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Carlo Massobrio, Irene Amiehe Essomba, Mauro Boero, Cheick Diarra, Mohammed Guerboub, et al.. On the actual difference between the Nosé and the Nosé-Hoover thermostats: a critical review of canonical temperature control by molecular dynamics. *physica status solidi (b)*, 2023, 10.1002/pssb.202300209 . hal-04280276

HAL Id: hal-04280276

<https://hal.science/hal-04280276>

Submitted on 10 Nov 2023

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On the actual difference between the Nosé and the Nosé-Hoover thermostats : a critical review of canonical temperature control by molecular dynamics

Carlo Massobrio Irene Amiehe Essomba Mauro Boero Cheick Diarra Mohammed Guerboub Kana Ishisone Achille Lambrecht Evelyne Martin Icare Morrot-Woisard Guido Ori Christine Tugène Steve Dave Wansi Wendji

Carlo Massobrio

Université de Strasbourg, CNRS, Institut de Physique et Chimie des Matériaux de Strasbourg, UMR 7504, Strasbourg F-67034, France

Email Address: Carlo.Massobrio@ipcms.unistra.fr

Irene Amiehe Essomba

Université de Strasbourg, CNRS, Institut de Physique et Chimie des Matériaux de Strasbourg, UMR 7504, Strasbourg F-67034, France

Email Address: Irene.Amiehe@ipcms.unistra.fr

Mauro Boero

Université de Strasbourg, CNRS, Institut de Physique et Chimie des Matériaux de Strasbourg, UMR 7504, Strasbourg F-67034, France

Email Address: Mauro.Boero@ipcms.unistra.fr

Cheick Oumar Diarra

Université de Strasbourg, CNRS, Laboratoire ICube, UMR 7357, F-67037 Strasbourg, France

Email Address: Cheick-Oumar.Diarra@etu.unistra.fr

Mohammed Guerboub

Université de Strasbourg, CNRS, Institut de Physique et Chimie des Matériaux de Strasbourg, UMR 7504, Strasbourg F-67034, France

Email Address: Mohammed.Guerboub@ipcms.unistra.fr

Kana Ishisone

Université de Strasbourg, CNRS, Institut de Physique et Chimie des Matériaux de Strasbourg, UMR 7504, Strasbourg F-67034, France

Email Address: Kana.Ishisone@ipcms.unistra.fr

Achille Lambrecht

Université de Strasbourg, CNRS, Institut de Physique et Chimie des Matériaux de Strasbourg, UMR 7504, Strasbourg F-67034, France

Université de Strasbourg, CNRS, Laboratoire ICube, UMR 7357, F-67037 Strasbourg, France

Email Address: Achille.Lambrecht@etu.unistra.fr

Evelyne Martin

Université de Strasbourg, CNRS, Laboratoire ICube, UMR 7357, F-67037 Strasbourg, France

Email Address: Evelyne.Martin@unistra.fr

Icare Morrot-Woisard

Université de Strasbourg, CNRS, Institut de Physique et Chimie des Matériaux de Strasbourg, UMR 7504, Strasbourg F-67034, France

Email Address: icare.morrotwoisard@etu.unistra.fr

Guido Ori

Université de Strasbourg, CNRS, Institut de Physique et Chimie des Matériaux de Strasbourg, UMR 7504, Strasbourg F-67034, France

Email Address: Guido.Ori@ipcms.unistra.fr

Christine Tugène

Université de Strasbourg, CNRS, Institut de Physique et Chimie des Matériaux de Strasbourg, UMR 7504, Strasbourg F-67034, France

Email Address: Christine.Tugene@ipcms.unistra.fr

Steve Dave Wansi Wendji

Université de Strasbourg, CNRS, Institut de Physique et Chimie des Matériaux de Strasbourg, UMR 7504, Strasbourg F-67034, France

Email Address: stevedave.wansi@ipcms.unistra.fr

Keywords: *Statistical Mechanics, Molecular Dynamics, Computational Materials Science, Temperature control, Car-Parrinello method*

This paper has to be intended both as a review and as an historical tribute to the ideas developed almost forty years ago by S. Nosé establishing the theoretical foundations of the implementation and use of thermostats in molecular dynamics. The original motivation of this work is enriched by an observation related to the connection between the Nosé seminal expression of temperature control and the extension proposed in 1985 by W. G. Hoover, known as the Nosé-Hoover thermostat. By carefully rederiving the equations of motion in both formalisms, it appears that all features of Nosé-Hoover framework (replacement of the Nosé variables by a single friction coefficient in the equations of motion) are already built in the Nosé approach. Therefore, one is able to work directly within the Nosé formalism with the addition of a single variable only, by greatly extending its general impact and simplicity and somewhat making redundant the Nosé-Hoover extension. Having been implicitly (and somewhat inadvertently) put to good use by a multitude of users over the past 40 years (in the context of classical and first-principles molecular dynamics), this finding does not need any specific application to be assessed.

1 Purpose and context

This paper reviews concepts and ideas inherent in the use of thermostats in molecular dynamics (MD). It has been stimulated by the author’s continued use of the Nosé and Nosé-Hoover formalism (for some of them over the past thirty years), both in the classical and first-principles MD frameworks. Also, interactions with young colleagues and more established scientists have prompted us to realize that, unfortunately, running into users partially (or even totally) unaware of the basics of control temperature in molecular dynamics is not infrequent. Therefore, one of the purposes is to be pedagogical and informative while explaining where the “best” thermostat within MD comes from and why. This work has come to maturity during the final stages of writing of a recent book (monography) on molecular dynamics in disordered systems [1].¹ It occurred that treating theory appropriately in the monography required not only a thorough account of past contributions in the area of temperature control within MD but also a careful rehearsal of the underlying concepts. This exercise has proved highly profitable, since allowing to take a “fresh” look at the Nosé and Nosé-Hoover formalism. It was a big surprise for us to realize the existence of unmistakable evidence proving that the Nosé formalism, in its very first formulation, includes already all features of the supposedly “more manageable” Nosé-Hoover scheme. This is by itself a valuable complement that gives to the present article the multifold flavor of historical review, critical analysis and insightful revisiting of theory. We would like to stress that, in this context, there is no need to show any practical applications, since we are neither proposing a new scheme nor extending the validity of an existing one. The rational developed here is purely analytical and does not affect the validity of any of the results published over the past 40 years by using the strategies referred to above. All this will appear clearly in what follows.

