Designing reversible measure invariant algorithms with applications to molecular dynamics

Frédéric Legoll[a,b] and Régis Monneau[a]

[a] *CERMICS, Ecole Nationale des Ponts et Chaussées,*

6 et 8 avenue Blaise Pascal, Cité Descartes,

77455 Marne-la-Vallée Cedex 2, France

[b] *EDF DRD, Mécanique et Modèles Numériques,*

1, avenue du Général de Gaulle,

92140 Clamart, France

legoll@cermics.enpc.fr,

monneau@cermics.enpc.fr

(Dated: June 6, 2002)

A new method for generating measure invariant algorithms is presented. This method is based on a reformulation of the equations of Molecular Dynamics. These new equations are non-Hamiltonian but have a *normal form* which guarantees that the invariant measure is the canonical one for the new variables. Furthermore, from this normal form, one can easily build algorithms to integrate these equations. Using a Trotter-type factorization of the classical Liouville propagator, we build (time) reversible measure invariant integrators as successive direct translations. We apply this method to propose new algorithms to generate the Nosé-Hoover chain dynamics and the isothermal-isobaric dynamics. We also give a measure invariant integrator for the Generalized Gaussian Moment Thermostatting dynamics recently introduced by Liu and Tuckerman. Finally, we present numerical results which show comparable performances with previously proposed algorithms.

I. INTRODUCTION

Continuous dynamical methods for generating statistical ensembles are, by now, standard. In this approach, we consider a single trajectory which generates a given sampling of the phase space. So, the integration over the trajectory of some physical quantities provides an estimate of some thermodynamic properties of a material. To calculate these estimates, we need to numerically simulate the trajectory. In general, these continuous dynamics preserve at least an energy and a measure. One may want to find algorithms that exactly preserve the energy, or the measure, or both. It has been shown[1] that for some dynamical systems, under some hypotheses, one can not have algorithms that exactly and at the same time preserve the measure, the energy, and the other quantities preserved by the dynamics. In our case, preserving at the same time the energy and the measure seems therefore difficult. Recently, it has been shown that measure invariant algorithms play a key role to make a good sampling of the phase space. So exactly preserving the measure is more interesting than exactly preserving the energy.

Many measure invariant algorithms have been proposed in the literature. We refer to the beautiful paper of Tuckerman, Martyna[2] for a survey of recent progress in Molecular Dynamics. The first Molecular Dynamics equations proposed to simulate the canonical ensemble were given by Nosé[3] and Hoover[4]. An improvement of this dynamics, called the Nosé-Hoover chain dynamics, has been proposed by Martyna, Klein and Tuckerman[5]. Tuckerman, Berne and Martyna[6] have proposed a first reversible measure invariant algorithm in the case of two thermostats. A generalization of this algorithm to the case of M thermostats has been given by Martyna et al.[7,8]. Recently, Liu and Tuckerman[9,10] have proposed a new dynamics to simulate the canonical ensemble, called the Generalized Gaussian Moment Thermostatting (GGMT) dynamics.

There are also many works on constant pressure Molecular Dynamics and on path integral Molecular Dynamics[11-15]. Let us also note that multiple time scale methods have been used to improve the previous algorithms[16-23].

As underlined previously, preserving at the same time the measure and the energy exactly is difficult, if not impossible. Thus, it is not surprising that the proposed measure invariant algorithms do not exactly preserve the energy of the system. This energy is only approximately conserved[24-29]. More generally, the Molecular Dynamics of non-microcanonical ensembles is refered to as non-Hamiltonian dynamics[30]. In practice, even if the energy is not exactly conserved by the measure invariant algorithms, there is no constant draft on it. This can be considered as very surprising. For instance, the well-known fourth-order Runge-Kutta method applied on the Kepler two-body problem gives a quadratic long term error growth[31]. The surprisingly good conservation of the energy is actually due to the fact that the algorithms are measure-invariant. More precisely, let us suppose that we work with a Hamiltonian dynamics, and we use a p-order measure-invariant algorithm to integrate it. The energy at the beginning is H_0, and the numerical energy at time step k is $H_{num}(k\,\Delta t)$. Then, under some regularity conditions on the Hamiltonian, and for small enough time steps Δt, one can prove[32,33] that the numerical error on the energy satisfies,

$$\forall k \leq \frac{1}{\Delta t}\, e^{c_1/\Delta t}\,, \quad \mid H_{num}(k\,\Delta t) - H_0 \mid \leq \; c_2\, \Delta t^p$$

where c_1 and c_2 are two constants which do not depend on the time step Δt (they depend on the Hamiltonian function which defines the dynamical system and on the measure invariant algorithm chosen). This means that the longtime error remains bounded for exponentially large times.

In this paper we go one step further in the research of measure invariant algorithms.

We present a *systematic method* to build reversible measure invariant algorithms (see Sec. II). Our approach allows us to generate many algorithms. In order to proceed pedagogically, we first apply our method on a simple example (see Sec. III). Actually, this example is a simplified case of the equations used to simulate the isothermal-isobaric ensemble[7]. We show in appendix (see Sec. V A) how to get measure invariant algorithms for the whole set of equations. Then, in the main part of the article, we focus on the GGMT dynamics[9]. First, we show how to get new algorithms, then give some numerical results (see Sec. IV). In the appendix, we take a close look at measure invariance for the GGMT dynamics. For this dynamics, the algorithm proposed by Liu and Tuckerman[9] is numerically efficient. However, it is actually only approximately measure invariant (see Sec. V D and V E). Our method gives us an algorithm which is *exactly measure invariant.*

II. A METHOD TO GENERATE MEASURE INVARIANT ALGORITHMS

Our method simply consists in rewriting (when it is possible) systems of ordinary differential equations

$$\dot{X}_j = F_j(X_1, ..., X_n), \quad j = 1, \ldots, n \tag{2.1}$$

in the *normal form*

$$\dot{Y}_i = G_i\left(\overset{\vee}{Y}_i\right), \quad i = 1, \ldots, n \tag{2.2}$$

where $\overset{\vee}{Y}_i = (Y_1, \ldots, Y_{i-1}, Y_{i+1}, \ldots, Y_n)$ is the whole set of variables *except* Y_i. The Y_i are obtained from the X_j by a change of variables. So, the normal form is caracterized by the fact that $\dot{Y}_i$ does not depend on Y_i. Following the usual method[2], one can check

that system (2.2) preserves the following measure

$$\tilde{m} = dY_1 \ \ldots \ dY_n$$

Now, we want to build measure-invariant algorithms. One can notice that the system (2.2) is a divergence-free dynamical system. Many ways to build volume-preserving algorithms for this kind of dynamics are known[34]. In this article, we take advantage of the fact that the system (2.2) is more than divergence-free, it is in a normal form. We follow a usual method[2], and build algorithms by Trotter factorizations of Liouville propagators. This gives simple algorithms by successives translations:

$$e^{\Delta t\, L_{eff}} = \prod_k e^{\Delta t_{p(k)}\, G_{p(k)}\, \partial_{Y_{p(k)}}}$$

The k^{th} operation is a translation on the variable $Y_{p(k)}$, where $p(k)$ is a subscript in $[1, n]$. This translation preserves the measure $\tilde{m}$, since it reads $Y_{p(k)} \rightarrow Y_{p(k)} + \Delta t_{p(k)}\, G_{p(k)}$. So the complete operator $e^{\Delta t\, L_{eff}}$ also preserves the measure $\tilde{m}$.

Let us now briefly discuss the existence of a transformation such as the one considered at the beginning of this section. Is it always possible to find variables Y_i so that the dynamics on these new variables is in a normal form? In general, it is not possible to have an explicit expression for a good change of variables. So, in general, it is not possible to explicitly transform a dynamics such as Eq. (2.1) into a normal form dynamics such as Eq. (2.2). However, for some particular cases, such a transformation exists and can be explicitly written. In the following parts of this article, we consider specific examples of dynamics (the ones usually used to generate NVT and NPT ensembles), and we explicitly transform them into normal form dynamics.

III. A SIMPLE APPLICATION

To illustrate our purpose, we consider Nosé-Hoover equations. Actually, we are going to work on a simplified example of these equations. So we simulate a one-dimensional particle coupled with a thermostat of Nosé-Hoover[2]:

$$\begin{aligned} \dot{q} &= \frac{p}{m} \\ \dot{p} &= F(q) - \frac{p_\xi}{Q} p \\ \dot{p}_\xi &= \frac{p^2}{m} - k_B T \end{aligned} \tag{3.1}$$

Here, the particle position is q, its impulsion is p, and its mass is m. The temperature is T, and k_B is the Boltzmann constant. The forces are $F(q) = -V'(q)$. The particle is coupled to the thermostat by the variable p_ξ, and Q is a coupling parameter (it can be considered as the thermostat mass). It is known that system (3.1) preserves the following "Maxwell-Boltzmann" measure

$$m_1 = e^{-\beta\left(\frac{p^2}{2m}+V(q)+\frac{p_\xi^2}{2Q}\right)} dq\ dp\ dp_\xi$$

for $\beta = 1/(k_B T)$.

To be efficient, an algorithm in Molecular Dynamics applied to Eqs. (3.1) has to preserve as much as possible the same measure. In practice all algorithms only approximately preserve this measure. In the last years the approach which has predominated has consisted in introducing an additional variable, let us say ξ, which here satisfies

$$\dot{\xi} = \frac{p_\xi}{Q} \tag{3.2}$$

and to remark that system (3.1)-(3.2) preserves the following energy and measure:

$$H' = \frac{p^2}{2m} + V(q) + \frac{p_\xi^2}{2Q} + \xi\, k_B T$$

$$m_0 = e^{\xi}\, dq\; dp\; dp_\xi\; d\xi$$

The usual method consists in finding an algorithm which exactly preserves the measure m_0. Actually, for many dynamical systems, the same approach has been used. The continuous dynamics preserves a measure, one has to find an algorithm that exactly preserves this measure. The discrete conservation of a measure similar to m_0 can be checked analytically or numerically. In this paper we propose a unified approach to design measure invariant reversible integrators. So no *a posteriori* check is required anymore.

