum without an external force. In Tuckerman's subsequent analysis [12], the MTK algorithm is presented with Nosé–Hoover chain of thermostats. Tuckerman *et al.* state that the use of Nosé–Hoover chains can modify the distribution so that one obtains correct distributions, despite the fact that the COM momentum is thermostatted [12]. In this work, we showed that the root of the inability of the conventional Nosé NVT or NpT algorithms to work in the presence of non-zero system momentum or external forces was due to the application of the thermostat and barostat to the COM coordinates. At this time, it is not clear to us how the use of a Nosé–Hoover chain of thermostats allows one to thermostat COM degrees of freedom and obtain rigorous trajectories.

In this work, we have not employed any kind of chain thermostat. As a result, we have shown that chain thermostats are not necessary to obtain rigorous trajectories in either the NVT or the NpT ensembles. We feel that there are some practical advantages with the algorithm outlined here. First, the new NpT algorithm has a Hamiltonian and the behavior of the system is entirely due to Hamiltonian mechanics. Therefore, we maintain a strong connection to Hamiltonian-based statistical mechanics. Second, the nature of our solution—namely the thermostatting and barostatting of only the peculiar degrees of freedom—is a very natural and logical way to avoid the historical problems associated with non-zero system momentum and external forces. Third, we have explicitly separated the internal and external forces in our algorithm, making it very clear how each term contributes. Fourth, we have an unambiguous definition of the temperature and pressure of the system in equation based on peculiar coordinates (2.14). These features make this new algorithm not only rigorous but unambiguous in its application.

5. Conclusions

In this work, we have used a Hamiltonian-based procedure to generalize the Nosé NpT algorithm so that it is capable of rigorously generating trajectories in the NpT ensemble in the presence of either (i) a non-zero total system momentum or (ii) non-negligible external forces. We have proven that the generalized algorithm is rigorous in a statistical mechanical sense using the two criteria that exist in the literature, namely the Hamiltonian-based criterion of Nosé [1] and the non-Hamiltonian criterion of Tuckerman *et al.* [12,13]. We have provided a numerical example, which clearly illustrates that the generalized algorithm generates correct thermodynamic and transport properties regardless of whether the two constraints listed above are satisfied.

This Hamiltonian-based procedure has now been successfully used to (i) generalize the SLLOD algorithm to maintain rigor in NEMD simulation of arbitrary homogeneous flows [10,11], (ii) to generalize the Nosé–Hoover thermostat [4,5], and to generalize the Nosé NpT algorithm. We believe that this Hamiltonian-based procedure has creative potential to develop new simulation algorithms of systems previously inaccessible to MD.

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Appendix A

In this appendix, we derive the equations of motion for the NpT ensemble in terms of the peculiar and COM coordinates in the physical frame of reference. Using equation (2.10a), we can write the time derivative of property q in terms of our transformed time as

$$\frac{\mathrm{d}q}{\mathrm{d}t} = \frac{\mathrm{d}q}{\mathrm{d}t'}\frac{\mathrm{d}t'}{\mathrm{d}t} = s\frac{\mathrm{d}q}{\mathrm{d}t'} \tag{A.1}$$

As a result, equation (2.7) can be written in terms of the new time as

$$\frac{\mathrm{d}r'_{i,\alpha}}{\mathrm{d}t} = s\frac{\mathrm{d}r'_{i,\alpha}}{\mathrm{d}t'} = \frac{p'_{i,\alpha}}{s\ell^2_\alpha m'_i} + \left(s - \frac{1}{s\ell^2_\alpha}\right)\frac{P'_\alpha}{M'} \tag{A.2a}$$

$$\frac{\mathrm{d}p'_{i,\alpha}}{\mathrm{d}t} = s\frac{\mathrm{d}p'_{i,\alpha}}{\mathrm{d}t'}$$

$$= s\ell_\alpha F^{\mathrm{int}}_{i,\alpha} + s\ell_\alpha F^{\mathrm{ext,pec}}_{i,\alpha}$$

$$- s\ell_\alpha \frac{m'_i}{M'}\sum_{j=1}^{N} F^{\mathrm{ext,pec}}_{j,\alpha} + s\frac{m'_i}{M'}F^{\mathrm{ext,COM}}_{\alpha} \quad \text{(A.2b)}$$

$$\frac{\mathrm{d}s}{\mathrm{d}t} = s\frac{\mathrm{d}s}{\mathrm{d}t'} = s\frac{p_s}{Q_s} \quad \text{(A.2c)}$$

$$\frac{\mathrm{d}p_s}{\mathrm{d}t} = s\frac{\mathrm{d}p_s}{\mathrm{d}t'}$$

$$= \sum_{i=1}^{N}\sum_{\alpha=1}^{3}\frac{p'^2_{i,\alpha}}{s^2\ell^2_\alpha m'_i} - \frac{1}{s^2\ell^2_\alpha}\sum_{\alpha=1}^{3}\frac{P'^2_\alpha}{M} - fk_{\mathrm{B}}T_{\mathrm{set}} \quad \text{(A.2d)}$$