2 Introduction

The implementation of the notion of thermostat within molecular dynamics has marked an important step toward the proper use of statistical mechanics concepts to produce atomic-scale temporal trajectories. It has to be recognized that molecular dynamics have long faced the challenge of obtaining a de-

¹Such an accomplishment appeared at the end of 2022 shortly after having received, by this Editor, the invitation to publish this paper in the context of an invited talk at the EMRS 2022 Fall meeting.

sired target temperature (as a macroscopic quantity) by acting on the equations of motion (the microscopic counterpart) for a collection of N_p atoms (or, equivalently, $3N_p$ degrees of freedom). Early attempts showed the need of a rigorous theoretical framework to achieve a consistent realization of the canonical NVT ensemble (with N playing the role of the above N_p , V being the volume and T the temperature) in the framework of a computer simulation based on time evolution [2, 3]. Also, the expected formalism has to comply with the attainment of a thermodynamic limit. This means that all concepts relevant to thermodynamics have to find their applications within a description purely based on the atomic-scale behavior of a collection of degrees of freedom giving access to properties averaged on time.

3 The Nosé thermostat

This issue has been solved in the eighties by Shuichi Nosé [4, 5]. Nosé showed that a molecular dynamics trajectory can be created to produce a canonical ensemble within a formalism that preserves the Hamiltonian character of the equations of motion. This goal can be achieved by coupling a system of N_{ind} independent degrees of freedom to a new dynamical variable s in a way compatible with the Hamiltonian character of the extended global dynamical quantity, provided the time t inherent in Equations 1 through 6 can be considered as a *virtual* physical parameter. The virtual time t and the real time t^r are linked by the equality $t = st^r$. Accordingly, the Nosé Hamiltonian reads:

$$\mathcal{H}_{Nosé} = \sum_{i=1}^{N_p} \frac{\mathbf{p}_i^2}{2ms^2} + E_{pot}[\mathbf{r}_i] + \frac{p_s^2}{2\eta} + (3N_p + 1)K_b T^{TG} \ln s \quad (1)$$

with the equations of motion derived straightforwardly as follows for the coordinates \mathbf{r}_i , the momentum \mathbf{p}_i , the variable s and its momentum p_s

$$\frac{d\mathbf{r}_i}{dt} = \dot{\mathbf{r}}_i = \frac{\partial \mathcal{H}}{\partial \mathbf{p}_i} = \frac{\mathbf{p}_i}{ms^2} \quad \frac{d\mathbf{p}_i}{dt} = \dot{\mathbf{p}}_i = \frac{\partial \mathcal{H}}{\partial \mathbf{r}_i} = -\frac{\partial E_{pot}[\mathbf{r}_i]}{\partial \mathbf{r}_i} \quad (2)$$

$$\frac{ds}{dt} = \dot{s} = \frac{\partial \mathcal{H}}{\partial p_s} = \frac{p_s}{\eta} \quad \frac{dp_s}{dt} = \dot{p}_s = -\frac{\partial \mathcal{H}}{\partial s} = \sum_{i=1}^{N_p} \frac{\mathbf{p}_i^2}{ms^3} - \frac{(3N_p + 1)K_b T^{TG}}{s} \quad (3)$$

Note that η is the mass associated with s and p_s and T^{TG} is the target temperature to be obtained (in average on time) via application of the thermostat. For sake of completeness, it is worth pointing out that the above formalism can be also expressed in Lagrangian terms by maintaining the same framework well adapted to be checked numerically, i.e. the existence of a constant of motion from which the time behavior of \mathbf{r}_i , $\dot{\mathbf{r}}_i$, \dot{s} , \ddot{s} can be directly derived:

$$\mathcal{L}_{Nosé} = \sum_{i=1}^{N_p} \frac{m\dot{\mathbf{r}}_i^2 s^2}{2} - E_{pot}[\mathbf{r}_i] + \frac{\dot{s}^2 \eta}{2} - (3N_p + 1)K_b T^{TG} \ln s \quad (4)$$

$$\frac{d}{dt}(ms^2 \dot{\mathbf{r}}_i) = -\frac{\partial E_{pot}[\mathbf{r}_i]}{\partial \mathbf{r}_i} \quad \text{or} \quad \ddot{\mathbf{r}}_i = -\frac{1}{ms^2} \frac{\partial E_{pot}[\mathbf{r}_i]}{\partial \mathbf{r}_i} - 2\dot{s} \dot{\mathbf{r}}_i s^{-1} \quad (5)$$

$$\frac{d}{dt}(\eta \dot{s}) = \sum_{i=1}^{N_p} m\dot{\mathbf{r}}_i^2 s - \frac{(3N_p + 1)K_b T^{TG}}{s} \quad (6)$$

The presence of the potential energy, namely $\ln s$, pertaining to the variable s is critical to ensure that the time average taken over the extended Nosé phase space (the one defined with respect to the virtual time t and the associated variables \mathbf{r}_i , \mathbf{p}_i) is equivalent to a time average in the canonical ensemble for the real variable in real time t^r , namely \mathbf{p}_i^r and \mathbf{r}_i^r . This assertion has been explicitly demonstrated by Nosé in Ref. [4] and Ref. [5] to which we refer to interested reader, together with other relevant papers by the same author (see, for instance, Ref. [6] and Ref. [7]). The quoted proof shows also explicitly that

the above equivalence holds provided the factor $(3N_p+1)$ multiplying $K_b T^{TG} \ln s$ in Equation 1 is employed in conjunction with the virtual variables at the place of $3N_p$, to be selected when real variables \mathbf{p}_i^r and \mathbf{r}_i^r evolving in real time t^r are adopted.