Let us apply our method to the system (3.1). We introduce

$$\tilde{p} = e^{\xi}\, p \tag{3.3}$$

Then the variables $(q, \tilde{p}, p_\xi, \xi)$ satisfy

$$\begin{aligned} \dot{q} &= \frac{\tilde{p}}{m}\, e^{-\xi} \\ \dot{\tilde{p}} &= e^{\xi}\, F(q) \\ \dot{p}_\xi &= \frac{\tilde{p}^2}{m}\, e^{-2\xi} - k_B T \\ \dot{\xi} &= \frac{p_\xi}{Q} \end{aligned} \tag{3.4}$$

Now, we have a dynamical system in a normal form. So, it is clear that the measure

$$\tilde{m} = dq\; d\tilde{p}\; dp_\xi\; d\xi$$

is preserved. When writing $\tilde{m}$ in the original variables, one can check that $\tilde{m} = m_0$. Furthermore, from the normal form, building a reversible measure invariant algorithm is quite easy. Using the Trotter formula:

$$e^{\Delta t(A+B)} = e^{\frac{\Delta t}{2}B}\; e^{\Delta t A}\; e^{\frac{\Delta t}{2}B} + O(\Delta t^3) \tag{3.5}$$

and using the fact that $[\dot{q}\,\partial_q, \dot{p}_\xi\,\partial_{p_\xi}] = 0$ we get

$$L = L_1 + L_2 + L_3$$

with

$$\begin{aligned} L_1 &= \dot{\xi}\,\partial_\xi \\ L_2 &= \dot{\tilde{p}}\,\partial_{\tilde{p}} \\ L_3 &= \dot{q}\,\partial_q + \dot{p}_\xi\,\partial_{p_\xi} \end{aligned}$$

We can now generate 3! different algorithms of the form

$$e^{\Delta t\, L_{eff}} = e^{\frac{\Delta t}{2} L_a}\; e^{\frac{\Delta t}{2} L_b}\; e^{\Delta t L_c}\; e^{\frac{\Delta t}{2} L_b}\; e^{\frac{\Delta t}{2} L_a} \tag{3.6}$$

with $\{a, b, c\} = \{1, 2, 3\}$. All these algorithms are measure invariant. From Eq. (3.5), we deduce:

$$e^{\Delta t\, L_{eff}} = e^{\Delta t\, L} + O(\Delta t^3) \tag{3.7}$$

With variables $(q, \tilde{p}, p_\xi, \xi)$, the energy reads

$$\tilde{H}' = \frac{\tilde{p}^2}{2m}\, e^{-2\xi} + V(q) + \frac{p_\xi^2}{2Q} + \xi k_B T$$

It is preserved up to the order 2 in Δt. For instance, the particular choice $(a, b, c) =$

$(1,2,3)$ in Eq. (3.6) gives the following algorithm:

$$(1)\ \ \xi \to \xi + \frac{1}{2}\Delta t\ \frac{p_\xi}{Q}$$

$$(2)\ \ \tilde{p} \to \tilde{p} + \frac{1}{2}\Delta t\ e^{\xi}\, F(q)$$

$$(3)\ \ \begin{cases} q \ \to\ q + \Delta t\ \dfrac{\tilde{p}}{m}\, e^{-\xi} \\ \\ p_\xi \ \to\ p_\xi + \Delta t \left(\dfrac{\tilde{p}^2}{m}\, e^{-2\xi} - k_B T \right) \end{cases}$$

$$(2)\ \ \tilde{p} \to \tilde{p} + \frac{1}{2}\Delta t\ e^{\xi} F(q)$$

$$(1)\ \ \xi \to \xi + \frac{1}{2}\Delta t\ \frac{p_\xi}{Q}$$

So, the dynamics given by Eqs. (3.4) is exactly the same as the dynamics given by Eqs. (3.1)-(3.2), provided that p and $\tilde{p}$ are linked according to Eq. (3.3). However, working with new variables allows us to derive measure invariant algorithms in a quite simple way. The numerical properties of these algorithms are studied in the following parts on some examples.

Finally, let us notice than more sophisticated algorithms than the one given in Eq. (3.6) are also possible. For instance, we can write

$$e^{\Delta t\, L_{eff}} = e^{\frac{\Delta t}{4} L_a}\ e^{\frac{\Delta t}{2} L_b}\ e^{\frac{\Delta t}{4} L_a}\ e^{\Delta t L_c}\ e^{\frac{\Delta t}{4} L_a}\ e^{\frac{\Delta t}{2} L_b}\ e^{\frac{\Delta t}{4} L_a}$$

It is also possible to use a Yoshida-Suzuki like decomposition[7,35,36]. Thanks to these more complex decompositions, energy conservation properties are probably better.

IV. GENERALIZED GAUSSIAN MOMENT THERMOSTATTING

A. Normal form for the GGMT dynamics

Let us now take the example of the Generalized Gaussian Moment Thermostatting (GGMT) equations. In this case, transforming the system into its normal form is more complex than in the simple example described in the beginning of the article.

We simulate N particules in d dimensions. The temperature is T, and the forces are $\mathbf{F}_i(\mathbf{q}) = -\dfrac{\partial V}{\partial \mathbf{q}_i}(\mathbf{q})$. The GGMT dynamics is:

$$\begin{aligned}
\dot{\mathbf{q}}_i &= \frac{\mathbf{p}_i}{m_i} && 1 \le i \le N \\
\dot{\mathbf{p}}_i &= \mathbf{F}_i(\mathbf{q}) - \left(\sum_{k=1}^{M} R_k \right) \mathbf{p}_i && 1 \le i \le N \\
\dot{p}_{\xi_k} &= \frac{S^k}{C_{k-1}} - dN \left(k_B T\right)^k && 1 \le k \le M
\end{aligned} \tag{4.1}$$

The constants $(C_k)_{k \ge -1}$ are given by

$$C_{-1} = \frac{1}{dN} \qquad C_0 = 1 \qquad C_k = \prod_{j=1}^{k} (dN + 2j)$$

We also set

$$S = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{m_i}$$

$$R_k = \frac{S^{k-1}}{C_{k-1}} \sum_{j=k}^{M} \frac{p_{\xi_j}}{Q_j} \left(k_B T\right)^{j-k} \qquad 1 \le k \le M$$

It is proved[9] that Eqs. (4.1) preserve the measure:

$$m_1 = e^{-\beta H(\mathbf{p},\mathbf{q}) - \beta \sum_{k=1}^{M} \frac{p_{\xi_k}^2}{2Q_k}} \; d^N\mathbf{p} \; d^N\mathbf{q} \; d^M p_\xi$$

with $\beta = 1/(k_B T)$ and $H(\mathbf{p},\mathbf{q}) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} + V(\mathbf{q})$. Furthermore, with the help of some additionnal variables η_k, one can find[9] a conserved energy and a conserved measure m_0.

The previous dynamical system is clearly not a system in a normal form, since $\dot{\mathbf{p}}_i$ depends on $\mathbf{p}_i$. As we did in the first simple application, we now add M variables ξ_k, whose dynamics is given by

$$\dot{\xi}_k = \mathcal{F}_k \left[(\mathbf{q}_i)_{i=1,N}, (\mathbf{p}_i)_{i=1,N}, (p_{\xi_k})_{k=1,M}, (\xi_k)_{k=1,M} \right]$$

where $\mathcal{F}_k$ is a function we are going to precise later on. We also need to take some initial conditions on these additional variables ξ_k. With all these data, we have a new dynamical system, written with variables $(\mathbf{q}_i, \mathbf{p}_i, p_{\xi_k}, \xi_k)$. This system is not in a normal form. We are going to transform it, finding new variables, in order for the new system to be in a normal form. Actually, the new variables will be $(\mathbf{q}_i, \tilde{\mathbf{p}}_i, p_{\xi_k}, \xi_k)$. So $\mathbf{p}_i$ is going to be replaced by $\tilde{\mathbf{p}}_i$.

Let us choose the following dynamics for ξ_k:

$$\begin{aligned} \dot{\xi}_1 &= \tilde{R}_1 \\ \dot{\xi}_k &= e^{-2(k-1)\left(\xi_1 + \sum_{j\neq k, j=2,\dots,M} \frac{1}{2(j-1)} \ln \xi_j\right)} \tilde{R}_k \qquad 2 \leq k \leq M \end{aligned} \tag{4.2}$$

The expressions of the $\tilde{R}_k$ are similar to the expressions of the R_k:

$$\tilde{R}_1 = \sum_{j=1}^{M} \frac{p_{\xi_j}}{Q_j} (k_B T)^{j-1}$$

$$\tilde{R}_k = 2(k-1) \frac{\tilde{S}^{k-1}}{C_{k-1}} \sum_{j=k}^{M} \frac{p_{\xi_j}}{Q_j} (k_B T)^{j-k} \qquad 2 \leq k \leq M$$

where $\tilde{S} = \sum_{i=1}^{N} \frac{\tilde{\mathbf{p}}_i^2}{m_i}$. So the quantity $\tilde{S}$ is the same as S, except that it is defined from variables $\tilde{\mathbf{p}}_i$ instead of variables $\mathbf{p}_i$. The new impulsions are linked to the old ones by

$$\tilde{\mathbf{p}}_i = e^{\chi} \mathbf{p}_i$$

with

$$\begin{aligned} \chi_1 &= \xi_1 \\ \chi_k &= \frac{1}{2(k-1)} \ln \xi_k \qquad 2 \leq k \leq M \\ \chi &= \textstyle\sum_{k=1}^{M} \chi_k \end{aligned} \tag{4.3}$$

Let us notice that it is possible to rewrite the dynamics on ξ_k for $k \geq 2$ as

$$\dot{\xi}_k = e^{-2(k-1)\left(\sum_{j \neq k, j=1,\dots,M} \chi_j\right)} \tilde{R}_k$$

From this equation, we can deduce that the dynamics of the M variables χ_k reads $\dot{\chi}_k = R_k$.

Let us now explain the transformation. In the initial dynamical system (4.1), $\dot{\mathbf{p}}_i$ depends on $\mathbf{p}_i$. It is thus natural to add the M variables χ_k defined by $\dot{\chi}_k = R_k$, and to transform $\mathbf{p}_i$ into $\tilde{\mathbf{p}}_i$ according to $\tilde{\mathbf{p}}_i = e^{\chi_1 + \dots + \chi_M}\, \mathbf{p}_i$. We want now to write the complete dynamical system only using variables $((\mathbf{q}_i)_{i=1,N}, (\tilde{\mathbf{p}}_i)_{i=1,N}, (p_{\xi_k})_{k=1,M}, (\chi_k)_{k=1,M})$. Reminding χ is the sum of the χ_k, we get

$$\begin{aligned} \dot{\mathbf{q}}_i &= \frac{\tilde{\mathbf{p}}_i}{m_i} e^{-\chi} && 1 \leq i \leq N \\ \dot{\tilde{\mathbf{p}}}_i &= e^{\chi} F_i(\mathbf{q}) && 1 \leq i \leq N \\ \dot{p}_{\xi_k} &= \frac{\tilde{S}^k}{C_{k-1}} e^{-2k\chi} - dN \left(k_B T\right)^k && 1 \leq k \leq M \end{aligned} \tag{4.4}$$

and

$$\dot{\chi}_k = \frac{\tilde{S}^{k-1}}{C_{k-1}} e^{-2(k-1)\chi} \sum_{j=k}^{M} \frac{p_{\xi_j}}{Q_j} \left(k_B T\right)^{j-k} \qquad 1 \leq k \leq M$$

So the system is not yet in a normal form, since $\dot{\chi}_k$ depends on χ_k (for $k \geq 2$). That is why we need to go from the χ_k to the ξ_k, defined as $\xi_k = e^{2(k-1)\,\chi_k}$ (for $k \geq 2$).

