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Stochastic thermostats and temperature expressions

A Samoletov and B Vasiev

Department of Mathematical Sciences, University of Liverpool, UK

E-mail: A.Samoletov@liverpool.ac.uk

E-mail: B.Vasiev@liverpool.ac.uk

Abstract. Molecular dynamics (MD) is in the core of fundamental research for a range of disciplines in natural sciences and is known for its applications in the design of new functional materials and the drug discovery. MD simulations are performed under certain thermodynamic conditions, typically at fixed temperature and pressure. The thermodynamic variables in the MD are modeled using equations that are called thermostats. Many different thermostats have been proposed. Recently (Samoletov A and Vasiev B 2017 *J. Chem. Phys.* **147** 204106), we have shown that a range of thermostats can be derived in the framework of a unified approach based on the fundamental principles of statistical physics, so that the relevant dynamic schemes are based on the concept of temperature expression (in short, ϑ -expression). However, only a few specific ϑ -expressions have been used so far and reported in the literature. In this paper, we are using a wider set of ϑ -expressions and their mathematical properties that allow us to modify the known and offer new thermostats with improved computational efficiency and ergodicity. We focus on the Nosé-Hoover-Langevin stochastic scheme and extend it with additional temperature control tools. Simultaneous thermostatting of all phase space variables with minimal additional computational costs is an advantage of the modified dynamics.

1. Introduction

Molecular dynamics (MD) [1–5] is an inevitable companion of research in a range of disciplines in natural sciences and in engineering including such popular branches as the design of new functional materials and the drug discovery. MD simulations are performed under certain environmental (thermodynamic) conditions, typically at fixed temperature or pressure. It is no wonder that many different dynamic temperature control tools that are called thermostats, deterministic and stochastic, have been proposed [4–9]. Recently, we have shown that a range of thermostats can be derived in the framework of a unified approach based on the fundamental principles of statistical physics [10]. However, this result has been presented in a rather formal form, so the benefits of unified approach presented may not seem obvious in terms of practical use. To address this issue, it is necessary to compare particular cases of abstract results with well-known dynamic thermostat schemes, although, obviously, with a loss of mathematical generality.

The Nosé–Hoover–Langevin (NHL) method [6–8] is commonly used in applications. This stochastic thermostat scheme allows one to obtain the canonical distribution for the simulated physical system using single additional degree of freedom subject to stochastic perturbation. The reliability of using the NHL scheme, as well as its deterministic counterpart, is based on the ergodic hypothesis, which claims that a physical system phase-space trajectory will spend an equal amount of time in each phase-space volume of equal probability [11]. In other words, this hypothesis equates the long-time average of a physical observable to its ensemble average.



While it is known that deterministic thermostats often violate ergodicity, *e.g.*, [12–14], they are assumed to be applicable for practical purposes. At the same time, the ergodicity of NHL thermostats, for which some rigorous results have been obtained [8], seems to be a very likely property.

Characteristic features of the NHL thermostat are 1) a single extra variable is added to physical equations of motion; 2) kinetic temperature expression is used. Initially, in the NHL scheme as it described in article [6], an additional dynamics variable was introduced formally, so there was no physical interpretation of it. On the contrary, theoretical scheme [10] is firmly based on the fundamental laws of statistical physics and allows reproducing the previous results as a very special case of a more general theory.

It is assumed that the physical system of interest to us, S, placed in the thermal reservoir, Σ , (such that is considered as a dynamical system of a very large (infinite) number of phase variables, which determines the general statistical properties of the S system) should to some extent perturb it and will itself be affected by the backward influence of this perturbation. Thus, the thermal reservoir is naturally divided into two parts, namely, the part that involved in joint dynamics with system, S^* , and the unperturbed part, $\Sigma \setminus S^*$, which is constantly in thermal equilibrium. An important assumption is made that all systems participating in joint dynamics are statistically independent at thermal equilibrium. In such a scheme, an additional thermostat variables are associated with the perturbed part S^* of the thermal reservoir. Therefore, the dynamic temperature control associated with this additional degree of freedom is as important as the kinetic energy control of the S system. Of course, the actual description of S^* system depends on the physical system of interest to us, as well as on the experimental methods used to extract the information, as they determine the temporal and spatial scales of data measurement and interpretation.