4 From the Nosé to the Nosé-Hoover thermostat

4.1 Origin and motivations: from virtual time to real time

When it came out in 1984, the breakthrough by Nosé was unanimously considered as the most important achievement of the late 20th century for both statistical mechanics and atomic-scale modelling. As such, it was readily implemented in molecular dynamics codes available or on the verge of being developed as softwares open to the whole community. However, some experts acknowledged to feel uncomfortable with the appearance of additional variables and the notion of *virtual* time by pointing out that their physical meaning could be hard to grasp since all statistical averages are expected to refer to a *real* time. This objection was partially counteracted by Nosé himself in Ref. [4] by showing how Equation 2 and Equation 3 can be expressed by working in a *real* time framework, the time evolution of the variable s and its momentum p_s to be followed along with atomic coordinates \mathbf{r}_i^r and momenta \mathbf{p}_i^r in real time. The first step consists in defining the relationships involving the dynamical variables in the descriptions of the Nosé formalism based on *real* and *virtual* time, respectively. The basic definitions to begin with are the following:

$$\mathbf{r}_i^r = \mathbf{r}_i \quad \mathbf{p}_i^r = \mathbf{p}_i/s \quad s^r = s \quad t^r = \int^t dt/s \quad p_s^r = p_s/s \quad (7)$$

where we have introduced the superscript r for all variables evolving in real time. Given the above relationship, and by employing the previous Equations 5 and 6 for evolution in virtual time, we obtain the time derivative of the above quantities and the related expression ready to use to implement numerically the Nosé formalism in the *real*, physical time.

$$\frac{d\mathbf{r}_i^r}{dt^r} = s \frac{d\mathbf{r}_i^r}{dt} = s \frac{d\mathbf{r}_i}{dt} = \frac{\mathbf{p}_i}{ms} = \frac{\mathbf{p}_i^r}{m} \quad (8)$$

$$\frac{d\mathbf{p}_i^r}{dt^r} = s \frac{d\mathbf{p}_i^r}{dt} = s \frac{d(\mathbf{p}_i/s)}{dt} = \frac{d\mathbf{p}_i}{dt} - \frac{1}{s} \frac{ds}{dt} \mathbf{p}_i \quad (9)$$

$$\frac{d\mathbf{p}_i^r}{dt^r} = -\frac{\partial E_{pot}[\mathbf{r}_i^r]}{\partial \mathbf{r}_i^r} - \frac{1}{s} \frac{p_s}{\eta} \mathbf{p}_i = -\frac{\partial E_{pot}[\mathbf{r}_i^r]}{\partial \mathbf{r}_i^r} - \frac{s^r p_s^r \mathbf{p}_i^r}{\eta} \quad (10)$$

$$\frac{ds^r}{dt^r} = s \frac{ds^r}{dt} = s \frac{ds}{dt} = \frac{s^r p_s}{\eta} = \frac{s^{r2} p_s^r}{\eta} \quad (11)$$

$$\frac{dp_s^r}{dt^r} = s \frac{dp_s^r}{dt} = s \frac{d(p_s/s)}{dt} = \frac{dp_s}{dt} - \frac{1}{s} \frac{ds}{dt} p_s \quad (12)$$

$$\frac{dp_s^r}{dt^r} = \sum_{i=1}^{N_p} \frac{(\mathbf{p}_i^r)^2}{ms^r} - \frac{3N_p K_b T^{TG}}{s^r} - \frac{s^r (p_s^r)^2}{\eta} \quad (13)$$

Therefore, by using these new set of equations of motion one can totally disregard the notion of virtual time and work in a framework strictly equivalent to the one employed to follow the evolution in the microcanonical (NVE) ensemble. A straightforward rewriting allows obtaining the equivalent of Equation 1 in terms of the real variables:

$$\mathcal{H}_{Nosé}^r = \sum_{i=1}^{N_p} \frac{(\mathbf{p}_i^r)^2}{2m} + E_{pot}[\mathbf{r}_i^r] + \frac{(s^r)^2 (p_s^r)^2}{2\eta} + 3N_p K_b T^{TG} \ln s^r \quad (14)$$

and the corresponding equivalent of Equation 4 in the form

$$\mathcal{L}_{Nosé}^r = \sum_{i=1}^{N_p} \frac{m(\mathbf{r}_i^r)^2}{2} - E_{pot}[\mathbf{r}_i^r] + \frac{(\dot{s}^r)^2 \eta}{2(s^r)^2} - 3N_p K_b T^{TG} \ln s^r \quad (15)$$

together with the Lagrangian equations of motion expressed in real time:

$$\frac{d}{s^r dt^r} \left(\frac{m(s^r)^2 \dot{\mathbf{r}}_i^r}{s^r} \right) = - \frac{\partial E_{pot}[\mathbf{r}_i^r]}{\partial \mathbf{r}_i^r} \quad \frac{d}{dt^r} (m(s^r) \dot{\mathbf{r}}_i^r) = -s^r \frac{\partial E_{pot}[\mathbf{r}_i^r]}{\partial \mathbf{r}_i^r} \quad (16)$$

$$\frac{d}{dt^r} \left(\frac{\eta}{s^r} \frac{ds^r}{dt^r} \right) = \sum_{i=1}^{N_p} m \left(\frac{d\mathbf{r}_i^r}{dt^r} \right)^2 - 3N_p K_b T^{TG} \quad (17)$$

It is important to realize that the Nosé equations as depending on the real variables change the purely Hamiltonian character of the formalism, since Equations 8 through 13 cannot be derived directly from Equation 14. In other terms, Equation 14 is not a Hamiltonian (i.e. Equation 15 is not a Lagrangian), both expressing now “mere” constants of motion. Also, what we have obtained above as the Hamiltonian and Lagrangian equations of motion in real time have been derived *directly* from the equations of motion in virtual time, since one could not obtain them from Equation 14 and Equation 15. Once again, the reason being that the Nosé formalism is a Hamiltonian one only in virtual time.