From this definition, it is possible to write the dynamics on ξ_k, which is exactly what we announced in Eq. (4.2). Then the dynamics for $(\mathbf{q}_i, \tilde{\mathbf{p}}_i, p_{\xi_k}, \xi_k)$ is given by the system (4.2)-(4.3)-(4.4). One can check that this set of differential equations is now a normal form system. It clearly preserves the measure

$$\tilde{m} = d^N\tilde{\mathbf{p}}\; d^N\mathbf{q}\; d^M p_\xi\; d^M\xi$$

If we write the measure $\tilde{m}$ with the original variables, we can check that $\tilde{m} = m_0$, where m_0 is the conserved measure given by Liu and Tuckerman[9]. In addition, the energy

$$\begin{aligned}\tilde{H}' = &\sum_{i=1}^{N} \frac{\tilde{\mathbf{p}}_i^2}{2m_i}\, e^{-2\chi} + V(\mathbf{q}) + \sum_{k=1}^{M} \frac{p_{\xi_k}^2}{2Q_k} \\ &+k_B T\, \left(\frac{C_0}{C_{-1}}\,\xi_1 + \frac{C_1}{C_0}\,\frac{\ln\xi_2}{2} + \frac{C_2}{C_1}\,\frac{\ln\xi_3}{2\times 2} + \ldots + \frac{C_{M-1}}{C_{M-2}}\,\frac{\ln\xi_M}{2(M-1)} \right)\end{aligned} \tag{4.5}$$

is preserved. A proof of this conservation is given in appendix (see Sec. V C).

B. Numerical results

On their web site[37], Frenkel and Smit propose many Molecular Dynamics codes, including sources. To get the results we present in this paper, we worked from one of these codes.

We want now to compare the algorithms given by our method with algorithms given by Liu and Tuckerman[9]. We choose to simulate one particle ($N = 1$), in one dimension ($d = 1$), in the quartic double well potential given by:

$$V(q) = D_0\,(a^2 - q^2)^2$$

Usually, Molecular Dynamics algorithms are first tested with the harmonic potential. However, when using this potential, the invariant measure is a Gaussian function. We

want to test algorithms given by our method on more demanding potentials. That is why we choose a double quartic well potential. We work with $D_0 = 1$, $a = 1.5$, and $k_B T = 1$. So, the barrier height is close to $5\, k_B T$. Initial conditions are $q(0) = 0$ and $p(0) = 1$. Thus, at the beginning of the simulation, the particle is in a non-equilibrium position, and goes toward the right well. In order to control the temperature, we use two thermostats ($M = 2$). Equations of motion in this case are given in appendix (see Sec. V B). We set the masses Q_1 and Q_2 of the thermostats according to adviced values[9], so $Q_1 = 1$ and $Q_2 = 8/3$.

To generate trajectories, two algorithms have been used. The first one is a reversible measure invariant algorithm. It is given in appendix (see Sec. V B). Generally speaking, we have focused on measure invariance, and not on energy conservation. So this algorithm is a simple one rather than a sophisticated one (see end of Sec. III for more details on this distinction).

The other algorithm is the one given by Liu and Tuckerman[9]. The authors present a general algorithm using a Yoshida-Suzuki decomposition[35,36]. We work with $n_c = n_{sy} = 1$. We have made this choice in order to compare our algorithm, which is not really improved in term of energy conservation, with an algorithm having the same feature. Of course, it is also possible to use a Yoshida-Suzuki decomposition on both algorithms.

For the Liu and Tuckerman algorithm, initial conditions for thermostat variables are $\eta_1(0) = \eta_2(0) = 0$ and $p_{\xi_1}(0) = -p_{\xi_2}(0) = 1$. For the measure invariant algorithm, initial conditions are $\xi_1(0) = 0$, $\xi_2(0) = 1$ and $p_{\xi_1}(0) = -p_{\xi_2}(0) = 1$. Thus, the energy has the same initial value in both simulations. With both algorithms, we generate trajectories of length $2.5\, 10^6$ steps, using a time step of $\Delta t = 0.001$.

With this dynamics, analytical position and impulsion distribution functions are

known. As the potential is symmetric, the particle spends equal amounts of time into both wells (let us notice that the particle has enough energy to cross the barrier). So the analytical position distribution function is symmetric. On a numerical point of view, getting the proper function is a challenge.

Results on position distribution functions are given in Fig. 1. One can see the functions generated by the algorithms, as well as the analytical solution. No algorithm gives a perfectly symmetrical function. However, the asymmetry is lower for the measure invariant algorithm.

Figure 1

In Fig. 2, we plot the quantity $< f(q) - f_{exact}(q) > (t)$ as a function of time. This quantity is an estimator of the difference between the analytical distribution function and the calculated function, and it is defined[9] by

$$< f(q) - f_{exact}(q) > (t) = \frac{1}{\mathcal{N}(t)} \sum_{i=1}^{\mathcal{N}(t)} \mid \overline{f}_t(q_i) - f_{exact}(q_i) \mid$$

At time t, $\mathcal{N}(t)$ bins have been generated. With these bins, it is possible to calculate a distribution function, which is $\overline{f}_t$. We can see that the distribution function generated by the measure invariant algorithm converges more quickly to the proper one. So, in term of position distribution function, the measure invariant algorithm gives better results.

Figure 2

We show on Fig. 3 the impulsion distribution functions generated by the algorithms, as well as the analytical solution.

Figure 3

The Liu and Tuckerman algorithm function is closer to the analytical solution. However, when one looks at the convergence of the calculated distribution function to the

exact one, algorithms performances are similar. The convergence can be estimated by many ways. We can look at the quantity $< f(p) - f_{exact}(p) >$ (cf. Fig. 4), but also at the moments of the distribution function. The second moment (which is linked to the temperature) is given on Fig. 5, whereas the fourth moment is given on Fig. 6. Obviously, both algorithms have the same performances.

Figure 4

Figure 5

Figure 6

Finally, let us give results on the conservation of the energy. The expression of the conserved energy is given in Eq. (4.5) when using the new variables. Let us underline the fact that we have chosen initial conditions for both simulations so that the initial values of the energy are the same: $\tilde{H}'_{mi}(t=0) = H'_{lt}(t=0) = 6.25$. Results are given in Fig. 7. The Liu and Tuckerman algorithm better preserves the energy. At all times, its numerical energy is close to the correct value. Our algorithm quite well preserves the energy for times $t \leq 1800$. At that moment, there is a sudden change. For times $t \geq 1800$, the numerical energy keeps constant, but at another value. However, one can notice that this change has no consequence on the quality of the distribution functions generated by our algorithm. We can see this kind of "shock" neither on the position distribution function (see Fig. 2) nor on the impulsion functions (see Figs. 4, 5 and 6). We think that it can be possible to improve our algorithm by changing the Trotter decomposition order.

Figure 7

ACKNOWLEDGMENTS

We would like to thank Eric Cancès and Philippe Chartier for stimulating discussions

and useful indications of the literature. We would also like to thank the referee for his suggestions.

V. APPENDIX

A. Nosé-Hoover chains for NVT and NPT ensembles

In this part, we want to show how to proceed to find equations in the normal form from the NPT equations, that simulate particles at constant temperature and constant pressure. So, we study N particles in d dimensions, that are coupled to M thermostats and one barostat. Let N_f be the number of degrees of freedom of the system that we have to thermostate. For the NPT equations, given below, $N_f = dN + 1$.

This formalism also includes the NVT ensemble. To go back to it, we first need to set $N_f = dN$. We need also to set $1/W = 0$, so V becomes a constant. The NVT ensemble equations only involve $(\mathbf{q}_i, \mathbf{p}_i, p_{\xi_k}, \xi_k)$.

We consider the following NPT equations[7]. The particles positions are $\mathbf{q}_i$, their impulsion are $\mathbf{p}_i$. They are coupled to a single barostat described by p_ε. The volume V is allowed to fluctuate, but we want the pressure to stay constant at P_{ext}. The barostat and the particles are coupled to the same chain of thermostats, described by p_{ξ_k}, in order for the simulation to run at constant temperature T (let us notice that slightly different dynamics are possible, that also generate the NPT ensemble).

$$
\begin{aligned}
\dot{\mathbf{q}}_i &= \frac{\mathbf{p}_i}{m_i} + \frac{p_\varepsilon}{W}\,\mathbf{q}_i && 1 \le i \le N \\
\dot{\mathbf{p}}_i &= \mathbf{F}_i - \frac{p_{\xi_1}}{Q_1}\,\mathbf{p}_i - \left(1+\frac{1}{N}\right)\frac{p_\varepsilon}{W}\,\mathbf{p}_i && 1 \le i \le N \\
\dot{p}_{\xi_1} &= \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{m_i} + \frac{p_\varepsilon^2}{W} - N_f k_B T - \frac{p_{\xi_2}}{Q_2}\,p_{\xi_1} \\
\dot{p}_{\xi_k} &= \frac{p_{\xi_{k-1}}^2}{Q_{k-1}} - k_B T - \frac{p_{\xi_{k+1}}}{Q_{k+1}}\,p_{\xi_k} && 2 \le k \le M-1 \qquad (5.1) \\
\dot{p}_{\xi_M} &= \frac{p_{\xi_{M-1}}^2}{Q_{M-1}} - k_B T \\
\dot{V} &= \frac{dV p_\varepsilon}{W} \\
\dot{p}_\varepsilon &= dV\,(P_{int} - P_{ext}) \;+\; \frac{1}{N}\sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{m_i} - \frac{p_{\xi_1}}{Q_1}\,p_\varepsilon
\end{aligned}
$$

Internal pressure and forces are defined by

$$
P_{int} = \frac{1}{dV}\left(\sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{m_i} + \sum_{i=1}^{N}\mathbf{q}_i\cdot\mathbf{F}_i - dV\,\frac{\partial\phi(\mathbf{q},V)}{\partial V}\right) \qquad (5.2)
$$

and $\mathbf{F}_i = -\dfrac{\partial\phi(\mathbf{q},V)}{\partial\mathbf{q}_i}$. Let us set $H(\mathbf{p},\mathbf{q},V) = \displaystyle\sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{2m_i} + \phi(\mathbf{q},V)$. It is known that the system (5.1) preserves the following measure

$$
m_1 = e^{-\beta H'}\,d^N\mathbf{p}\;d^N\mathbf{q}\;d^M p_\xi\;dp_\varepsilon\;dV
$$

with

$$
H' = H(\mathbf{p},\mathbf{q},V) + \frac{p_\varepsilon^2}{2W} + \sum_{k=1}^{M}\frac{p_{\xi_k}^2}{2Q_k} + P_{ext}V
$$

The system (5.1) is obviously not in a normal form. So we add M variables ξ_k, whose dynamics is:

$$\dot{\xi}_k = \frac{p_{\xi_k}}{Q_k} \quad 1 \leq k \leq M$$

Now we have a system written in variables $(\mathbf{q}_i, \mathbf{p}_i, p_{\xi_k}, \xi_k, V, p_\varepsilon)$. We are going to change of variables. The new ones are $(\tilde{\mathbf{q}}_i, \tilde{\mathbf{p}}_i, \tilde{p}_{\xi_k}, \xi_k, \tilde{V}, \tilde{p}_\varepsilon)$. We set

$$\begin{aligned}
\tilde{\mathbf{q}}_i &= V^{-\frac{1}{d}}\ \mathbf{q}_i & 1 \leq i \leq N \\
\tilde{\mathbf{p}}_i &= V^{\frac{N+1}{dN}}\ e^{\xi_1}\ \mathbf{p}_i & 1 \leq i \leq N \\
\tilde{p}_{\xi_k} &= e^{\xi_{k+1}}\ p_{\xi_k} & 1 \leq k \leq M-1 \\
\tilde{p}_{\xi_M} &= p_{\xi_M} \\
\tilde{V} &= \ln V \\
\tilde{p}_\varepsilon &= e^{\xi_1}\ p_\varepsilon
\end{aligned} \tag{5.3}$$