$$\frac{\mathrm{d}\ell_\alpha}{\mathrm{d}t} = s\frac{\mathrm{d}\ell_\alpha}{\mathrm{d}t'} = s\frac{p_{\ell,\alpha}}{Q_{\ell,\alpha}} \quad \text{(A.2e)}$$

$$\frac{\mathrm{d}p_{\ell,\alpha}}{\mathrm{d}t} = \sum_{i=1}^{N}\sum_{\alpha=1}^{3}\frac{p'^2_{i,\alpha}}{s\ell^3_\alpha m'_i} - \sum_{\alpha=1}^{3}\frac{1}{s\ell^3_\alpha}\frac{P'^2_\alpha}{M'} + s\sum_{i=1}^{N}F^{\mathrm{in}}_{i,\alpha}r'_{i,\alpha}$$

$$+ s\sum_{i=1}^{N}F^{\mathrm{ext,pec}}_{i,\alpha}\rho'_{i,\alpha} - sp_{\mathrm{set}}V_{\mathrm{o}}\prod_{\substack{\beta=1\\ \alpha\neq\beta}}^{3}\ell_\beta \quad \text{(A.2f)}$$

Next, we differentiate equation (2.10) and substitute into it equations (2.1) and (2.2) to obtain

$$\frac{\mathrm{d}\rho_{i,\alpha}}{\mathrm{d}t} = \frac{\mathrm{d}\ell_\alpha\rho'_{i,\alpha}}{\mathrm{d}t}$$

$$= \ell_\alpha\left(\frac{\mathrm{d}r'_{i,\alpha}}{\mathrm{d}t} - \frac{\mathrm{d}R'_\alpha}{\mathrm{d}t}\right) + (r'_{i,\alpha} - R'_\alpha)\frac{\mathrm{d}\ell_\alpha}{\mathrm{d}t} \quad \text{(A.3a)}$$

$$\frac{\mathrm{d}\pi_{i,\alpha}}{\mathrm{d}t} = \frac{\mathrm{d}\left(\frac{\pi'_{i,\alpha}}{s\ell_\alpha}\right)}{\mathrm{d}t}$$

$$= \frac{1}{s\ell_\alpha}\left(\frac{\mathrm{d}p'_{i,\alpha}}{\mathrm{d}t} - \frac{m'_i}{M'}\frac{\mathrm{d}P'_\alpha}{\mathrm{d}t}\right)$$

$$- \frac{1}{s^2\ell_\alpha}\left(p'_{i,\alpha} - \frac{m'_i}{M'}P'_\alpha\right)\frac{\mathrm{d}s}{\mathrm{d}t}$$

$$- \frac{1}{s\ell^2_\alpha}\left(p'_{i,\alpha} - \frac{m'_i}{M'}P'_\alpha\right)\frac{\mathrm{d}\ell_\alpha}{\mathrm{d}t} \quad \text{(A.3b)}$$

$$\frac{\mathrm{d}R_\alpha}{\mathrm{d}t} = \frac{\mathrm{d}R'_\alpha}{\mathrm{d}t} = \frac{1}{M'}\sum_{i=1}^{N}m'_i\frac{\mathrm{d}r'_{i,\alpha}}{\mathrm{d}t} \quad \text{(A.3c)}$$

$$\frac{\mathrm{d}P_\alpha}{\mathrm{d}t} = \frac{\mathrm{d}P'_\alpha}{\mathrm{d}t} = \sum_{i=1}^{N}\frac{\mathrm{d}p'_{i,\alpha}}{\mathrm{d}t} \quad \text{(A.3d)}$$

$$\frac{\mathrm{d}\eta_T}{\mathrm{d}t} = \frac{\mathrm{d}s}{\mathrm{d}t} \quad \text{(A.3e)}$$

$$\frac{\mathrm{d}\zeta_T}{\mathrm{d}t} = \frac{1}{Q_s}\frac{\mathrm{d}p_s}{\mathrm{d}t} \quad \text{(A.3f)}$$

$$\frac{\mathrm{d}\eta_{P,\alpha}}{\mathrm{d}t} = \frac{\mathrm{d}\ell_\alpha}{\mathrm{d}t} \quad \text{(A.3g)}$$

$$\frac{\mathrm{d}\zeta_{P,\alpha}}{\mathrm{d}t} = \frac{s}{\ell_\alpha}\frac{1}{Q_{\ell,\alpha}}\frac{\mathrm{d}p_{\ell,\alpha}}{\mathrm{d}t} + \frac{p_{\ell,\alpha}}{\ell_\alpha}\frac{1}{Q_{\ell,\alpha}}\frac{\mathrm{d}s}{\mathrm{d}t}$$

$$- \frac{sp_{\ell,\alpha}}{\ell^2_\alpha}\frac{1}{Q_{\ell,\alpha}}\frac{\ell_\alpha}{\mathrm{d}t} \quad \text{(A.3h)}$$