4.2 Can we attach to the Nosé variables a physical meaning ?

We have seen that the Nosé framework, although established in *virtual* time and holding a fully hamiltonian character in this framework *only*, can be reformulated within the customary temporal scale (the *real* one) inherent in any molecular dynamics application. Is this going to settle the issue of its straightforward and manageable use to implement a temperature control ? What makes it still cumbersome to the eyes of practitioners is the presence of the s variable to which one cannot attach a transparent physical meaning. However, it appears that careful analysis of the equations provides a clear hint to address favorably this issue and recover a more palatable analytical expression. The route followed in this paper is alternative to the one proposed by Hoover [8] even though we shall demonstrate later that the present derivation and the one of Hoover are strictly identical. More, we would like to demonstrate that what Nosé has shown in his seminal papers is largely sufficient to obtain a theory of thermostats for molecular dynamics bearing a clear physical meaning and not carrying any unneeded awkwardness because of the presence of the s variable.

Let's first concentrate on Equation 10 by defining $\xi = s^r p_s^r / \eta$. One can first rewrite Equation 10 in the following form:

$$\frac{d\mathbf{p}_i^r}{dt^r} = - \frac{\partial E_{pot}[\mathbf{r}_i^r]}{\partial \mathbf{r}_i^r} - \frac{s^r p_s^r \mathbf{p}_i^r}{\eta} = - \frac{\partial E_{pot}[\mathbf{r}_i^r]}{\partial \mathbf{r}_i^r} - \xi \mathbf{p}_i^r \quad (18)$$

by showing that an actual friction term can be identified as acting on the time evolution of \mathbf{p}_i^r . At first sight, this postulate does not correspond to any simplification in the equations of motions, since one is bound to follow the time evolution of both s^r and p_s^r .

However, it turns out that *focusing on the product of the two variables s^r and p_s^r* (defined above as proportional to $\xi\eta$) has a quite insightful meaning when attention is drawn on its time derivative $\dot{\xi}$ as it results from the following equations:

$$\frac{d(s^r p_s^r)}{dt^r} = s^r \frac{dp_s^r}{dt^r} + p_s^r \frac{ds^r}{dt^r} = s^r \left(\sum_{i=1}^{N_p} \frac{(\mathbf{p}_i^r)^2}{m s^r} - \frac{3N_p K_b T^{TG}}{s^r} - \frac{s^r (p_s^r)^2}{\eta} \right) + p_s^r \frac{s^{r2} p_s^r}{\eta} \quad (19)$$

$$\frac{d(s^r p_s^r)}{dt^r} = s^r \frac{dp_s^r}{dt^r} + p_s^r \frac{ds^r}{dt^r} = s^r \left(\sum_{i=1}^{N_p} \frac{(\mathbf{p}_i^r)^2}{m s^r} - \frac{3N_p K_b T^{TG}}{s^r} \right) = \left(\sum_{i=1}^{N_p} \frac{(\mathbf{p}_i^r)^2}{m} - 3N_p K_b T^{TG} \right) \quad (20)$$

$$\frac{d\xi}{dt^r} = \left(\sum_{i=1}^{N_p} \frac{(\mathbf{p}_i^r)^2}{m} - 3N_p K_b T^{TG} \right) / \eta \quad (21)$$

Equation 21 has a form clearly reminiscent of the time evolution of a friction variable, as it appears when grouping and considering as a whole the three equations expressing the Nosé evolution in real time of the variables \mathbf{r}_i^r , \mathbf{p}_i^r and ξ :

$$\frac{d\mathbf{r}_i^r}{dt^r} = s \frac{d\mathbf{r}_i^r}{dt} = s \frac{d\mathbf{r}_i}{dt} = \frac{\mathbf{p}_i}{ms} = \frac{\mathbf{p}_i^r}{m} \quad (22)$$

$$\frac{d\mathbf{p}_i^r}{dt^r} = - \frac{\partial E_{pot}[\mathbf{r}_i^r]}{\partial \mathbf{r}_i^r} - \frac{s^r p_s^r \mathbf{p}_i^r}{\eta} = - \frac{\partial E_{pot}[\mathbf{r}_i^r]}{\partial \mathbf{r}_i^r} - \xi \mathbf{p}_i^r \quad (23)$$

$$\frac{d\xi}{dt^r} = \left(\sum_{i=1}^{N_p} \frac{(\mathbf{p}_i^r)^2}{m} - 3N_p K_b T^{TG} \right) / \eta \quad (24)$$

What is the form taken by the constant of motion as a result of the introduction of the ξ variable ? It appears that the first expression one can come up with (obtained from Equation 14 with the appropriate changes) can contain ξ explicitly and yet, the s^r variable is still present, undermining the postulate that only ξ has to be followed in time:

$$\mathcal{H}_{Nosé}^r = \sum_{i=1}^{N_p} \frac{(\mathbf{p}_i^r)^2}{2m} + E_{pot}[\mathbf{r}_i^r] + \eta \frac{\xi^2}{2} + 3N_p K_b T^{TG} \ln s^r \quad (25)$$

However, it is possible to eliminate the s^r variable by exploiting Equation 11

$$\xi = \frac{1}{s^r} \frac{ds^r}{dt^r} = \frac{s^r p_s^r}{\eta} \quad \int \frac{1}{s^r} \frac{ds^r}{dt^r} dt^r = \ln s^r \quad (26)$$

This gives an expression for the Nosé constant of motion in real time in which the ξ variable appears both in the kinetic and in the potential part of the time evolution of the thermostat, the only inconvenient feature being the presence of a time integral that, in principle, one should perform over the running time trajectory to make sure that the constant of motion is well conserved.

$$\mathcal{H}_{Nosé}^r = \sum_{i=1}^{N_p} \frac{(\mathbf{p}_i^r)^2}{2m} + E_{pot}[\mathbf{r}_i^r] + \eta \frac{\xi^2}{2} + 3N_p K_b T^{TG} \int \xi dt^r \quad (27)$$

The rationale developed in this section shows unambiguously that the Nosé formalism as developed in Refs. [4, 5] does not imply (as claimed in the literature, see Ref. [8] and reiterated over the years) any mandatory use of the s variable in the equation of motions. Also the Nosé formalism is not characterized by an unnecessary “scaling of the time”, since a set of equations in real variables (time and coordinates) can be straightforwardly obtained, by reducing the application of a thermostat to a skillful use of the ξ variable.