With these new variables, the dynamical system can be rewritten as

$$
\begin{aligned}
\dot{\tilde{\mathbf{q}}}_i &= \frac{\tilde{\mathbf{p}}_i}{m_i}\, e^{-\xi_1}\, e^{-\tilde{V}\left(\frac{1}{dN}+\frac{2}{d}\right)} && 1 \le i \le N \\
\dot{\tilde{\mathbf{p}}}_i &= e^{\tilde{V}\frac{N+1}{dN}}\, e^{\xi_1}\, \mathbf{F}_i && 1 \le i \le N \\
\dot{\tilde{p}}_{\xi_1} &= e^{\xi_2}\left[e^{-2\xi_1}\, e^{-2\tilde{V}\frac{N+1}{dN}}\left(\sum_{i=1}^{N}\frac{\tilde{\mathbf{p}}_i^2}{m_i}\right) + e^{-2\xi_1}\,\frac{\tilde{p}_\varepsilon^2}{W} - N_f k_B T\right] \\
\dot{\tilde{p}}_{\xi_k} &= e^{\xi_{k+1}}\left(\frac{\tilde{p}_{\xi_{k-1}}^2}{Q_{k-1}}\, e^{-2\xi_k} - k_B T\right) && 2 \le k \le M-1 \\
\dot{\tilde{p}}_{\xi_M} &= \frac{\tilde{p}_{\xi_{M-1}}^2}{Q_{M-1}}\, e^{-2\xi_M} - k_B T && (5.4) \\
\dot{\xi}_k &= \frac{\tilde{p}_{\xi_k}}{Q_k}\, e^{-\xi_{k+1}} && 1 \le k \le M-1 \\
\dot{\xi}_M &= \frac{\tilde{p}_{\xi_M}}{Q_M} \\
\dot{\tilde{V}} &= \frac{d}{W}\, e^{-\xi_1}\tilde{p}_\varepsilon \\
\dot{\tilde{p}}_\varepsilon &= e^{\xi_1}\left[d\, e^{\tilde{V}}\,(P_{int} - P_{ext}) + \frac{1}{N}\, e^{-2\xi_1}\, e^{-2\tilde{V}\frac{N+1}{dN}}\sum_{i=1}^{N}\frac{\tilde{\mathbf{p}}_i^2}{m_i}\right]
\end{aligned}
$$

In the last equation, P_{int} is defined as in (5.2), but has to be written with variables introduced in (5.3). The important thing is that we can check by (5.2) that P_{int} does not depend on $\tilde{p}_\varepsilon$.

It is straightforward to notice that this last system of equations is in a normal form.

So the measure

$$\tilde{m} = d^N\tilde{\mathbf{p}}\; d^N\tilde{\mathbf{q}}\; d^M\tilde{p}_\xi\; d^M\xi\; d\tilde{p}_\varepsilon\; d\tilde{V}$$

is conserved. Thanks to (5.3), we can express $\tilde{m}$ with the original variables, and check that we find the same measure as the one already known[2]. With the new variables, the energy reads:

$$\begin{aligned}\tilde{H}' \;=\; & e^{-2\xi_1}\, e^{-2\tilde{V}\frac{N+1}{dN}} \sum_{i=1}^{N} \frac{\tilde{\mathbf{p}}_i^2}{2m_i} \;+\; \phi(e^{\tilde{V}/d}\,\tilde{\mathbf{q}}, e^{\tilde{V}}) \;+\; \sum_{k=1}^{M-1} \frac{\tilde{p}_{\xi_k}^2}{2Q_k}\, e^{-2\xi_{k+1}} \;+\; \frac{\tilde{p}_{\xi_M}^2}{2Q_M} \\ & +\; e^{-2\xi_1}\, \frac{\tilde{p}_\varepsilon^2}{2W} \;+\; N_f\, k_B T\, \xi_1 + k_B T \sum_{k=2}^{M} \xi_k \;+\; P_{ext}\, e^{\tilde{V}}\end{aligned} \tag{5.5}$$

From the system (5.4), it is straightforward to generate an algorithm. In the particular case $M = 2$, the classical Liouville propagator can be factorized as

$$L = L_1 + L_2 + L_3 + L_4 + L_5 + L_6 + L_7 + L_8$$

with

$$\begin{aligned} L_1 &= \dot{\xi}_1\, \partial_{\xi_1} \\ L_2 &= \dot{\xi}_2\, \partial_{\xi_2} \\ L_3 &= \dot{\tilde{p}}_{\xi_1}\, \partial_{\tilde{p}_{\xi_1}} \\ L_4 &= \dot{\tilde{p}}_{\xi_2}\, \partial_{\tilde{p}_{\xi_2}} \\ L_5 &= \textstyle\sum_{i=1}^{N} \dot{\tilde{\mathbf{p}}}_i\, \partial_{\tilde{\mathbf{p}}_i} \\ L_6 &= \textstyle\sum_{i=1}^{N} \dot{\tilde{\mathbf{q}}}_i\, \partial_{\tilde{\mathbf{q}}_i} \\ L_7 &= \dot{\tilde{V}}\, \partial_{\tilde{V}} \\ L_8 &= \dot{\tilde{p}}_\varepsilon\, \partial_{\tilde{p}_\varepsilon} \end{aligned}$$

We took advantage of the fact that the operators $\dot{\tilde{\mathbf{p}}}_i\, \partial_{\tilde{\mathbf{p}}_i}$ commute one with each other, as well as the operators $\dot{\tilde{\mathbf{q}}}_i\, \partial_{\tilde{\mathbf{q}}_i}$. From then on, we go on as in the first example. We expand $e^{\Delta t\, L}$ as in equations (3.6) - (3.7), or in a more sophisticated way to better preserve the energy.

B. GGMT dynamics, Case $M = 2, N = 1, d = 1$

In section IV, we present numerical results for the simulation of one particle coupled to a chain of two thermostats. In the following lines, we are going to detail the algorithm we implemented. Let us first rewrite the system (4.2)-(4.4) in this particular case. We have $e^{\chi} = \sqrt{\xi_2}\, e^{\xi_1}$. The dynamics for $(q, \tilde{p}, p_{\xi_1}, p_{\xi_2}, \xi_1, \xi_2)$ is

$$\begin{aligned}
\dot{q} &= \frac{\tilde{p}}{m}\,\frac{e^{-\xi_1}}{\sqrt{\xi_2}} \\
\dot{\tilde{p}} &= \sqrt{\xi_2}\, e^{\xi_1}\, F(q) \\
\dot{p_{\xi_1}} &= \frac{\tilde{p}^2}{m}\,\frac{e^{-2\xi_1}}{\xi_2} - k_B T \\
\dot{p_{\xi_2}} &= \frac{\tilde{p}^4}{3m^2}\,\frac{e^{-4\xi_1}}{\xi_2^2} - (k_B T)^2 \\
\dot{\xi}_1 &= \frac{p_{\xi_1}}{Q_1} + \frac{p_{\xi_2}}{Q_2}\, k_B T \\
\dot{\xi}_2 &= \frac{2}{3}\, e^{-2\xi_1}\,\frac{\tilde{p}^2}{m}\,\frac{p_{\xi_2}}{Q_2}
\end{aligned} \tag{5.6}$$

and the energy reads

$$\tilde{H}' = \frac{\tilde{p}^2}{2m}\,\frac{e^{-2\xi_1}}{\xi_2} + V(q) + \frac{p_{\xi_1}^2}{2Q_1} + \frac{p_{\xi_2}^2}{2Q_2} + k_B T\left(\xi_1 + \frac{3}{2}\,\ln \xi_2\right)$$

The preserved measure is

$$\tilde{m} = dq\; dp\; dp_{\xi_1}\; dp_{\xi_2}\; d\xi_1 d\xi_2$$

Let

$$
\begin{aligned}
L_1 &= \dot{\xi}_1 \, \partial_{\xi_1} \\
L_2 &= \dot{\xi}_2 \, \partial_{\xi_2} \\
L_3 &= \dot{\tilde{p}} \, \partial_{\tilde{p}} \\
L_4 &= \dot{q} \, \partial_q + \dot{p}_{\xi_1} \, \partial_{p_{\xi_1}} + \dot{p}_{\xi_2} \, \partial_{p_{\xi_2}}
\end{aligned}
$$

We can generate 4! algorithms of the form

$$
e^{\frac{\Delta t}{2} L_a} \; e^{\frac{\Delta t}{2} L_b} \; e^{\frac{\Delta t}{2} L_c} \; e^{\Delta t L_d} \; e^{\frac{\Delta t}{2} L_c} \; e^{\frac{\Delta t}{2} L_b} \; e^{\frac{\Delta t}{2} L_a} \;=\; e^{\Delta t L_{eff}}
$$

with $\{a, b, c, d\} = \{1, 2, 3, 4\}$. We implemented this algorithm with $(a, b, c, d) = (1, 2, 3, 4)$.

C. Proof of the conservation of the energy for the GGMT dynamics

We want to prove that the energy written in (4.5) is conserved by the dynamics (4.2)-(4.3)-(4.4). Thanks to the relations $\xi_1 = \chi_1$, $\xi_k = e^{2(k-1)\chi_k}$ for $k \geq 2$, we can first rewrite the energy as

$$
\tilde{H}' = \sum_{i=1}^{N} \frac{\tilde{\mathbf{p}}_i^2}{2m_i} \, e^{-2\chi} + V(\mathbf{q}) + \sum_{k=1}^{M} \frac{p_{\xi_k}^2}{2Q_k}
$$

$$
+ k_B T \left(\frac{C_0}{C_{-1}} \, \chi_1 + \frac{C_1}{C_0} \, \chi_2 + \frac{C_2}{C_1} \, \chi_3 + \ldots + \frac{C_{M-1}}{C_{M-2}} \, \chi_M \right)
$$

We know[9] that the following energy is preserved:

$$
H' = \sum_{i=1}^{N} \frac{\tilde{\mathbf{p}}_i^2}{2m_i} \, e^{-2\chi} + V(\mathbf{q}) + \sum_{k=1}^{M} \frac{p_{\xi_k}^2}{2Q_k} + dN \, k_B T \sum_{k=1}^{M} \eta_k
$$

where the dynamics on η_k is

$$
\dot{\eta}_k = \frac{p_{\xi_k}}{Q_k} \; \frac{1}{dN} \; \sum_{j=1}^{k} (k_B T)^{k-j} \; \frac{S^{j-1}}{C_{j-2}}
$$

We then only have to check that:

$$dN \sum_{k=1}^{M} \dot{\eta}_k \;=\; \left(\frac{C_0}{C_{-1}} \dot{\chi}_1 + \frac{C_1}{C_0} \dot{\chi}_2 + \frac{C_2}{C_1} \dot{\chi}_3 + \ldots + \frac{C_{M-1}}{C_{M-2}} \dot{\chi}_M \right) \qquad (5.7)$$