We substitute equation (A.2) into equation (A.3):

$$\frac{\mathrm{d}\rho_{i,\alpha}}{\mathrm{d}t} = \frac{p'_{i,\alpha}}{s\ell_\alpha m'_i} - \frac{1}{s\ell_\alpha}\frac{P'_\alpha}{M'} + (r'_{i,\alpha} - R'_\alpha)s\frac{p_{\ell,\alpha}}{Q_{\ell,\alpha}} \quad \text{(A.4a)}$$

$$\frac{\mathrm{d}\pi_{i,\alpha}}{\mathrm{d}t} = F^{\mathrm{int}}_{i,\alpha} + F^{\mathrm{ext,pec}}_{i,\alpha} - \frac{m'_i}{M'}\sum_{j=1}^{N}F^{\mathrm{ext,pec}}_{j,\alpha}$$

$$- \frac{1}{s\ell_\alpha}\left(p'_{i,\alpha} - \frac{m'_i}{M'}P'_\alpha\right)\frac{p_s}{Q_s}$$

$$- \frac{1}{s\ell^2_\alpha}\left(p'_{i,\alpha} - \frac{m'_i}{M'}P'_\alpha\right)s\frac{p_{\ell,\alpha}}{Q_{\ell,\alpha}} \quad \text{(A.4b)}$$

$$\frac{\mathrm{d}R_\alpha}{\mathrm{d}t} = \frac{\mathrm{d}R'_\alpha}{\mathrm{d}t} = s\frac{P'_\alpha}{M'} \quad \text{(A.4c)}$$

$$\frac{\mathrm{d}P_\alpha}{\mathrm{d}t} = \frac{\mathrm{d}P'_\alpha}{\mathrm{d}t} = sF^{\mathrm{ext,COM}}_{\alpha} \quad \text{(A.4d)}$$

$$\frac{\mathrm{d}\eta_T}{\mathrm{d}t} = s\frac{p_s}{Q_s} \quad \text{(A.4e)}$$

$$\frac{\mathrm{d}\zeta_T}{\mathrm{d}t} = \frac{1}{Q_s}\left(\sum_{i=1}^{N}\sum_{\alpha=1}^{3}\frac{p'^2_{i,\alpha}}{s^2\ell^2_\alpha m'_i} - \frac{1}{s^2\ell^2_\alpha}\sum_{\alpha=1}^{3}\frac{P'^2_\alpha}{M} - fk_{\mathrm{B}}T_{\mathrm{set}}\right) \quad \text{(A.4f)}$$

$$\frac{\mathrm{d}\eta_{P,\alpha}}{\mathrm{d}t} = s\frac{p_{\ell,\alpha}}{Q_{\ell,\alpha}} \quad \text{(A.4g)}$$

$$\frac{\mathrm{d}\zeta_{P,\alpha}}{\mathrm{d}t} = \frac{s^2}{\ell^2_\alpha}\frac{1}{Q_{\ell,\alpha}}\left(\sum_{i=1}^{N}\sum_{\alpha=1}^{3}\frac{p'^2_{i,\alpha}}{s^2\ell^2_\alpha m'_i} - \sum_{\alpha=1}^{3}\frac{1}{s^2\ell^2_\alpha}\frac{P'^2_\alpha}{M'}\right.$$

$$+ \sum_{i=1}^{N}F^{in}_{i,\alpha}r'_{i,\alpha}\ell_\alpha + \sum_{i=1}^{N}F^{\mathrm{ext,pec}}_{i,\alpha}\rho'_{i,\alpha}\ell_\alpha$$

$$\left. - p_{\mathrm{set}}V_{\mathrm{o}}\prod_{\beta=1}^{3}\ell_\beta\right) + \frac{p_{\ell,\alpha}}{\ell_\alpha}\frac{1}{Q_{\ell,\alpha}}s\frac{p_s}{Q_s}$$

$$- \frac{sp_{\ell,\alpha}}{\ell^2_\alpha}\frac{1}{Q_{\ell,\alpha}}s\frac{p_{\ell,\alpha}}{Q_{\ell,\alpha}} \quad \text{(A.4h)}$$