To summarize what shown in the above sections, the following points have to be underlined

- To preserve the Hamiltonian (or, equivalently, Lagrangian) character of the equations of motion, the Nosé formalism has to be expressed, at the outset, in *virtual* time by connecting *virtual* and *real* time in the form $dt^r = dt^v/s = dt/s$ through the s variable, where the superscript r stands for real, and we do not use throughout the paper the superscript v standing for virtual (note also that for “real” and “virtual” we use both *italic* and standard characters depending on the context).
- The Nosé formalism can be expressed in real time by applying the suitable relationship connecting these two frameworks (Equations 7 through 13). However this can be done at the price of the Hamiltonian character of Eq. 1, that becomes a constant of motion only, quite useful to be followed in time to monitor the correctness of the time integration of the equations of motion.

- By focusing on the variable $\xi = s^r p_s^r / \eta$ and on its time derivative, one can reformulate the entire Nosé formalism by using three equations of motion for the variables \mathbf{r}_i^r , \mathbf{p}_i^r and ξ .

4.3 The Hoover derivation of the Nosé thermostat

Shortly after the publication of the two main papers by Nosé (Refs. [4, 5]) featuring the breakthrough methodology of rigorous thermostats for molecular dynamics, W. G. Hoover proposed alternative expressions for the equations of motion meeting exactly the same purposes (see Ref. [8]). He pointed out that friction coefficients could be employed at the place of the original s and p_s , by claiming that the set of equations developed were “free of time scaling”. The formalism by Hoover, known as Nosé-Hoover thermostat, became immediately very popular in the field of molecular dynamics, to the point of (almost) supplanting the original Nosé ideas as if the actual discovery of right thermostats for molecular dynamics were the offspring of Ref. [8]. This is somewhat unfair since, Hoover has only rewritten a set of equation *already existing in Ref. [4]* by interpreting in his own way the concepts of real time and variables. This will become quite evident in the following.

In practice, Hoover introduces first a change in the time variable by imposing $dt_{Nosé} = s dt_{Hoover}$ ($dt_{Hoover} = dt$ hereafter for simplicity, for instance as in $d\mathbf{r}_i/dt$). This amounts to rewriting Equation 2 and Equation 3 as multiplied by s :

$$\frac{d\mathbf{r}_i}{dt} = \dot{\mathbf{r}}_i = \frac{\partial \mathcal{H}}{\partial \mathbf{p}_i} = \frac{\mathbf{p}_i}{ms} \quad \frac{d\mathbf{p}_i}{dt} = \dot{\mathbf{p}}_i = \frac{\partial \mathcal{H}}{\partial \mathbf{r}_i} = -s \frac{\partial E_{pot}[\mathbf{r}_i]}{\partial \mathbf{r}_i} \quad (28)$$

$$\frac{ds}{dt} = \dot{s} = \frac{\partial \mathcal{H}}{\partial p_s} = \frac{sp_s}{\eta} \quad \frac{dp_s}{dt} = \dot{p}_s = -\frac{\partial \mathcal{H}}{\partial s} = \sum_{i=1}^{N_p} \frac{\mathbf{p}_i^2}{ms^2} - (3N_p + 1)K_b T^{TG} \quad (29)$$

$$\ddot{\mathbf{r}}_i = \frac{\dot{\mathbf{p}}_i}{ms} - \frac{\mathbf{p}_i}{ms} \frac{\dot{s}}{s} = -\frac{1}{m} \frac{\partial E_{pot}[\mathbf{r}_i]}{\partial \mathbf{r}_i} - \frac{p_s}{\eta} \dot{\mathbf{r}}_i \quad (30)$$

At this point, Hoover introduces the variable $\zeta = p_s/\eta$ (analogous to the variable ξ first used in Equation 18) to rewrite Equation 30 as

$$\ddot{\mathbf{r}}_i = \frac{\dot{\mathbf{p}}_i}{ms} - \frac{\mathbf{p}_i}{ms} \frac{\dot{s}}{s} = -\frac{1}{m} \frac{\partial E_{pot}[\mathbf{r}_i]}{\partial \mathbf{r}_i} - \zeta \dot{\mathbf{r}}_i \quad (31)$$

By taking advantage of Equation 29 one has for the time derivative of ζ

$$\dot{\zeta} = \frac{\dot{p}_s}{\eta} = \frac{1}{\eta} \left(\sum_{i=1}^{N_p} \frac{\mathbf{p}_i^2}{ms^2} - (3N_p + 1)K_b T^{TG} \right) = \frac{1}{\eta} \left(\sum_{i=1}^{N_p} m \dot{\mathbf{r}}_i^2 - (3N_p + 1)K_b T^{TG} \right) \quad (32)$$

At this point, the formalism expressed in Ref. [8] can be made equivalent to the original one by Nosé by redefining $\dot{\mathbf{r}}_i = \mathbf{p}_i/m$ and by replacing $3N_p+1$ by $3N_p$. The final set of equations according to Hoover’s strategy reads:

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m} \quad m \ddot{\mathbf{r}}_i = -\frac{\partial E_{pot}[\mathbf{r}_i]}{\partial \mathbf{r}_i} - m \zeta \dot{\mathbf{r}}_i \quad \dot{\mathbf{p}}_i = -\frac{\partial E_{pot}[\mathbf{r}_i]}{\partial \mathbf{r}_i} - \zeta \mathbf{p}_i \quad \dot{\zeta} = \frac{1}{\eta} \left(\sum_i^{N_p} \frac{\dot{\mathbf{p}}_i^2}{m} - 3N_p K_b T^{TG} \right) \quad (33)$$

It appears that the three relationships contained in Equation 33 have the same physical meaning than what we have expressed through Equation 22, Equation 23 and Equation 24, with ξ in the Nosé formalism acting as ζ in the Hoover’s one. However, we reiterate that the route taken by Hoover to obtain Equation 33 does not follow any specific protocol based on the introduction of a *real* time together with *real* variables, the only advantage of it being the simpler link $\zeta = p_s/\eta$ between friction and Nosé variables.