We have $\dot{\chi}_k = \sum_{j=k}^{M} \frac{p_{\xi_j}}{Q_j} \, (k_B T)^{j-k} \, \frac{S^{k-1}}{C_{k-1}}$. So

$$\dot{\chi}_1 \;=\; \frac{p_{\xi_1}}{Q_1} \;+\; \frac{p_{\xi_2}}{Q_2} (k_B T) \;+\; \frac{p_{\xi_3}}{Q_3} (k_B T)^2 \;+\; \ldots \;+\; \frac{p_{\xi_M}}{Q_M} (k_B T)^{M-1}$$

$$\dot{\chi}_2 \;=\; \frac{p_{\xi_2}}{Q_2} \frac{S}{C_1} \;+\; \frac{p_{\xi_3}}{Q_3} \frac{S}{C_1} (k_B T) \;+\; \ldots \;+\; \frac{p_{\xi_M}}{Q_M} \frac{S}{C_1} (k_B T)^{M-2}$$

$$\dot{\chi}_M \;=\; \frac{p_{\xi_M}}{Q_M} \frac{S^{M-1}}{C_{M-1}}$$

whereas

$$dN \, \dot{\eta}_1 \;=\; \frac{1}{C_{-1}} \frac{p_{\xi_1}}{Q_1}$$

$$dN \, \dot{\eta}_2 \;=\; \frac{1}{C_{-1}} \frac{p_{\xi_2}}{Q_2} (k_B T) \;+\; \frac{p_{\xi_2}}{Q_2} \frac{S}{C_0}$$

$$dN \, \dot{\eta}_3 \;=\; \frac{1}{C_{-1}} \frac{p_{\xi_3}}{Q_3} (k_B T)^2 \;+\; \frac{p_{\xi_3}}{Q_3} \frac{S}{C_0} (k_B T) \;+\; \frac{p_{\xi_3}}{Q_3} \frac{S^2}{C_1}$$

$$dN \, \dot{\eta}_M \;=\; \frac{1}{C_{-1}} \frac{p_{\xi_M}}{Q_M} (k_B T)^{M-1} \;+\; \frac{p_{\xi_M}}{Q_M} \frac{S}{C_0} (k_B T)^{M-2} \;+\; \frac{p_{\xi_M}}{Q_M} \frac{S^2}{C_1} (k_B T)^{M-3} \;+\; \ldots \;+\; \frac{p_{\xi_M}}{Q_M} \frac{S^{M-1}}{C_{M-2}}$$

So the equation (5.7) is true.

D. Non-exact preservation of the measure for the algorithm Liu et al.[9] proposed for GGMT dynamics, case of the free particle

We show here that the algorithm proposed by Liu and Tuckerman[9] does not exactly preserve the measure analytically, in the very special case of a free particle (a more general case is studied in the next section). However, we will see that, for some initial conditions, the preservation, if not exact, is very good. This may explain the good numerical properties that Liu and Tuckerman noticed.

We work in the case $M = 2$ (two thermostats), $N = 1$ and $d = 1$ (one particle in a one-dimensionnal space), and with the variables used by the authors, i.e. $X = (q, p, p_{\xi_1}, p_{\xi_2}, \eta_1, \eta_2)$. We use MAPLE to get explicit formulas when needed.

The GGMT equations:

For the present moment, we recall the GGMT equations and the algorithm proposed by Liu and Tuckerman, without any assumption on the force. The equations are

$$\begin{aligned}
\dot{q} &= \frac{p}{m} \\
\dot{p} &= F(q) - \frac{p_{\xi_1}}{Q_1}\, p - \frac{p_{\xi_2}}{Q_2}\left((k_B T)p + \frac{p^3}{3m}\right) \\
\dot{\eta}_1 &= \frac{p_{\xi_1}}{Q_1} \\
\dot{\eta}_2 &= \left(k_B T + \frac{p^2}{m}\right)\frac{p_{\xi_2}}{Q_2} \\
\dot{p}_{\xi_1} &= \frac{p^2}{m} - k_B T \\
\dot{p}_{\xi_2} &= \frac{p^4}{3m^2} - (k_B T)^2
\end{aligned}$$

They preserve the following measure

$$m_0 = e^{\eta_1+\eta_2}\; dp\; dq\; dp_{\xi_1}\; dp_{\xi_2}\; d\eta_1\; d\eta_2 \tag{5.8}$$

The algorithm proposed by Liu and Tuckerman is the following

$$e^{\Delta t\, L_{eff}} \;=\; e^{\frac{\Delta t}{2} L_{GGMT}}\; e^{\frac{\Delta t}{2} F(q)\,\partial_p}\; e^{\Delta t \frac{p}{m}\,\partial_q}\; e^{\frac{\Delta t}{2} F(q)\,\partial_p}\; e^{\frac{\Delta t}{2} L_{GGMT}} \tag{5.9}$$

The central part of this decomposition corresponds to the simple Velocity Verlet algorithm. The external operator is

$$\exp\left(\frac{\Delta t}{2}\, L_{GGMT}\right) = A(\Delta t)\; B(\Delta t)\; C(\Delta t)\; B(\Delta t)\; A(\Delta t)$$

The operators $A(\Delta t)$, $B(\Delta t)$ and $C(\Delta t)$ are defined by

$$A(\Delta t) \;=\; \exp\left(\frac{\Delta t}{4}\, G_1(p)\,\partial_{p_{\xi_1}}\right)\; \exp\left(\frac{\Delta t}{4}\, G_2(p)\,\partial_{p_{\xi_2}}\right)$$

$$B(\Delta t) \;=\; \exp\left(-\frac{\Delta t}{8}\lambda\, p\,\partial_p\right)\; \exp\left(-\frac{\Delta t}{4}\,\frac{p_{\xi_2}}{Q_2}\,\frac{p^3}{3m}\,\partial_p\right)\; \exp\left(-\frac{\Delta t}{8}\lambda\, p\,\partial_p\right)$$

$$C(\Delta t) \;=\; \exp\left(\frac{\Delta t}{2}\,\frac{p_{\xi_1}}{Q_1}\,\partial_{\eta_1}\right)\; \exp\left(\frac{\Delta t}{2}\, g(p)\,\frac{p_{\xi_2}}{Q_2}\,\partial_{\eta_2}\right)$$

We set

$$\lambda(X) \;=\; \frac{p_{\xi_1}}{Q_1} + k_B T\,\frac{p_{\xi_2}}{Q_2}$$

$$g(p) \;=\; k_B T + \frac{p^2}{m}$$

$$G_1(p) \;=\; \frac{p^2}{m} - k_B T$$

$$G_2(p) \;=\; \frac{p^4}{3m^2} - (k_B T)^2$$

$$\mathcal{G}(p) \;=\; \frac{G_1(p)}{Q_1} + k_B T\,\frac{G_2(p)}{Q_2}$$

$$U(X) \;=\; \eta_1 + \eta_2$$

If the vector X' is a function of the vector X, the Jacobian matrix is noted $\frac{\partial X'}{\partial X}$. The Jacobian of the transformation is $\mathrm{Jac}\left(\frac{\partial X'}{\partial X}\right)$.

If the complete algorithm (5.9) preserves the measure m_0 defined by Eq. (5.8), we have

$$m_0\left[X'(X)\right] = m_0\left[X\right]$$

Using the Jacobian of the function $X'(X)$, and the function $U(X)$ already defined, we get

$$\mathrm{Jac}\left(\frac{\partial X'}{\partial X}\right) = e^{U(X)-U(X')} \tag{5.10}$$

Study in the case $F(q) = 0$:

The equation (5.10) must be true for all parameters m, Q_1, Q_2, T, Δt, and for all initial conditions X. Let us now choose some specific values for some parameters:

$$m = 1.0, \qquad Q_1 = 1.0, \qquad Q_2 = 8/3, \qquad k_B T = 1.0$$

Then $\mathcal{G}(p) = \frac{p^4}{8} + p^2 - \frac{11}{8}$. Let μ be the real positive root of $\mathcal{G}$: $\mu = \sqrt{-4 + 3\sqrt{3}}$.

We also choose some specific initial conditions $X = (q, p, p_{\xi_1}(p), p_{\xi_2}(p), \eta_1, \eta_2)$. So, in

X, there are only 4 free variables, and we choose p_{ξ_1} and p_{ξ_2} according to

$$\begin{aligned} p_{\xi_2}(p) &= 3\,m\,Q_2\,\frac{p^2-\mu^2}{\Delta t\;\mu^2 p^2} - \frac{\Delta t}{4} G_2(p) \\ &= 8\,\frac{p^2-\mu^2}{\Delta t\;\mu^2 p^2} - \frac{\Delta t}{4}\left(\frac{p^4}{3} - 1.0\right) \\ \text{and} \qquad p_{\xi_1}(p) &= -Q_1\left(\frac{k_B T}{Q_2} p_{\xi_2}(p) + \frac{\Delta t}{4}\mathcal{G}(p)\right) \\ &= -\left(\frac{3}{8} p_{\xi_2}(p) + \frac{\Delta t}{4}\mathcal{G}(p)\right) \end{aligned} \tag{5.11}$$

where μ is the real positive root of $\mathcal{G}(p)$ (we assumed that $\Delta t > 0$). Reasons to make this choice can be found in the next section, in which we give a general proof of the non preservation of the measure.

Using MAPLE, we compute $\eta_1(\Delta t)$ and $\eta_2(\Delta t)$. Working only with $p \geq 0$, we have

$$\eta_1(\Delta t) = -\frac{1}{4}\,\frac{16\,\eta_1\,p^2 - 12\,\eta_1\,p^2\,\sqrt{3} + 12\,p^2 + 48 - 36\,\sqrt{3} - 47\,\Delta t^2\,p^2 + 27\,\Delta t^2\,p^2\,\sqrt{3}}{(-4+3\sqrt{3})\;p^2}$$

and

$$\begin{aligned} &\eta_1 + \eta_2 - \eta_1(\Delta t) - \eta_2(\Delta t) \\ &\quad = 6\,\frac{p^2\;\left(-36\,p^2\,\sqrt{3} + 249\,\Delta t^2\,p^2\,\sqrt{3} - 288\,\sqrt{3} - 431\,\Delta t^2\,p^2 + 48\,p^2 + 516\right)}{(-4+3\,\sqrt{3})\;(-4+3\,\sqrt{3}+p^2)\;(18\,p^2 + 24 - 18\,\sqrt{3} - 47\,\Delta t^2\,p^2 + 27\,\Delta t^2\,p^2\,\sqrt{3})} \end{aligned}$$

where η_1 stands for $\eta_1(0)$ and η_2 for $\eta_2(0)$.

We can also compute

$$\text{Jac}\left(\frac{\partial X'}{\partial X}\right) = 6\,\frac{\left(-4+3\,\sqrt{3}\right)^{3/2}\;\sqrt{3}\;\sqrt{2}}{\left(12\,p^2 + 24 - 18\,\sqrt{3} - 47\,\Delta t^2\,p^2 + 27\,\Delta t^2\,p^2\,\sqrt{3}\right)^{3/2}}$$

If $\Delta t = 0$, we choose $p = \mu$, so initial values for p_{ξ_1} and p_{ξ_2} are well defined. With these values, one can check that $\eta_1 + \eta_2 - \eta_1(\Delta t) - \eta_2(\Delta t) = 0$ and that $\text{Jac}\left(\frac{\partial X'}{\partial X}\right) = 1$.