In this paper, we solve the problem of formulating the dynamics of the NHL type, which includes temperature expressions related to both systems, S and S^* , temperature control is applied to all degrees of freedom of the physical system of interest to us, and assuming that in general thermostated dynamics, a single thermostat variable can still be viewed for comparison, as in a standard NHL scheme.

2. Temperature expressions and thermostats

The design of dynamic thermostats is based on the concept of temperature expression [10]. Let us briefly recall the details of corresponding theoretical scheme, which are essential for this article.

Let the probability density $\sigma(x)$, $x \in \mathcal{M} = \mathbb{R}^n$ be given (the phase space is not necessarily even dimensional). We set the probability density in the form $\sigma_{\vartheta}(x) \propto \exp\{-\vartheta^{-1}\mathcal{V}(x)\}$ where $\mathcal{V}(x) : \mathcal{M} \rightarrow \mathbb{R}$ is a coercive function, that is, $\mathcal{V}(x) \rightarrow +\infty$, as $\|x\| \rightarrow +\infty$, so that $\mathcal{V}(x) = -\vartheta \ln \sigma_{\vartheta}(x)$, where $\vartheta > 0$ is a parameter. Consider a pair of vector fields, gradient $\nabla\mathcal{V}(x)$ and incompressible $\mathbf{G}(x)$, that is, $\nabla \cdot \mathbf{G}(x) = 0$ for all $x \in \mathcal{M}$, such that $\nabla\mathcal{V}(x) \cdot \mathbf{G}(x) = 0$ for all $x \in \mathcal{M}$ (in other words, $\nabla\mathcal{V}(x)$ and $\mathbf{G}(x)$ form a cosymmetric pair as defined in [15]). Then we relate to the system S the equations of motion

$$\dot{x} = \mathbf{G}(x).$$

Thus, we arrive at the following properties, $\dot{\mathcal{V}} = \nabla\mathcal{V}(x) \cdot \mathbf{G}(x) = 0$ and $\nabla \cdot (\mathbf{G}(x) \sigma(x)) = 0$, that is, $\mathcal{V}(x)$ is a first integral and the density $\sigma(x)$ is invariant for the dynamics $\dot{x} = \mathbf{G}(x)$.

When the S system contacts the thermal reservoir Σ at thermodynamic temperature T , $\vartheta = k_B T$, where k_B is the Boltzmann constant, then we define the temperature expression, $\Theta(x, \vartheta)$, based on the ergodic hypothesis as much as the concept of a thermostat itself.

Function $\Theta(x, \vartheta)$, $x \in \mathcal{M}$ is called a temperature expression if it explicitly depends on the parameter $\vartheta = k_B T$ and satisfies the condition,

$$\int_{\mathcal{M}} \Theta(x, \vartheta) d\mu_{\vartheta}(x) = 0 \quad \text{for all } \vartheta > 0,$$

where $d\mu_{\vartheta}(x) = \sigma_{\vartheta}(x) dx$. Similarly, for the S^* system $\int_{\mathcal{M}^*} \Theta^*(y, \vartheta) d\mu_{\vartheta}^*(y) = 0$ for all $\vartheta > 0$, where $d\mu_{\vartheta}^*(y) \propto \exp\{-\vartheta^{-1} \mathcal{V}^*(y)\} dy$, $y \in \mathcal{M}^* = \mathbb{R}^{n^*}$.

The ergodic hypothesis implies that for invariant densities

$$\lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^{\tau} \left\{ \begin{array}{l} \Theta(x(t), \vartheta) \\ \Theta^*(y(t), \vartheta) \end{array} \right\} dt = 0,$$

for almost all trajectories.