Next we substitute equation (2.10) into equation (A.4):

$$\frac{\mathrm{d}\rho_{i,\alpha}}{\mathrm{d}t} = \frac{\pi_{i,\alpha}}{m_i} + \rho_{i,\alpha}\zeta_{P,\alpha} \quad \text{(A.5a)}$$

$$\frac{\mathrm{d}\pi_{i,\alpha}}{\mathrm{d}t} = F^{\mathrm{int}}_{i,\alpha} + F^{\mathrm{ext,pec}}_{i,\alpha} - \frac{m'_i}{M'}\sum_{j=1}^{N} F^{\mathrm{ext,pec}}_{j,\alpha} - \pi_{i,\alpha}(\zeta_T + \zeta_{P,\alpha}) \tag{A.5b}$$

$$\frac{\mathrm{d}R_\alpha}{\mathrm{d}t} = \eta_T \frac{P_\alpha}{M} \tag{A.5c}$$

$$\frac{\mathrm{d}P_\alpha}{\mathrm{d}t} = \eta_T F^{\mathrm{ext,COM}}_\alpha \tag{A.5d}$$

$$\frac{\mathrm{d}\eta_T}{\mathrm{d}t} = \eta_T \zeta_T \tag{A.5e}$$

$$\frac{\mathrm{d}\zeta_T}{\mathrm{d}t} = \frac{\nu_T^2}{f k_{\mathrm{B}} T_{\mathrm{set}}}\left(\sum_{i=1}^{N}\sum_{\alpha=1}^{3}\frac{\pi^2_{i,\alpha}}{m_i} - f k_{\mathrm{B}} T_{\mathrm{set}}\right) \tag{A.5f}$$

$$\frac{\mathrm{d}\eta_{P,\alpha}}{\mathrm{d}t} = \eta_{P,\alpha}\zeta_{P,\alpha} \tag{A.5g}$$

$$\frac{\mathrm{d}\zeta_{P,\alpha}}{\mathrm{d}t} = \frac{\eta_T^2}{\eta^2_{P,\alpha}}\frac{\nu^2_{P,\alpha}}{f k_{\mathrm{B}} T_{\mathrm{set}}} \times \left(\sum_{i=1}^{N}\sum_{\alpha=1}^{3}\frac{\pi^2_{i,\alpha}}{m_i} + \sum_{i=1}^{N} F^{\mathrm{in}}_{i,\alpha}\rho_{i,\alpha} + \sum_{i=1}^{N} F^{\mathrm{ext,pec}}_{i,\alpha}\rho_{i,\alpha} - p_{\mathrm{set}} V_{\mathrm{o}} \prod_{\beta=1}^{3}\ell_\beta\right) + \zeta_{P,\alpha}\zeta_T - \zeta^2_{P,\alpha} \tag{A.5h}$$

These are the equations of motion in terms of the peculiar and COM coordinates for the physical system. They can be further simplified by identifying the temperature as

$$T(t) = \frac{1}{f k_{\mathrm{B}}}\sum_{i=1}^{N}\sum_{\alpha=1}^{3}\frac{\pi^2_{i,\alpha}}{m_i} \tag{A.6}$$

and the $\alpha\alpha$ component of the pressure tensor, $p_{\alpha\alpha}$, as

$$p_{\alpha\alpha}(t) = \frac{1}{V(t)}\left[\sum_{i=1}^{N}\frac{\pi^2_{i,\alpha}}{m_i} + \sum_{i=1}^{N}(F^{\mathrm{in}}_{i,\alpha} + F^{\mathrm{ext,pec}}_{i,\alpha})\rho_{i,\alpha}\right] \tag{A.7}$$

The system volume is again

$$V(t) = V_{\mathrm{o}}\prod_{\beta=1}^{3}\ell_\beta \tag{A.8}$$

so that the equation of motion for the momenta of the barostat and thermostat are

$$\frac{\mathrm{d}\zeta_T}{\mathrm{d}t} = \nu_T^2\left(\frac{T(t)}{T_{\mathrm{set}}} - 1\right) \tag{A.9a}$$

and

$$\frac{\mathrm{d}\zeta_{P,\alpha}}{\mathrm{d}t} = \frac{\eta_T^2}{\eta^2_{P,\alpha}}\frac{\nu^2_{P,\alpha}V(t)}{f k_{\mathrm{B}} T_{\mathrm{set}}}(p_{\alpha\alpha}(t) - p_{\mathrm{set}}) + \zeta_{P,\alpha}\zeta_T - \zeta^2_{P,\alpha} \tag{A.9b}$$

Appendix B

In this appendix, we prove that the Hamiltonian of the extended system proposed in this work for the NpT case generates the correct NpT ensemble using the two criteria that exist in the literature, namely, the Hamiltonian-based criterion of Nosé [1] and the non-Hamiltonian criterion of Tuckerman *et al.* [12,13]. We first present the proof that the generalized algorithm satisfies the criterion of Nosé [1]. For a direct comparison with the standard form of the NpT ensemble in statistical mechanics, here we will use volume V of system instead of the space-dilation variable ℓ for each direction.