Now we have to check whether $\text{Jac}\left(\frac{\partial X'}{\partial X}\right)$ is equal to $e^{\eta_1+\eta_2-\eta_1(\Delta t)-\eta_2(\Delta t)}$. We notice that these two functions depend only on p and Δt, and not on q, η_1 or η_2. In Fig. 8, we plot the ratio $\text{Jac}\left(\frac{\partial X'}{\partial X}\right) / e^{\eta_1+\eta_2-\eta_1(\Delta t)-\eta_2(\Delta t)}$ for $\Delta t = 0.001$ and for $p \in [2.0; 5.0]$, and we compare it with 1.

Figure 8

We clearly see that, for some values of the impulsion p, the ratio is different from 1. However, in Fig. 9, we plot the same ratio for $p \in [0.9; 1.1]$ (with the same value for Δt):

Figure 9

Functions are close to each other. We can check that their values for $p = 1$ are really close:

$$\text{Jac}\left(\frac{\partial X'}{\partial X}\right)(p=1) \;=\; 1.81517$$

$$e^{\eta_1+\eta_2-\eta_1(\Delta t)-\eta_2(\Delta t)}(p=1) \;=\; 1.81153$$

When $p = 1$, the initial condition is $X = (q, 1, 491.96, -1311.89, \eta_1, \eta_2)$.

So, for some initial conditions, the measure is very well preserved. However, for some other initial conditions, it is not at all preserved.

E. Non-exact preservation of the measure for the algorithm Liu et al.[9] proposed for GGMT dynamics, a more general case

In the previous section, we study the very special case of a free particle, $F(q) = 0$. Now, we have a look at a more general case: we suppose that the force $F(q)$ is a polynomial function of q, which degree is odd (for instance, this is the force given by the harmonic oscillator). We still work with $M = 2$ (two thermostats), $N = 1$ and $d = 1$ (one

particle in a one-dimensionnal space), and with the variables used by the authors, i.e. $X = (q, p, p_{\xi_1}, p_{\xi_2}, \eta_1, \eta_2)$. The GGMT equations and the algorithm to integrate them are the same as in the previous section.

The main idea:

Previously, thanks to the simple choice made for the force, we used MAPLE to get explicit formulas. Here, we do not use MAPLE, but we rather give a more general proof. It will enlighten the choice of the functions $p_{\xi_1}(p)$ and $p_{\xi_2}(p)$ made in Eq. (5.11).

Our proof is based on the concept of algebraicity[38]. We will use the following facts. A polynomial function is algebraic. Any function obtained by addition, multiplication or composition of a finite number of algebraic functions is algebraic. Any root of a polynomial function is an algebraic function of the coefficients. However, the function $x \mapsto e^x$, with x real, is not algebraic. We suppose that the algorithm (5.9) is measure invariant, and we look for a contradiction.

Let us set $X^a = A(\Delta t)\, X$. It can be checked that the vector X^a is a polynomial function of X, and thus a real algebraical function of X. Let us suppose for a moment that $X' = e^{\Delta t\, L_{eff}}\ X$ is an algebraical function of X. We assume that the complete algorithm (5.9) preserves the measure m_0 defined by Eq. (5.8). So we have

$$\mathrm{Jac}\left(\frac{\partial X'}{\partial X}\right) = e^{U(X)-U(X')}$$

We know that $X'(X)$ and $U(X)$ are algebraical functions of X. Furthermore, they are not constant. So we conclude that the exponential of an algebraical function is an algebraical function, which is not true. We reach the contradiction.

The difficulty and how to solve it:

The previous proof is incorrect, since X' is actually not an algebraical function of X. The issue is on the operator $B(\Delta t)$, which only modifies the value of the impulsion. Let us set $X^b = B(\Delta t)X$. The impulsion in X and X^b are respectively p and p^b, and the second thermostat impulsion in X is p_{ξ_2}. Setting $\alpha = \frac{p_{\xi_2}}{3mQ_2}$ and $\lambda = \lambda(X)$, we have

$$p^b = \frac{p\, e^{-\lambda \frac{\Delta t}{4}}}{\sqrt{1 + \alpha \frac{\Delta t}{2} p^2 e^{-\lambda \frac{\Delta t}{4}}}}$$

$$\mathrm{Jac}\left(\frac{\partial X^b}{\partial X}\right)(X) = \frac{\partial p^b}{\partial p}(p) = \frac{e^{-\lambda \frac{\Delta t}{4}}}{\left(1 + \alpha \frac{\Delta t}{2} p^2 e^{-\lambda \frac{\Delta t}{4}}\right)^{3/2}}$$

Because p^b depends on $\lambda(X)$ by an exponential function, the vector X^b is not an algebraical function of X.

Now, let us suppose that, instead of working with X, we work with $\tilde{X} = (q, p, p_{\xi_2})$. We define X as a function of $\tilde{X}$ by $X(\tilde{X}) = (q, p, -Q_1\, k_B T\, p_{\xi_2}/Q_2, p_{\xi_2}, 0, 0)$. Let us now set $X^b = B(\Delta t)\, X(\tilde{X})$. As $\lambda(X) = 0$, we check, thanks to the formulas previously written, that

- X^b is an algebraical function of $\tilde{X}$
- $\mathrm{Jac}\left(\frac{\partial X^b}{\partial X}\right)(X(\tilde{X}))$ is also an algebraical function of $\tilde{X}$.

So we solved our issue.

The solution on the whole algorithm:

In the algorithm (5.9), the operator $B(\Delta t)$ appears four times. However, between the first and the second time, and between the third and the fourth time, the value of λ is not modified. All we need to ensure is that $\lambda = 0$ just before the first application of

$B(\Delta t)$, and also just before the third application. We set

$$X \overset{A(\Delta t)}{\longrightarrow} X^a \overset{B(\Delta t)}{\longrightarrow} X^b \overset{C(\Delta t)}{\longrightarrow} X^c \overset{B(\Delta t)}{\longrightarrow} X^d \overset{A(\Delta t)}{\longrightarrow} X^e$$

$$X^e \overset{L_p(\Delta t/2)}{\longrightarrow} X^f \overset{L_q(\Delta t)}{\longrightarrow} X^g \overset{L_p(\Delta t/2)}{\longrightarrow} X^h$$

$$X^h \overset{A(\Delta t)}{\longrightarrow} X^i \overset{B(\Delta t)}{\longrightarrow} X^j \overset{C(\Delta t)}{\longrightarrow} X^k \overset{B(\Delta t)}{\longrightarrow} X^l \overset{A(\Delta t)}{\longrightarrow} X^m$$

with $X = (q, p, p_{\xi_1}, p_{\xi_2}, \eta_1, \eta_2)$, $X^a = (q^a, p^a, p^a_{\xi_1}, p^a_{\xi_2}, \eta^a_1, \eta^a_2)$, and so on. So we need to ensure that $\lambda(X^a) = \lambda(X^i) = 0$.

Expression of the constraints:

We compute

$$\lambda(X^a) = \frac{1}{Q_1}\left(p_{\xi_1} + \frac{\Delta t}{4}\, G_1(p)\right) + \frac{k_B T}{Q_2}\left(p_{\xi_2} + \frac{\Delta t}{4}\, G_2(p)\right)$$

and

$$\begin{aligned}
\lambda(X^i) &= \lambda(X^h) + \frac{\Delta t}{4}\left(\frac{G_1(p^h)}{Q_1} + k_B T\, \frac{G_2(p^h)}{Q_2}\right) \\
&= \lambda(X^e) + \frac{\Delta t}{4}\, \mathcal{G}(p^h) \\
&= \lambda(X^d) + \frac{\Delta t}{4}\, \mathcal{G}(p^d) + \frac{\Delta t}{4}\, \mathcal{G}(p^h) \\
&= \lambda(X^a) + \frac{\Delta t}{4}\, \mathcal{G}(p^d) + \frac{\Delta t}{4}\, \mathcal{G}(p^h)
\end{aligned}$$

We set $\Phi(p^d, q) = p^d + \dfrac{\Delta t}{2}\left[F(q) + F\left(q + \Delta t\, p^d + \dfrac{\Delta t^2}{2}\, F(q)\right)\right]$, so that $p^h = \Phi(p^d, q)$.

We want to choose X so that

$$\frac{1}{Q_1}\left(p_{\xi_1}+\frac{\Delta t}{4}G_1(p)\right)+\frac{k_BT}{Q_2}\left(p_{\xi_2}+\frac{\Delta t}{4}G_2(p)\right) \;=\; 0 \tag{5.12}$$

$$\mathcal{G}\left(\Phi(p^d,q)\right)+\mathcal{G}(p^d) \;=\; 0 \tag{5.13}$$

Choosing X:

The goal of this part is to show how to choose X in order for the two previous constraints to be fulfilled. The variable q will be free, and we will define X by $X=(q,p=\psi(q,\Delta t),p_{\xi_1}=\psi_1(q,\Delta t),p_{\xi_2}=\psi_2(q,\Delta t),\eta_1=0,\eta_2=0)$.

Let us first show that there exists a value of p^d, which is $\theta(q,\Delta t)$, so that the second constraint (5.13) is fullfilled.

Let us suppose that $q=0$. Since F is a odd degree polynomial function, we see that $\lim_{|p^d|\to\infty}\mathcal{G}\left(\Phi(p^d,q=0)\right)=+\infty$. So the function $p^d\mapsto\mathcal{G}\left(\Phi(p^d,q=0)\right)+\mathcal{G}\left(p^d\right)$ goes to $+\infty$ when $\mid p^d \mid$ goes to $+\infty$, and has a negative value when $p^d=0$. So there exists $\theta(q=0,\Delta t)>0$ so that $(p^d,q)=(\theta(0,\Delta t),0)$ fulfills the second constraint. When q is small enough, we can do the same. So we define a function $\theta(q,\Delta t)$ which is algebraic in q, positive, and which satisfies $\mathcal{G}\left(\Phi(\theta(q,\Delta t),q)\right)+\mathcal{G}\left(\theta(q,\Delta t)\right)=0$. Let us call μ the strictly positive root of $\mathcal{G}$. We can check that $\lim_{\Delta t\to 0}\theta(q,\Delta t)=\mu>0$, where μ is independent of q.