Our approach to designing thermostats with desired properties is based on the following observations. First, it is easy to make sure that the set of ϑ -expressions is a linear space. Then we associate this linear space with a vector space whose components are phase space functions that grow no faster than polynomials. Therefore, we use the expansion of a ϑ -expression in the basis in \mathcal{M} , $\{\mathbf{e}_i\}$, $\boldsymbol{\varphi}(x, \vartheta) = \sum \varphi_i(x, \vartheta) \mathbf{e}_i$, and similarly, the basis in \mathcal{M}^* , $\{\mathbf{e}_i^*\}$, $\boldsymbol{\varphi}^*(y, \vartheta) = \sum \varphi_i^*(y, \vartheta) \mathbf{e}_i^*$. It is acceptable that the functions $\varphi_i(x, \vartheta)$ and $\varphi_i^*(y, \vartheta)$ are themselves ϑ -expressions. Further, in respect of functions $\varphi_i(x, \vartheta)$ and $\varphi_i^*(y, \vartheta)$, we use expansion in terms of polynomials. We can also define the mapping of a ϑ -expression (or a vector of ϑ -expressions) to a ϑ -expression. In this article, we do not develop this scheme in a general mathematical form. Instead, we will look at examples.

Now we modify the equations of motion according to the dynamic principle [10], that is,

$$\nabla_x \mathcal{V}(x) \cdot \mathbf{G}(x) \propto \Theta(x, \vartheta),$$

assuming the validity of the ergodic hypothesis. Note that it is always possible to expand $\mathbf{G}(x)$ into two parts, first, the cosymmetry of $\nabla_x \mathcal{V}(x)$, $\nabla_x \mathcal{V}(x) \cdot \mathbf{G}_1(x) = 0$ for all $x \in \mathcal{M}$, and the other $\nabla_x \mathcal{V}(x) \cdot \mathbf{G}_2(x)$ that is vanishing on average only. Similarly, we relate to the S^* system the equations of motion $\dot{y} = \mathbf{G}^*(y)$, $y \in \mathcal{M}^*$, the appropriate potential function $\mathcal{V}^*(y)$, and the equilibrium probability density $\sigma_{\vartheta}^*(y) \propto \exp\{-\vartheta^{-1} \mathcal{V}^*(y)\}$.

3. Stochastic equations of motion

The theoretical scheme [10] covers both stochastic and deterministic methods of dynamical sampling of a statistical ensemble, in particular, thermostats. It is based on the fundamental principles of statistical mechanics, so that the canonical density is *de facto* invariant for the resulting equations of motion. The canonical ensemble is maintained by interaction with (effectively infinite) thermal reservoir, Σ . Since a complete microscopic description of Σ is not possible, the simulation of thermal reservoirs is carried out using stochastic or deterministic thermostats. We arrive at deterministic equations of motion by ignorance the influence of the main part of the heat reservoir, $\Sigma \setminus S^*$, on the dynamics of physical system, which is a stochastic perturbation by necessary. This greatly simplifies the dynamics, but sharply raises the difficult question about the ergodicity of thermostats. The practical effectiveness of any deterministic thermostat is actually a matter of chance.

In this article, we restrict ourselves to considering the generic case when thermostats are applied to Hamiltonian systems. Let the S system, when it is isolated, be defined by the Hamiltonian function $H(x)$, $x \in \mathcal{M}$, and equations of motion $\dot{x} = \mathbf{G}(x) = \mathbf{J}_x \nabla_x H(x)$, and, similarly, let the S^* system be defined by \mathcal{M}^* , $H^*(y)$, $y \in \mathcal{M}^*$, and $\dot{y} = \mathbf{G}^*(y) = \mathbf{J}_y \nabla_y H^*(y)$. Here, \mathbf{J}_x and \mathbf{J}_y are symplectic units. It is easy to verify that $\nabla H \cdot \mathbf{J} \nabla H \equiv 0$ and $\nabla \cdot \mathbf{J} \nabla H \equiv 0$ as required.