The Hamiltonian, which corresponds to equation (2.6), in terms of the laboratory coordinates in the dilated frame of reference is given by

$$H'_{\mathrm{NpT}} = \sum_{i=1}^{N}\frac{\mathbf{p}'^2_i}{2m'_i s^2 V^{2/D}} + U(V^{1/D}\boldsymbol{\rho}', \mathbf{R}') + \left(1 - \frac{1}{s^2 V^{2/D}}\right)\frac{\mathbf{P}'^2}{2M'} + \frac{p_s^2}{2Q_s} + f k_{\mathrm{B}} T_{\mathrm{set}}\ln(s) + \frac{p_V}{2Q_V} + p_{\mathrm{set}} V \tag{B.1}$$

Here, we employ more flexibility in dimensionality of our frame of reference, as denoted by D. The above Hamiltonian is conserved during the evolution of our physical system. Thus, the partition function for the extended system is written as

$$Z'_{\mathrm{NpT}} = \frac{1}{N!}\int \mathrm{d}^N\mathbf{p}' \int \mathrm{d}^N\mathbf{r}' \int \mathrm{d}p_s \int \mathrm{d}s \int \mathrm{d}p_V \int \mathrm{d}V\,\delta\left[\sum_{i=1}^{N}\frac{\mathbf{p}'^2_i}{2m'_i s^2 V^{2/D}} + \left(1 - \frac{1}{s^2 V^{2/D}}\right)\frac{\mathbf{P}'^2}{2M'} + U(V^{1/D}\boldsymbol{\rho}', \mathbf{R}') + \frac{p_s^2}{2Q_s} + f k_{\mathrm{B}} T_{\mathrm{set}}\ln(s) + \frac{p_V}{2Q_V} + p_{\mathrm{set}} V - E\right] \tag{B.2}$$

where we used a shortened notation $\mathrm{d}^N\mathbf{p}' = \mathrm{d}\mathbf{p}'_1\mathrm{d}\mathbf{p}'_2\ldots\mathrm{d}\mathbf{p}'_N$ and $\mathrm{d}^N\mathbf{r}' = \mathrm{d}\mathbf{r}'_1\mathrm{d}\mathbf{r}'_2\ldots\mathrm{d}\mathbf{r}'_N$. From the following relations between the laboratory coordinates and peculiar coordinates

in the mathematical frame of reference,

$$\boldsymbol{\pi}_i' = \mathbf{p}_i' - \frac{m_i'}{M'}\left(\sum_{i=1}^{N}\mathbf{p}_i'\right), \quad \mathbf{P}' = \sum_{i=1}^{N}\mathbf{p}_i',$$

$$\boldsymbol{\rho}_i' = \mathbf{r}_i' - \frac{1}{M'}\left(\sum_{i=1}^{N} m_i'\mathbf{r}_i'\right),$$

$$\mathbf{R}' = \frac{1}{M'}\left(\sum_{i=1}^{N} m_i'\mathbf{r}_i'\right) \tag{B.3}$$

it is seen that $\mathrm{d}^N\mathbf{p}' = \mathrm{d}^{N-1}\boldsymbol{\pi}'\mathrm{d}\mathbf{P}'$ and $\mathrm{d}^N\mathbf{r}' = c_1\mathrm{d}^{N-1}\boldsymbol{\rho}'\mathrm{d}\mathbf{R}'$, where c_1 is a constant that depends on the mass of the particles. Then, the partition function can be written as

$$Z'_{\mathrm{NpT}} = \frac{c_1}{N!}\int \mathrm{d}^{N-1}\boldsymbol{\pi}'\int \mathrm{d}\mathbf{P}'\int \mathrm{d}^{N-1}\rho'\int \mathrm{d}\mathbf{R}'\int \mathrm{d}p_s\int \mathrm{d}s$$
$$\int \mathrm{d}p_V\int \mathrm{d}V\,\delta\left[\sum_{i=1}^{N}\frac{\boldsymbol{\pi}_i'^2}{2m_i' s^2 V^{2/D}} + \frac{\mathbf{P}'2}{2M'} + U(V^{1/D}\boldsymbol{\rho}', \mathbf{R}')\right.$$
$$\left. + \frac{\mathbf{p}_s^2}{2Q_s} + f k_{\mathrm{B}} T_{\mathrm{set}}\ln(s) + \frac{p_V}{2Q_V} + p_{\mathrm{set}}V - E\right] \tag{B.4}$$

Now let us make a proper transformation from the mathematical variables to the physical variables as follows: $\boldsymbol{\pi}_i = \boldsymbol{\pi}_i'/sV^{1/D}$, $\mathbf{P} = \mathbf{P}'$, $\boldsymbol{\rho}_i = V^{1/D}\boldsymbol{\rho}_i'$ and $\mathbf{R} = \mathbf{R}'$, $m_i = m_i'$ and $M = M'$. From these relations, it is found that $\mathrm{d}^{N-1}\boldsymbol{\pi}'\mathrm{d}^{N-1}\boldsymbol{\rho}' = s^{D(N-1)}\mathrm{d}^{N-1}\boldsymbol{\pi}\mathrm{d}^{N-1}\boldsymbol{\rho}$. Therefore, the partition function in terms of the physical variables can be expressed as