Let us set

$$\tau(q,\Delta t)=\frac{3\,m\,Q_2}{\Delta t+q^2+1}\;\frac{1}{\left[\theta(q,\Delta t)\right]^2+1} \tag{5.14}$$

We suppose that we can choose X so that $p^a_{\xi_2}=p^c_{\xi_2}=\tau(q,\Delta t)$ and $\lambda(X_a)=0$. So

$$p^d=\frac{p^c}{\sqrt{1+\tau(q,\Delta t)\,\frac{\Delta t}{6mQ_2}\,(p^c)^2}}\quad,\quad p^c=p^b\quad,\quad p^b=\frac{p}{\sqrt{1+\tau(q,\Delta t)\,\frac{\Delta t}{6mQ_2}\,p^2}}$$

The function $p \mapsto p^d(p, q, \Delta t)$ is an increasing function, and its limit when $p \to \pm\infty$ is $\pm\sqrt{\frac{3\,m\,Q_2}{\Delta t\,\tau(q,\Delta t)}}$. Thanks to the choice of τ, the equation

$$p^d(p, q, \Delta t) = \theta(q, \Delta t)$$

where p is the unknown, has a unique solution, $p = \psi(q, \Delta t)$. This function is algebraic in q. Using the limit of θ, one can check that $\lim_{\Delta t \to 0} \psi(q, \Delta t) = \mu > 0$. Let us notice that many other expressions for the function τ are possible. The main constraint is to ensure that the previous equation (where p is the unknown) has a unique solution, and that $\lim_{\Delta t \to 0} \tau(q, \Delta t)$ exists and depends on q.

Now we define $\psi_2(q, \Delta t) = \tau(q, \Delta t) - \frac{\Delta t}{4} G_2\left(\psi(q, \Delta t)\right)$, and we choose in X the value $p_{\xi_2} = \psi_2(q, \Delta t)$. Once again, this function is algebraic in q, and $\lim_{\Delta t \to 0} \psi_2(q, \Delta t) = \tau(q, 0)$.

Let us sum up what we have done until now. We show that it is possible to choose p and p_{ξ_2} as algebraic functions of q, so that the second contraint is fulfilled. Furthermore, we identified the limit when $\Delta t \to 0$ of these functions.

Now, we use the first constraint (5.12) and define $\psi_1(q, \Delta t) = -\frac{\Delta t}{4} Q_1\, G_1\left(\psi(q, \Delta t)\right) - k_B T \frac{Q_1}{Q_2}\left[\psi_2(q, \Delta t) + \frac{\Delta t}{4} G_2\left(\psi(q, \Delta t)\right)\right]$, and we choose in X the value $p_{\xi_1} = \psi_1(q, \Delta t)$. Once again, this function is algebraic in q, and $\lim_{\Delta t \to 0} \psi_1(q, \Delta t) = -k_B T \frac{Q_1}{Q_2} \tau(q, 0)$.

We proved what we announced at the beginning of this part.

Conclusion:

In the previous part, we show it was possible to define an algebraic function $q \mapsto X(q)$ so that:

- $X'(X(q))$ is an algebraical function of q
- $\mathrm{Jac}\left(\frac{\partial X'}{\partial X}\right)(X(q))$ is also an algebraical function of q.

where $X' = e^{\Delta t L_{eff}}\ X$. If the algorithm (5.9) is measure invariant, then we have the relation (5.10). We just need to prove that $U(X'(X(q))) - U(X(q))$ is not a constant function to reach a contradiction. In order to do so, we make a Taylor expansion on the variable Δt, and we check that the first term really depends on q. We can do so because we have checked that all the functions we defined to build the function $q \mapsto X(q)$ have a finite limit when $\Delta t \to 0$.

$$
\begin{aligned}
U(X'(X(q))) - U(X(q)) &= \eta_1' + \eta_2' - \eta_1 - \eta_2 \\
&= \frac{\Delta t}{2}\left(\frac{1}{Q_1} p^b_{\xi_1} + \frac{1}{Q_1} p^j_{\xi_1} + \frac{1}{Q_2} g(p^b)\, p^b_{\xi_2} + \frac{1}{Q_2} g(p^j)\, p^j_{\xi_2}\right) \\
&= \Delta t\left(\frac{1}{Q_1}\psi_1(q,0) + \frac{1}{Q_2} g\left(\psi(q,0)\right)\psi_2(q,0) + o(1)\right) \\
&= \Delta t\left(-\frac{k_B T}{Q_2}\,\tau(q,0) + \frac{1}{Q_2} g(\mu)\tau(q,0) + o(1)\right) \\
&= \Delta t\left(\frac{\mu^2}{m\,Q_2}\tau(q,0) + o(1)\right)
\end{aligned}
$$

One can check that $\tau(q,0)$ depends on q (thanks to the particular choice of τ in Eq. (5.14)). The real μ is a strictly positive constant. So we reach the contradiction.

---

[1] Z. Ge, J.E. Marsden, Phys. Lett. A **133**, 134 (1988).

[2] M.E. Tuckerman, G.J. Martyna, J. Phys. Chem. B, **104**, 159 (2000).

[3] S. Nosé, J. Chem. Phys. **81**, 561 (1985).

[4] W.G. Hoover, Phys. Rev. A **31**, 1695 (1985).

[5] G.J. Martyna, M.L. Klein, M.E. Tuckerman, J. Chem. Phys. **97**, 2635 (1992).

[6] M.E. Tuckerman, B.J. Berne, G.J. Martyna, J. Chem. Phys. **97**, 1990 (1992).

[7] G.J. Martyna, M.E. Tuckerman, D.J. Tobias, M.L. Klein, Mol. Phys. **87**, 1117 (1996).

[8] G.J. Martyna, M.E. Tuckerman, J. Chem. Phys. **102**, 8071 (1995).

[9] Y. Liu, M.E. Tuckerman, J. Chem. Phys. **112**, 1685 (2000).

[10] M.E. Tuckerman (submitted to J. Phys. Chem.).

[11] J. Cao, G.J. Martyna, J. Chem. Phys. **104**, 2028 (1996).

[12] G.J. Martyna, A. Hughes, M.E. Tuckerman, J. Chem. Phys. **110**, 3275 (1999).

[13] P. Procacci, B.J. Berne, Mol. Phys. **83**, 255 (1994).

[14] M.E. Tuckerman, T. von Rosenvinge, A. Hughes, G.J. Martyna, submitted to Mol. Phys. (received Jan. 1997).

[15] R. Martonak, C. Molteni, M. Parrinello, Comput. Mat. Science **20**, 293 (2001).

[16] M.E. Tuckerman, G.J. Martyna, B.J. Berne, J. Chem. Phys. **93**, 1287 (1990).

[17] D.D. Humphreys, R.A. Friesner, B.J. Berne, J. Phys. Chem. **98**, 6885 (1994).

[18] M.E. Tuckerman, B.J. Berne, J. Chem. Phys. **95**, 8362 (1991).

[19] M.E. Tuckerman, B.J. Berne, J. Chem. Phys. **95**, 4389 (1991).

[20] M.E. Tuckerman, B.J. Berne, G.J. Martyna, J. Chem. Phys. **94**, 6811 (1991).

[21] M.E. Tuckerman, B.J. Berne, A. Rossi, J. Chem. Phys. **94**, 1465 (1991).

[22] M.E. Tuckerman, M. Parrinello, J. Chem. Phys. **101**, 1316 (1994).

[23] S.J. Stuart, R. Zhou, B.J. Berne, J. Chem. Phys. **105**, 1426 (1996).

[24] S. Jang, G. Voth, J. Chem. Phys. **107**, 9514 (1997).

[25] S. Jang, G. Voth, J. Chem. Phys. **110**, 3626 (1999).

[26] S. Toxvaerd, J. Chem. Phys. **99**, 2277 (1993).

[27] M.E. Tuckerman, B.J. Berne, G.J. Martyna, J. Chem. Phys. **99**,2278 (1993).

[28] M.E. Tuckerman, G.J. Martyna, J. Chem. Phys. **110**, 3623 (1999).

[29] J.M. Sanz-Serna and M.P. Calvo, *Numerical Hamiltonian Problems* (Applied Mathematics and Mathematical Computation 7, Chapman & Hall, London, 1994).

[30] M.E. Tuckerman, C.J. Mundy, G.J. Martyna, Europhys. Lett. **45**, 149 (1999).

[31] G.R.W. Quispel, C.P. Dyt, Phys. Lett. A **242**, 25 (1998).

[32] E. Hairer, *Numerical Geometric Integration*, lectures available on the web (http://www.unige.ch/math/folks/hairer/polycop.html)

[33] E. Hairer, Chr. Lubich, G. Wanner, *Geometric Numerical Integration, Structure-Preserving Algorithms for Ordinary Differential Equations* (Springer-Verlag, 2002).

[34] K. Feng, Z. Shang, Numer. Math. **71**, 451 (1995).

[35] H. Yoshida, Phys. Lett. A **150**, 262 (1990).

[36] M. Suzuki, J. Math. Phys. **32**, 400 (1991).

[37] Codes for Molecular Dynamics can be found on the following site: http://molsim.chem.uva.nl/frenkel_smit

[38] E. Ramis, C. Deschamps, J. Odoux, *Special course on mathematics: Algebra* (Masson, Paris, 1997).

List of figure captions

FIG. 1: Position distribution functions for the double quartic well potential generated by measure invariant GGMT algorithm (solid line) and by Liu and Tuckerman GGMT algorithm (long dashed line), compared with the analytical result (short dashed line).

FIG. 2: Convergence of the position distribution functions for measure invariant GGMT algorithm (solid line) and for Liu and Tuckerman GGMT algorithm (dashed line) for the double quartic well potential.

FIG. 3: Impulsion distribution functions for the double quartic well potential generated by measure invariant GGMT algorithm (solid line) and by Liu and Tuckerman GGMT algorithm (long dashed line), compared with the analytical result (short dashed line).

FIG. 4: Convergence of the impulsion distribution functions for measure invariant GGMT algorithm (solid line) and for Liu and Tuckerman GGMT algorithm (dashed line) for the double quartic well potential.

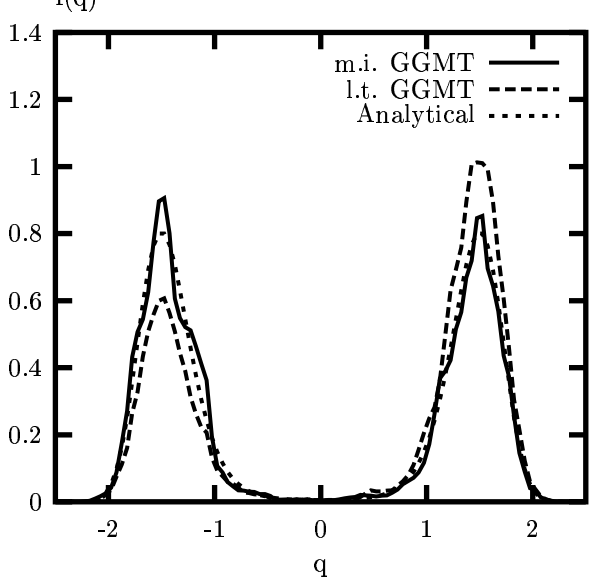
FIG. 5: Convergence of the second moment of the impulsion distribution functions for measure invariant GGMT algorithm (solid line) and for Liu and Tuckerman GGMT algorithm (dashed line) for the double quartic well potential.