First, let the S^* system be empty. Thus, the only stochastic thermostat dynamics is possible. Consider a special ϑ -expression of the form $\Theta_L(x, \vartheta) = \sum_{l=0}^L \Theta_l(x, \vartheta)\vartheta^{2l}$ for all $L \in \mathbb{Z}_{\geq 0}$, where $\Theta_l(x, \vartheta) = \varphi_l(x, \vartheta) \cdot \nabla H(x) - \vartheta \nabla \cdot \varphi_l(x, \vartheta)$, $l = 0, 1, \dots, L$, and $\{\varphi_l(x, \vartheta)\}_{l=0}^L$ is a set of vector fields on \mathcal{M} such that $\varphi_l(x, \vartheta)\sigma(x) \rightarrow \mathbf{0}$ as $\|x\| \rightarrow \infty$, introduce the set of independent vectors of white noises, $\{\xi(l; t)\}_{l=0}^L$, $L \in \mathbb{Z}_{\geq 0}$, such that $\langle \xi(l; t) \rangle = \mathbf{0}$, $\langle \xi_i(l; t)\xi_j(l'; t') \rangle = 2\lambda_l \theta \delta_{ij} \delta_{ll'} \delta(t - t')$, and the set of vector fields, $\{\zeta(l; x)\}_{l=0}^L$, $L \in \mathbb{Z}_{\geq 0}$, such that $\nabla \circ \zeta(l; x) = \mathbf{0}$ for any $l \geq 0$, where \circ denotes the component-wise (Hadamard) product of two vectors. Starting with the relationship, $\nabla H(x) \cdot \mathbf{G}_2(x, \lambda) = \sum_{l=0}^L \Theta_l(x, \vartheta)\vartheta^{2l}$, and following the procedure [10], we arrive at the stochastic dynamics:

$$\dot{x} = \mathbf{J}_x \nabla_x H(x) - \sum_{l=0}^L \lambda_l \boldsymbol{\eta}(l; x) \circ \nabla_x H(x) \vartheta^{2l} + \sum_{l=0}^L \zeta(l; x) \circ \xi(l; t) \vartheta^l,$$

where $\boldsymbol{\eta}(x) \equiv \zeta(x) \circ \zeta(x)$. One can verify by direct calculation that the density $\sigma_\vartheta(x)$ is invariant for this dynamics. It can be expected that such a Langevin-type dynamics is ergodic.

When the nontrivial S^* system is involved in a joint motion with the S system and an influence of $\Sigma \setminus S^*$, it has to be stochastic by necessary, on the dynamics is taking into consideration, then, following the procedure [10], we arrive at the stochastic equations of motion (where the case $y \in \mathbb{R}$ can be specified as in the standard NHL scheme [6]),

$$\begin{aligned} \dot{x} &= \mathbf{J}_x \nabla_x H(x) + \sum_{(k)} \Theta_k^*(y, \vartheta) \varphi_k(x, \vartheta), \\ \dot{y} &= \mathbf{J}_y \nabla_y H^*(y) - \sum_{(l)} \Theta_l(x, \vartheta) \varphi_l^*(y, \vartheta) - \sum_{l=0}^L \lambda_l^* \boldsymbol{\eta}^*(l; y) \circ \nabla_y H^*(y) \vartheta^{2l} + \sum_{l=0}^L \zeta^*(l; y) \circ \xi(l; t) \vartheta^l, \end{aligned}$$

under reasonable conditions on the growth of vector fields $\{\varphi_k(x, \vartheta)\}$. Here $\boldsymbol{\eta}^*(y) \equiv \zeta^*(y) \circ \zeta^*(y)$. and $\{\varphi_l^*(y, \vartheta)\}$. One can verify that the density $\sigma \propto \exp\{-\vartheta^{-1}[H(x) + H^*(y)]\}$ is invariant for this dynamics. Such an NHL-type stochastic dynamics can be expected to be ergodic.

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