$$Z_{\mathrm{NpT}} = \frac{c_1}{N!}\int \mathrm{d}^{N-1}\boldsymbol{\pi}\int \mathrm{d}\mathbf{P}\int \mathrm{d}^{N-1}\boldsymbol{\rho}\int \mathrm{d}\mathbf{R}\int \mathrm{d}p_s\int \mathrm{d}s$$
$$\int \mathrm{d}p_V\int \mathrm{d}V\, s^{D(N-1)}\delta\left[\sum_{i=1}^{N}\frac{\boldsymbol{\pi}_i'^2}{2m_i} + \frac{\mathbf{P}^2}{2M} + U(\boldsymbol{\rho}, \mathbf{R})\right.$$
$$\left. + \frac{p_s^2}{2Q_s} + f k_{\mathrm{B}} T_{\mathrm{set}}\ln(s) + \frac{p_V}{2Q_V} + p_{\mathrm{set}}V - E\right] \tag{B.5}$$

Now if we perform the integration over s in equation (B.5) using a δ-function property, $\delta[G(s)] = \sum_k \delta[s - s_k]/|\mathrm{d}G(s)/\mathrm{d}s|$, where s_k are all the zeroes satisfying $G(s) = 0$, then equation (B.5) becomes

$$Z'_{\mathrm{NpT}} = \frac{c_1}{N!}\frac{1}{f k_{\mathrm{B}} T_{\mathrm{set}}}\int \mathrm{d}^{N-1}\boldsymbol{\pi}\int \mathrm{d}\mathbf{P}\int \mathrm{d}^{N-1}\boldsymbol{\rho}\int \mathrm{d}\mathbf{R}\int \mathrm{d}p_s\int \mathrm{d}p_V\int \mathrm{d}V$$
$$\times \mathrm{e}^{-\frac{1}{k_{\mathrm{B}}T_{\mathrm{set}}}\left(\frac{D(N-1)+1}{f}\right)\left[\sum_{i=1}^{N}\frac{\boldsymbol{\pi}_i^2}{2m_i} + \frac{\mathbf{P}^2}{2M} + U(\boldsymbol{\rho},\mathbf{R}) + \frac{p_s^2}{2Q_s} + \frac{p_V}{2Q_V} + p_{\mathrm{set}}V - E\right]} \tag{B.6}$$

If we set $f = D(N-1) + 1$ and perform the integrations over both p_s and p_V, we finally find

$$Z_{\mathrm{NpT}} = c\int \mathrm{d}^{N-1}\boldsymbol{\pi}\int \mathrm{d}\mathbf{P}\int \mathrm{d}^{N-1}\boldsymbol{\rho}\int \mathrm{d}\mathbf{R}\int \mathrm{d}p_V$$
$$\int \mathrm{d}V\,\mathrm{e}^{-\frac{1}{k_B T_{\mathrm{set}}}\left[\sum_{i=1}^{N}\frac{\boldsymbol{\pi}_i^2}{2m_i} + \frac{\mathbf{P}^2}{2M} + U(\boldsymbol{\rho},\mathbf{R}) + p_{\mathrm{set}}V\right]} \tag{B.7a}$$

where

$$c = \frac{c_1}{N!}\frac{1}{f k_{\mathrm{B}} T_{\mathrm{set}}}\sqrt{2\boldsymbol{\pi} Q_s k_{\mathrm{B}} T_{\mathrm{set}}}\sqrt{2\boldsymbol{\pi} Q_V k_{\mathrm{B}} T_{\mathrm{set}}}\,\mathrm{e}^{E/k_{\mathrm{B}}T_{\mathrm{set}}} \tag{B.7b}$$

Beyond a constant, equation (B.7a) represents the well-known NpT ensemble in statistical mechanics. Furthermore, it is seen that in the absence of external forces, where the total linear momentum of the system, P, is conserved, the constraint on equation (B.7a) will result in the (N − 1)pT ensemble.

We can also verify the above results using the non-Hamiltonian approach developed by Tuckerman *et al.* [12,13]. In this approach, we start directly from the equations of motion and a conserved quantity in terms of the physical variables. Following the same procedure described in Section 2, the equations of motion from the Hamiltonian in equation (B.1) are found to be

$$\frac{\mathrm{d}\boldsymbol{\rho}_i}{\mathrm{d}t} = \frac{\boldsymbol{\pi}_i}{m_i} + \boldsymbol{\rho}_i\zeta_p \tag{B.8a}$$

$$\frac{\mathrm{d}\boldsymbol{\pi}_i}{\mathrm{d}t} = \mathbf{F}_i^{\mathrm{int}} + \mathbf{F}_i^{\mathrm{ext,pec}} - \frac{m_i}{M}\sum_{j=1}^{N}\mathbf{F}_j^{\mathrm{ext,pec}}$$
$$- \boldsymbol{\pi}_i(\zeta_T + \zeta_p) \tag{B.8b}$$

$$\frac{\mathrm{d}\mathbf{R}}{\mathrm{d}t} = \eta_T\frac{\mathbf{P}}{M} \tag{B.8c}$$