5 Extending the Nosé ideas: multiple thermostats and first-principles molecular dynamics

5.1 Constant of motion and the friction variable made simpler

As a prerequisite to any other thoughts on the Nosé scheme, particularly in the context of first-principles molecular dynamics (that is to say, a scheme where the potential energy depends on the electronic structure, unlike in classical molecular dynamics) it is useful to focus on the expression for the conserved quantity given in Equation 27 that we rewrite in the form

$$\mathcal{H}_{Conserved} = \sum_{i=1}^{N_p} \frac{(\mathbf{p}_i)^2}{2m} + E_{pot}[\mathbf{r}_i] + \eta \frac{\xi^2}{2} + 3N_p K_b T^{TG} \int \xi dt \quad (34)$$

by dropping the upperscript r standing for *real* since from now on we shall refer to real time. Careful analysis of Equation 34 reveals that the cumbersome presence of a time integral within a constant of motion can be eliminated by resorting to a new variable α such as $\dot{\alpha} = \xi$. Accordingly, Equation 33 and Equation 34 take the form:

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m} \quad m\ddot{\mathbf{r}}_i = -\frac{\partial E_{pot}[\mathbf{r}_i]}{\partial \mathbf{r}_i} - m\dot{\alpha}\dot{\mathbf{r}}_i \quad \dot{\mathbf{p}}_i = -\frac{\partial E_{pot}[\mathbf{r}_i]}{\partial \mathbf{r}_i} - \dot{\alpha}\mathbf{p}_i \quad \ddot{\alpha} = \frac{1}{\eta} \left(\sum_{i=1}^{N_p} \frac{\dot{\mathbf{p}}_i^2}{m} - 3N_p K_b T^{TG} \right) \quad (35)$$

$$\mathcal{H}_{Conserved} = \sum_{i=1}^{N_p} \frac{\mathbf{p}_i^2}{2m} + E_{pot}[\mathbf{r}_i] + \eta \frac{\dot{\alpha}^2}{2} + 3N_p K_b T^{TG} \alpha \quad (36)$$

The above equations, linking a quantity constant in time ($\mathcal{H}_{Conserved}$) to non-Hamiltonian equations of motion can be easily generalized to the case of multiple thermostats. One can consider the case of two subsystems made of N_{p1} and N_{p2} atoms of coordinates and momenta $\mathbf{r}_l, \mathbf{p}_l$ (for the subclass made of N_{p1} atoms) and $\mathbf{r}_k, \mathbf{p}_k$ ((for the subclass made of N_{p2} atoms) kept at two different temperatures T^{TG1}, T^{TG2} . Here we made the choice of two subsystems only for simplicity, the number of subsystems not being limited. Calculations of thermal conductivity with the AEMD are revealing examples of application of multiple thermostats to sub-sets of atoms belonging to the same system but kept at different (initial) temperatures [9, 10, 11, 12].

The corresponding equations of motion read (note that the friction variables $\dot{\alpha}$ and $\dot{\beta}$ have masses η and γ , respectively):

$$\dot{\mathbf{r}}_l = \frac{\mathbf{p}_l}{m} \quad m\ddot{\mathbf{r}}_l = -\frac{\partial E_{pot}[\mathbf{r}_l]}{\partial \mathbf{r}_l} - m\dot{\alpha}\dot{\mathbf{r}}_l \quad \dot{\mathbf{p}}_l = -\frac{\partial E_{pot}[\mathbf{r}_l]}{\partial \mathbf{r}_l} - \dot{\alpha}\mathbf{p}_l \quad \ddot{\alpha} = \frac{1}{\eta} \left(\sum_{l=1}^{N_{p1}} \frac{\dot{\mathbf{p}}_l^2}{m} - 3N_{p1} K_b T^{TG1} \right) \quad (37)$$

$$\dot{\mathbf{r}}_k = \frac{\mathbf{p}_k}{m} \quad m\ddot{\mathbf{r}}_k = -\frac{\partial E_{pot}[\mathbf{r}_k]}{\partial \mathbf{r}_k} - m\dot{\beta}\dot{\mathbf{r}}_k \quad \dot{\mathbf{p}}_k = -\frac{\partial E_{pot}[\mathbf{r}_k]}{\partial \mathbf{r}_k} - \dot{\beta}\mathbf{p}_k \quad \ddot{\beta} = \frac{1}{\gamma} \left(\sum_{k=1}^{N_{p2}} \frac{\dot{\mathbf{p}}_k^2}{m} - 3N_{p2} K_b T^{TG2} \right) \quad (38)$$

with the constant of motion H_{C12} accounting for the presence of two different friction variables $\dot{\alpha}$ and $\dot{\beta}$ and their associated kinetic and potential energy:

$$\mathcal{H}_{C12} = \sum_{l=1}^{N_{p1}} \frac{\mathbf{p}_l^2}{2m} + \sum_{k=1}^{N_{p2}} \frac{\mathbf{p}_k^2}{2m} + E_{pot}[\mathbf{r}_l, \mathbf{r}_k] + \eta \frac{\dot{\alpha}^2}{2} + 3N_{p1} K_b T^{TG1} \alpha + \gamma \frac{\dot{\beta}^2}{2} + 3N_{p2} K_b T^{TG2} \beta \quad (39)$$