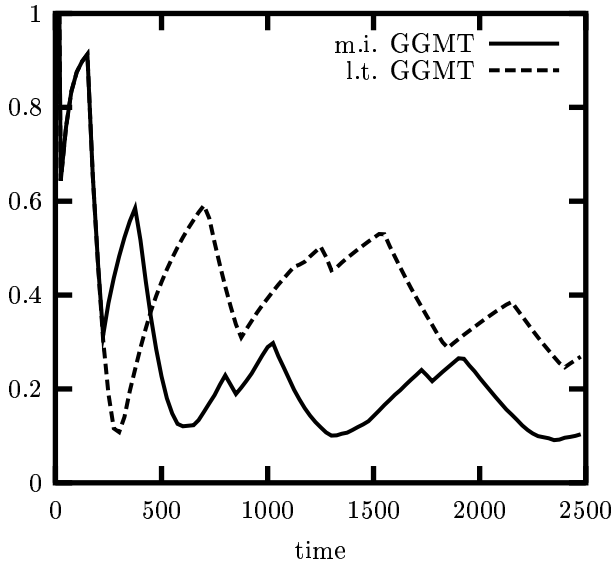
FIG. 6: Convergence of the fourth moment of the impulsion distribution functions for measure invariant GGMT algorithm (solid line) and for Liu and Tuckerman GGMT algorithm (dashed line) for the double quartic well potential.

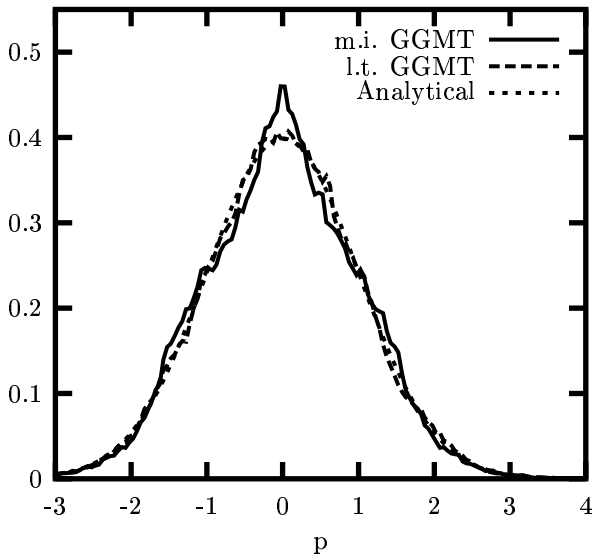
FIG. 7: Evolution of the numerical energy for measure invariant GGMT algorithm (solid line) and for Liu and Tuckerman GGMT algorithm (dashed line) for the double quartic well potential.

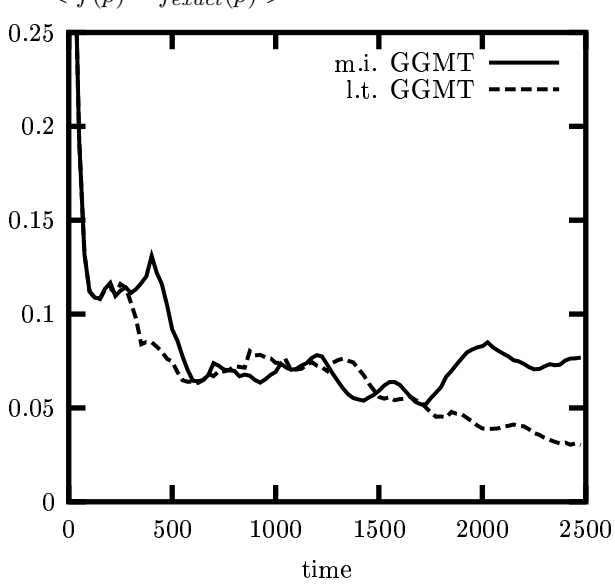
FIG. 8: Checking the preservation of the measure in the case of the free particle, for $p \in [2.0; 5.0]$: we compare Jac $\left(\frac{\partial X'}{\partial X}\right)(p)$ with $e^{\eta_1+\eta_2-\eta_1(\Delta t)-\eta_2(\Delta t)}(p)$ by plotting their ratio.

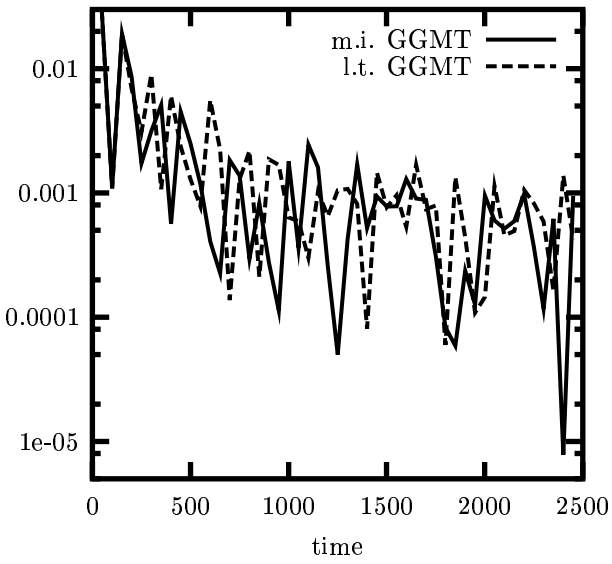
FIG. 9: Checking the preservation of the measure in the case of the free particle, for $p \in [0.9; 1.1]$: we compare Jac $\left(\frac{\partial X'}{\partial X}\right)(p)$ with $e^{\eta_1+\eta_2-\eta_1(\Delta t)-\eta_2(\Delta t)}(p)$ by plotting their ratio.

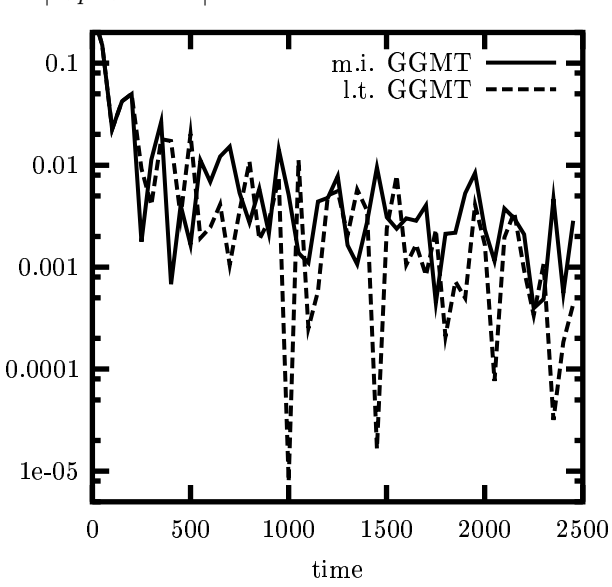

P(q)
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-2
-1
0
1
2
q
m.i. GGMT
l.t. GGMT
Analytical

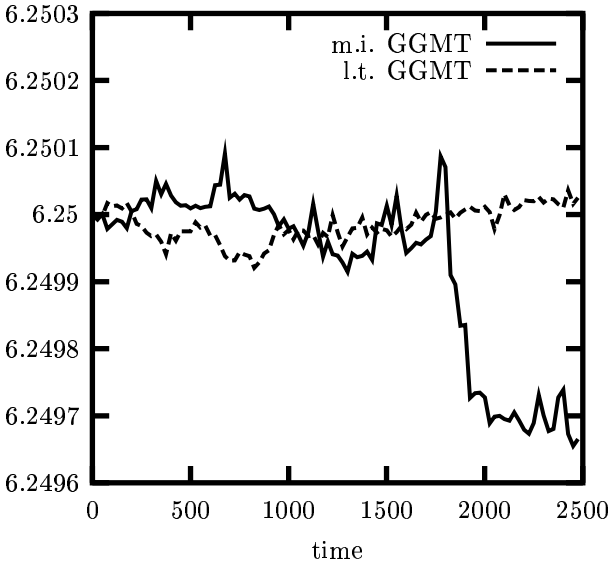

m.i. GGMT
l.t. GGMT
1
0.8
0.6
0.4
0.2
0
0
500
1000
1500
2000
2500
time

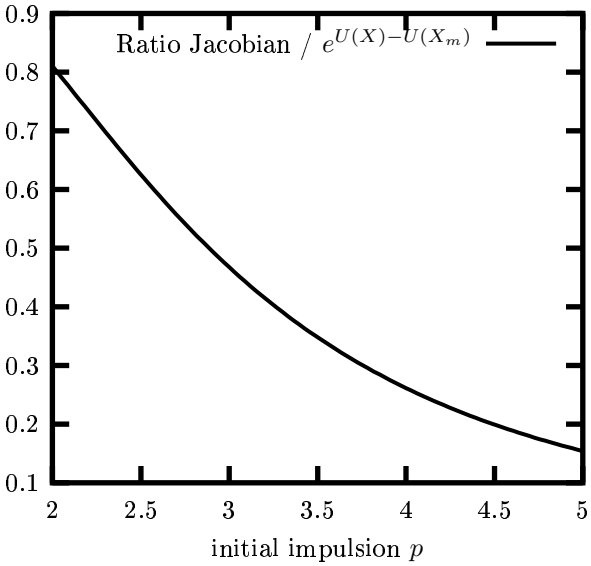

m.i. GGMT
l.t. GGMT
Analytical
0.5
0.4
0.3
0.2
0.1
0
-3
-2
-1
0
1
2
3
4
p

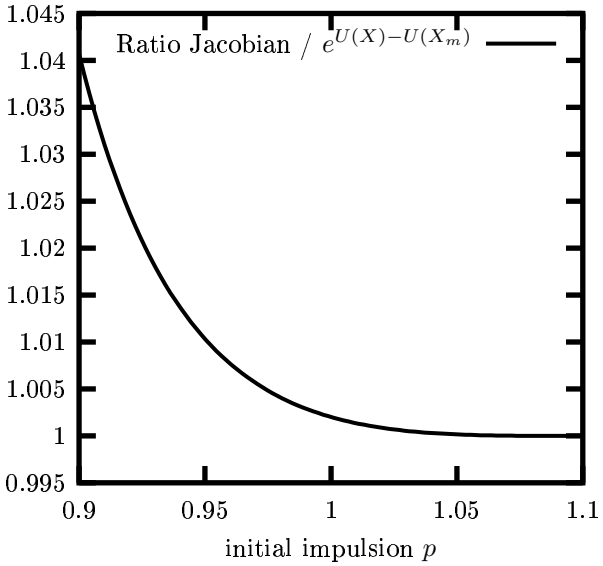

$< f(p) - f_{exact}(p) >$
0.25
0.2
0.15
0.1
0.05
0
0
500
1000
1500
2000
2500
time
m.i. GGMT
l.t. GGMT


m.i. GGMT
l.t. GGMT
0.01
0.001
0.0001
1e-05
0
500
1000
1500
2000
2500
time


0.1
0.01
0.001
0.0001
1e-05
0
500
1000
1500
2000
2500
time
m.i. GGMT
l.t. GGMT


6.2503
6.2502
6.2501
6.25
6.2499
6.2498
6.2497
6.2496
0
500
1000
1500
2000
2500
time
m.i. GGMT
l.t. GGMT


Ratio Jacobian / $e^{U(X)-U(X_m)}$
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
2
2.5
3
3.5
4
4.5
5
initial impulsion p


Ratio Jacobian / $e^{U(X)-U(X_m)}$
1.045
1.04
1.035
1.03
1.025
1.02
1.015
1.01
1.005
1
0.995
0.9
0.95
1
1.05
1.1
initial impulsion p