$$\frac{\mathrm{d}\mathbf{P}}{\mathrm{d}t} = \eta_T\mathbf{F}^{\mathrm{ext,COM}} \tag{B.8d}$$

$$\frac{\mathrm{d}\eta_T}{\mathrm{d}t} = \eta_T\zeta_T \tag{B.8e}$$

$$\frac{\mathrm{d}\zeta_T}{\mathrm{d}t} = \frac{f k_{\mathrm{B}} T_{\mathrm{set}}}{Q_s}\left(\frac{T}{T_{\mathrm{set}}} - 1\right) \tag{B.8f}$$

$$\frac{\mathrm{d}V}{\mathrm{d}t} = DV\zeta_p \tag{B.8g}$$

$$\frac{\mathrm{d}\zeta_p}{\mathrm{d}t} = \frac{\eta_T^2}{Q_V DV}(p(t) - p_{\mathrm{set}}) + \zeta_T\zeta_p - D\zeta_p^2 \tag{B.8h}$$

where use has been made of a similar transformation to equation (2.10): $m_i = m_i'$, $\boldsymbol{\rho}_i = V^{1/D}\boldsymbol{\rho}_i'$, $\boldsymbol{\pi}_i = \boldsymbol{\pi}_i'/sV^{1/D}$, $\mathbf{R} = \mathbf{R}'$, $\mathbf{P} = \mathbf{P}'$, $\eta_T = s$, $\zeta_T = p_s/Q_s$ and $\zeta_p = sp_V/DVQ_V$. The conserved quantity is the Hamiltonian defined in equation (B.1), which in terms of the physical variables

is written as

$$H_{\mathrm{NpT}} = \sum_{i=1}^{N} \frac{\boldsymbol{\pi}_i^2}{2m_i} + \frac{\mathbf{P}^2}{2M} + U(\boldsymbol{\rho}, \mathbf{R}) + \frac{Q_s}{2}\zeta_T^2 + f k_{\mathrm{B}} T_{\mathrm{set}} \ln(\eta_T) + \frac{Q_V}{2}\frac{D^2 V^2}{\eta_T^2}\zeta_p^2 + p_{\mathrm{set}} V \quad \text{(B.9)}$$

According to the non-Hamiltonian approach, the partition function is now written as

$$Z_{\mathrm{NpT}} = \frac{1}{N!}\int \mathrm{d}^{N-1}\boldsymbol{\pi} \int \mathrm{d}\mathbf{P} \int \mathrm{d}^{N-1}\boldsymbol{\rho} \int \mathrm{d}\mathbf{R} \int \mathrm{d}\zeta_T \int \mathrm{d}\eta_T \int \mathrm{d}\zeta_p \int \mathrm{d}V \delta(H_{\mathrm{NpT}} - E)\sqrt{g} \quad \text{(B.10)}$$

where $\sqrt{g} = 1/J$ and the variation of the Jacobian, J, with time is determined by $\mathrm{d}J/\mathrm{d}t = J\nabla\cdot\dot{x}$. Using equation (B.8), the divergence $\nabla\cdot\dot{x}$ is found to be

$$\nabla\cdot\dot{x} = \sum_{i=1}^{N-1}\left(\frac{\partial}{\partial\boldsymbol{\rho}_i}\cdot\dot{\boldsymbol{\rho}}_i + \frac{\partial}{\partial\boldsymbol{\pi}_i}\cdot\dot{\boldsymbol{\pi}}_i\right) + \frac{\partial}{\partial\mathbf{R}}\cdot\dot{\mathbf{R}} + \frac{\partial}{\partial\mathbf{P}}\cdot\dot{\mathbf{P}} + \frac{\partial\dot{\eta}_T}{\partial\eta_T} + \frac{\partial\dot{\zeta}_T}{\partial\zeta_T} + \frac{\partial\dot{V}}{\partial V} + \frac{\partial\dot{\zeta}_p}{\partial\zeta_p} = -[D(N-1)-2]\zeta_T - D\zeta_p \quad \text{(B.11)}$$

from which the Jacobian and $\sqrt{g}$ are found to be

$$J = \mathrm{e}^{-[D(N-1)-2]\ln(\eta_T) - \ln V} = \frac{1}{V}\eta_T^{-[D(N-1)-2]} \quad \text{(B.12a)}$$

$$\sqrt{g} = V\eta_T^{[D(N-1)-2]} \quad \text{(B.12b)}$$

Substituting equations (B.9) and (B.12b) into equation (B.10), we find

$$Z_{\mathrm{NpT}} = \frac{1}{N!}\int \mathrm{d}^{N-1}\boldsymbol{\pi} \int \mathrm{d}\mathbf{P} \int \mathrm{d}^{N-1}\boldsymbol{\rho} \int \mathrm{d}\mathbf{R} \int \mathrm{d}\zeta_T \int \mathrm{d}\eta_T \int \mathrm{d}\zeta_p \int \mathrm{d}V V \eta_T^{D(N-1)-2} \delta[\sum_{i=1}^{N}\frac{\boldsymbol{\pi}_i^2}{2m_i} + \frac{\mathbf{P}^2}{2M} + U(\boldsymbol{\rho},\mathbf{R}) + \frac{Q_s}{2}\zeta_T^2 + f k_{\mathrm{B}} T_{\mathrm{set}}\ln(\eta_T) + \frac{Q_V}{2}\frac{D^2V^2}{\eta_T^2}\zeta_p^2 + p_{\mathrm{set}}V - E]$$