5.2 First-principles (Car-Parrinello) molecular dynamics with thermostats: part 1

The ideas developed so far have found a natural application within first-principles molecular dynamics (in the version pioneered by Roberto Car and Michele Parrinello [13], FPMD-CP hereafter). First, it appears that the formalism by Nosé is perfectly suited to be employed in the FPMD-CP framework to control the temperature of the ionic degrees of freedom (corresponding to the atomic degrees of freedom in the classical MD description). Also, the combination of Nosé and FPMD-CP ideas is essential to achieve an overall manageable use of the whole FPMD-CP approach, by ensuring adiabatic separation between ionic and electronic dynamical sub-systems. This stems from the possibility to control the temperature of different families of degrees of freedom, as we have explicitly shown via Equation 37 and Equation 38. In what follows we shall slightly change our previous notation to allow for the introduction of electronic degrees of freedom coupling to the ionic ones. Let's consider a Lagrangian collection of ions of coordinates \mathbf{R}_I with masses M_I and orbitals $\psi_i(r)$ accounting for the electronic structure. μ is a mass inherent in the so-called fictitious movements of the orbitals, its value, in Hartree atomic units, being much smaller than the one of M_I . In this way, one has ions and orbitals dynamically decoupled since moving with drastically different frequencies. This postulate and its correct implementation are at the very heart of the FPMD-CP methodology, for which these conditions are best fulfilled by insulators and, at not too high temperatures, semiconductors, due to the presence of a gap separating valence and conduction states. By assuming that the total energy is obtained within the density functional Kohn-Sham framework (and by imposing as it should be the constraint that the orbitals are orthonormal via $E_{or_{cnstr}}(\psi_i(\mathbf{r}))$), one has:

$$\mathcal{L}_{CP} = E_{fic}(\psi_i(\mathbf{r})) + E_{kin}(\{\mathbf{R}_I\}) - E_{tot}[\{\psi_i\}; \{\mathbf{R}_I\}] + E_{or_{cnstr}}(\psi_i(\mathbf{r})) \quad (40)$$

$$\mathcal{L}_{CP} = \mu \sum_i \int |\dot{\psi}_i(\mathbf{r})|^2 d\mathbf{r} + \frac{1}{2} \sum_{I=1}^N M_I \dot{\mathbf{R}}_I^2 - E_{tot}[\{\psi_i\}; \{\mathbf{R}_I\}] - \sum_{ij} \lambda_{ij} \left(\int \psi_i^*(\mathbf{r}) \psi_j(\mathbf{r}) d\mathbf{r} - \delta_{ij} \right) \quad (41)$$

For future purposes (as it will be the case when making explicit the action of thermostats), it is convenient to express $E_{tot}[\{\psi_i\}; \{\mathbf{R}_I\}]$ in the form $E_{tot}[\{\psi_i\}; \{\mathbf{R}_I\}, \alpha_l]$, by implying that l variables can be included in the dynamical evolution of the system. Therefore, in analogy with what developed in Sec. 5.1 we can first rewrite Equation 41 in the generic form

$$\mathcal{L}_{CP_{Cons}} = \mu \sum_i \int |\dot{\psi}_i(\mathbf{r})|^2 d\mathbf{r} + \frac{1}{2} \sum_{I=1}^N M_I \dot{\mathbf{R}}_I^2 - E_{tot}[\{\psi_i\}; \{\mathbf{R}_I\}, \alpha_l] - \sum_{ij} \lambda_{ij} \left(\int \psi_i^*(\mathbf{r}) \psi_j(\mathbf{r}) d\mathbf{r} - \delta_{ij} \right) + \frac{1}{2} \sum_l \eta_l \dot{\alpha}_l^2 \quad (42)$$

that contains explicitly the potential and the kinetic parts due to a thermostat as follows:

$$\mathcal{L}_{CP_{Cons}} = \mu \sum_i \int |\dot{\psi}_i(\mathbf{r})|^2 d\mathbf{r} + \frac{1}{2} \sum_{I=1}^N M_I \dot{\mathbf{R}}_I^2 - E_{tot}[\{\psi_i\}; \{\mathbf{R}_I\}] - \sum_{ij} \lambda_{ij} \left(\int \psi_i^*(\mathbf{r}) \psi_j(\mathbf{r}) d\mathbf{r} - \delta_{ij} \right) + \frac{1}{2} \eta_I \dot{\alpha}_I^2 + F(\alpha_I) \quad (43)$$

This is exactly the FPMD-CP equivalent of the constant of motion made explicit in the previous sections for the case of a thermostat applied to the ionic (atomic) degrees of freedom (see Equation 36). Note that we have termed the new constant of motion $\mathcal{L}_{CP_{Cons}}$ to underline the conceptual difference between $\mathcal{L}_{CP_{Cons}}$ and \mathcal{L}_{CP} , the former having lost, due to the presence of the thermostat variables, the Lagrangian character of the latter, i.e. no Lagrangian equation of motion can be derived directly from it. In analogy with the above rationale on the Nosé formalism in real time (see Sec. 4.2) one can associate to the variable α_I the kinetic term $\frac{1}{2} \eta_I \dot{\alpha}_I^2$ as well as the potential energy term in the form

$$F(\alpha_I) = 2E_{kin}^{I-TG} \alpha_I \quad (44)$$

where $2E_{kin}^{I-TG}$ is the targetted average ionic kinetic energy, typically expressed via the target temperature so as $2E_{kin}^{I-TG} = N_{ind} k_B T^{TG}$, N_{ind} being the number of degrees of freedom (the strict equivalent of $3N_p$ employed to introduce the Nosé formalism within classical molecular dynamics). This holds true

provided one keeps in mind that only the average value of the kinetic energy can be taken to correspond to a temperature, even though often both kinetic energy and temperature are employed as instantaneous and average quantities. Having obtained the expression for a conserved quantity within FPMD-CP after application of a thermostat on the ionic family of degrees of freedom, it is now straightforward to write down the expression for the FPMD-CP equations of motions along the same lines followed in the classical case via Equation 35:

$$\mu\ddot{\psi}_i(\mathbf{r}, t) = -\frac{\delta E_{tot}[\{\psi_i\}, \{\mathbf{R}_I\}]}{\delta\psi_i^*(\mathbf{r}, t)} + \sum_j \lambda_{ij}\psi_j(\mathbf{r}, t) \quad (45)$$

$$M_I\ddot{\mathbf{R}}_I = -\nabla_I E_{tot}[\{\psi_i\}, \{\mathbf{R}_I\}] - M_I\dot{\mathbf{R}}_I\dot{\alpha}_I \quad (46)$$

$$\eta_I\ddot{\alpha}_I = 2\left(\frac{1}{2}\sum_{I=1}^N M_I\dot{\mathbf{R}}_I^2 - \frac{1}{2}N_{ind}k_B T^{TG}\right) \quad (47)$$