$$= \frac{1}{N!}\frac{1}{Q_V D}\int \mathrm{d}^{N-1}\boldsymbol{\pi} \int \mathrm{d}\mathbf{P} \int \mathrm{d}^{N-1}\boldsymbol{\rho} \int \mathrm{d}\mathbf{R} \int \mathrm{d}\zeta_T \int \mathrm{d}\eta_T \int \mathrm{d}p_V \int \mathrm{d}V \eta_T^{D(N-1)-1} \delta[\sum_{i=1}^{N}\frac{\boldsymbol{\pi}_i^2}{2m_i} + \frac{\mathbf{P}^2}{2M} + U(\boldsymbol{\rho},\mathbf{R}) + \frac{Q_s}{2}\zeta_T^2 + f k_{\mathrm{B}} T_{\mathrm{set}}\ln(\eta_T) + \frac{p_V^2}{2Q_V} + p_{\mathrm{set}}V - E] \quad \text{(B.13)}$$

In the second equality of equation (B.13), we have used the relation $\mathrm{d}\eta_T\mathrm{d}V\mathrm{d}\zeta_p = (\eta_T)/(Q_V DV)\,\mathrm{d}\eta_T\mathrm{d}V\mathrm{d}p_V$. Integrating over η_T, and using again the δ-function property, $\delta[G(s)] = \sum_k \delta[s - s_k]/|\mathrm{d}G(s)/\mathrm{d}s|$, equation (B.13) becomes

$$Z_{\mathrm{NpT}} = \frac{1}{N!}\frac{1}{Q_V}\frac{1}{Df k_{\mathrm{B}} T_{\mathrm{set}}} \int \mathrm{d}^{N-1}\boldsymbol{\pi} \int \mathrm{d}\mathbf{P} \int \mathrm{d}^{N-1}\boldsymbol{\rho} \int \mathrm{d}\mathbf{R} \int \mathrm{d}\zeta_T \int \mathrm{d}p_V \int \mathrm{d}V \times \mathrm{e}^{-\frac{1}{k_{\mathrm{B}}T_{\mathrm{set}}}\left(\frac{D(N-1)}{f}\right)\left[\sum_{i=1}^{N}\frac{\boldsymbol{\pi}_i^2}{2m_i} + \frac{\mathbf{P}^2}{2M} + U(\boldsymbol{\rho},\mathbf{R}) + \frac{Q_s}{2}\zeta_T^2 + \frac{p_V}{2Q_V} + p_{\mathrm{set}}V - E\right]} \quad \text{(B.14)}$$

By setting $f = D(N-1)$ and integrating over ζ_T and p_V, we finally find

$$Z_{\mathrm{NpT}} = c\int \mathrm{d}^{N-1}\boldsymbol{\pi} \int \mathrm{d}\mathbf{P} \int \mathrm{d}^{N-1}\boldsymbol{\rho} \int \mathrm{d}\mathbf{R} \int \mathrm{d}p_V \int \mathrm{d}V\, \mathrm{e}^{-\frac{1}{k_{\mathrm{B}}T_{\mathrm{set}}}\left[\sum_{i=1}^{N}\frac{\boldsymbol{\pi}_i^2}{2m_i} + \frac{\mathbf{P}^2}{2M} + U(\boldsymbol{\rho},\mathbf{R}) + p_{\mathrm{set}}V\right]} \quad \text{(B.15a)}$$

where

$$c = \frac{1}{N!}\frac{1}{Q_s}\frac{1}{Q_V D}\frac{1}{f k_{\mathrm{B}} T_{\mathrm{set}}}\sqrt{2\pi Q_s k_{\mathrm{B}} T_{\mathrm{set}}}\sqrt{2\pi Q_V k_{\mathrm{B}} T_{\mathrm{set}}}\,\mathrm{e}^{E/k_{\mathrm{B}}T_{\mathrm{set}}} \quad \text{(B.15b)}$$

Beyond a slight difference in the constant c, which is of no importance, equation (B.15a) is the same as equation (B.7a). That is, according to the non-Hamiltonian approach, the equations of motion derived from the Hamiltonian proposed in this work are proven to generate the correct NpT ensemble. As in the NVT case of [4], we again see due to the difference between the virtual and the real time sampling that while f is set equal to $D(N-1)+1$ in the first method, f is set equal to $D(N-1)$ in the non-Hamiltonian approach.

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