5.3 First-principles (Car-Parrinello) molecular dynamics with thermostats: part 2

In addition to the use of Nosé formalism to control the temperature of a system (as expressed through the average kinetic energy of the atoms, or, better, of the ions if one considers also electronic degrees of freedom), one can take advantage of the whole scheme to make sure the FPMD-CP time evolution is as much as possible adiabatic. This means that the notion of temperature control can be employed to hamper the increase of $E_{fic}(\psi_i(\mathbf{r}))$ that favors unwanted transfer of energy from the ionic to the fictitious electronic degrees of freedom. Based on what we have seen in Sec. 5.1, Equation 37, Equation 38 and Equation 39 this can be achieved by considering a variable α_l acting as a thermostat for $E_{fic}(\psi_i(\mathbf{r}))$ (as first proposed in Ref. [14]). While this approach is not bound to work on extended intervals for dramatic cases of gapless systems (as metals), it remains quite valid to ensure adiabaticity for a wide class of systems featuring electronic density of states at least depleted (exhibiting pseudogaps) around the Fermi energy level. The corresponding FPMD-CP conserved quantity reads

$$\mathcal{L}_{CPCons} = E_{fic}(\psi_i(\mathbf{r})) + E_{kin}(\{\mathbf{R}_I\}) - E_{tot}[\{\psi_i\}; \{\mathbf{R}_I\}, \alpha_I, \alpha_e] + E_{orcnstr}(\psi_i(\mathbf{r})) + E_{ext}(\alpha_I) + E_{ext}(\alpha_e) \quad (48)$$

$$\mathcal{L}_{CPCons} = E_{fic}(\psi_i(\mathbf{r})) + E_{kin}(\{\mathbf{R}_I\}) - E_{tot}[\{\psi_i\}; \{\mathbf{R}_I\}] + E_{orcnstr}(\psi_i(\mathbf{r})) + \frac{1}{2}\eta_I\dot{\alpha}_I^2 + 2E_{kin}^{I-TG}\alpha_I + \frac{1}{2}\eta_e\dot{\alpha}_e^2 + 2E_{kin}^{e-TG}\alpha_e \quad (49)$$

in which E_{kin}^{e-TG} plays the role of a value to be reached (in average) by $\mu\sum_i\int|\dot{\psi}_i(\mathbf{r})|^2d\mathbf{r}$. The corresponding equations of motion are as follows

$$\mu\ddot{\psi}_i(\mathbf{r}, t) = -\frac{\delta E_{tot}[\{\psi_i\}, \{\mathbf{R}_I\}]}{\delta\psi_i^*(\mathbf{r}, t)} + \sum_j \lambda_{ij}\psi_j(\mathbf{r}, t) - \mu\dot{\psi}_i\dot{\alpha}_e \quad (50)$$

$$M_I\ddot{\mathbf{R}}_I = -\nabla_I E_{tot}[\{\psi_i\}, \{\mathbf{R}_I\}] - M_I\dot{\mathbf{R}}_I\dot{\alpha}_I \quad (51)$$

$$\eta_I\ddot{\alpha}_I = 2\left(\frac{1}{2}\sum_{I=1}^N M_I\dot{\mathbf{R}}_I^2 - \frac{1}{2}N_{ind}k_B T^{TG}\right) \quad (52)$$

$$\eta_e\ddot{\alpha}_e = 2\left(\mu\sum_i\int|\dot{\psi}_i(\mathbf{r})|^2d\mathbf{r} - E_{kin}^{e-TG}\right) \quad (53)$$

where we have simply adapted and rewritten for the combined ionic/electronic degrees of freedom of the FPMD-CP method the set of equations shown in Sec. 5.1 when introducing the notion of multiple temperature control ².

²for a more complete and detailed view on the methodology and applications of FPMD-CP see Refs. [15, 1]

6 Conclusions

The main motivation of this paper was to review and highlight some very fundamental features of early temperature control approaches within molecular dynamics. Despite the fact that we are referring here to a formalism proposed back in 1985, we were driven by the conviction that some refocusing on the foundations and the underlying theory of thermostats application in atomic-scale dynamical simulation was very much needed. While reviewing the Nosé ideas for the benefit of those that did not have the opportunity to go through the original derivation, we realized that, quite surprisingly, the so-called extension and improvement due to Hoover (the Nosé-Hoover thermostat) can be easily traced back and identified in the original Nosé expressions. This is way the present paper, in addition to its predominant review character, contains also some new observation that can be taken as an valuable contribution to the temperature control ideas.

We showed that the Nosé formalism as it stands does not require, to increase its manageability and acquire a sound physical interpretation, any of the rearrangements put forth by Hoover and leading to the so-called Nosé-Hoover thermostat. Therefore, our analysis provides a form for the equations of motion easily understandable, containing the required friction force and yet based uniquely on a skillful reworking on what Nosé has presented in his seminal papers. As a complement to our rationale, we include the explicit expressions for the use of multiple thermostats by considering the case of separate families of degrees of freedom as it occurs in the Car-Parrinello version of first-principles molecular dynamics. We can also observe that the temperature of any additional dynamical variable, not necessarily atoms or fictitious electronic degrees of freedom, can be controlled with the scheme proposed by Nosé and revisited here. This is the case, for instance, of reaction coordinates or collective variables driving an activated process from reactants to products and included in the so-called metadynamics scheme [16, 17].

It would be unfair to conclude this paper without doing justice to those that, over the years, contributed to a better understanding of the theoretical foundations of the Nosé thermostat and the underlying non-hamiltonian dynamics. The references that follow (and those quoted therein) are not only highly representative of these theoretical efforts but provide important clues to capture the differences between microcanonical and canonical dynamics. As such, they have to be considered of the outmost importance when reviewing concepts and ideas related to temperature control within molecular dynamics [18, 19, 20, 21, 22].

Acknowledgements

We are grateful to Prof. Giovanni Ciccotti (Istituto per le Applicazioni del Calcolo, Consiglio Nazionale delle Ricerche, Roma (Italia)) for instructive comments.

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