Thermostats for "Slow" Configurational Modes

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Abstract Thermostats are dynamical equations used to model thermodynamic variables such as temperature and pressure in molecular simulations. For computationally intensive problems such as the simulation of biomolecules, we propose to average over fast momentum degrees of freedom and construct thermostat equations in configuration space. The equations of motion are *deterministic* analogues of the Smoluchowski dynamics in the method of stochastic differential equations.

1 Introduction

One of the most ambitious challenges in mathematical modeling of biological processes is to describe dynamics of two major biological events within a cell—DNA molecule replication and transcription. In both cases, dynamical properties, especially large amplitude conformational changes of the double-stranded DNA molecule play a vital part. The principal physical feature of biological functioning of biomolecules is that they operate at ambient physiological temperature, pressure and solvent conditions. Thus, the surrounding physiological solvent plays the role of a thermostat, among others. To properly thermostat this

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dynamics, especially on a biological ("slow") time scale, we propose a suitable and effective temperature control of interest both for the practice of numerical simulation and the general theory of dynamical systems.

For a recent and comprehensive review of the problem outlined above we refer to [1]. Current approaches commonly use the Nosé–Hoover thermostat method (for review see [2–6]). This canonical thermostat method involves integration of both position and momentum phase space variables. However, for problems that are related to slow conformational changes of biomolecules, integration of fast momentum variables appears superfluous from a theoretical point of view (unobservable variables) as well expensive in the sense of numerical simulation.

In this paper, a novel approach to the problem of slow conformational changes in thermostatting dynamics is presented. The method is based on an analogy with the derivation of the Smoluchowski dynamics (see (2) below) from the Langevin stochastic dynamics (see (1) below) [7–9]. The configurational deterministic thermostat is constructed so as to effect the temperature control via certain dynamics of the relaxation rate variable and also involves a dynamically fluctuated collective force to ensure the ergodicity property. As the result, the temperature control is connected to the specific configurational temperature recently introduced in [10, 11] in a different context. The new configurational thermostat can be combined with complementary temperature control via a dynamically fluctuated virial function [12–14] that helps to enhance the efficiency of the thermostat and, more importantly because biological molecules are functioning at a constant pressure, implements the pressure control into the corresponding dynamics. Moreover, the configurational thermostat admits stimulation by a chain of thermostats similar to Nosé–Hoover [15] and a stochastically driven method (see below). To test the new configurational thermostat, corresponding simulations of a one-dimensional harmonic and the Morse oscillator dynamics are given, providing a stringent test of the ergodicity property.

Remark Braga and Travis [16] have recently proposed a thermostat based on the Smoluchowski equation and configurational temperature ideas (but retaining the momentum variables), citing an early preprint of this paper [17].

2 Preliminaries

Section 2.1 briefly reviews the Langevin and Smoluchowski approaches to a system in contact with the environment. Section 2.2 presents the Nosé–Hoover thermostat scheme in brief in the form of consequent steps and logic that we follow in Sect. 3. Section 2.3 presents the virial thermostat scheme. Section 2.4 presents a stochastically stimulated thermostat scheme in the context of Nose–Hoover dynamics. Following these preliminary sections our proposed configurational thermostats are presented in Sects. 3 and 4 and tested numerically in Sect. 5. Section 6 concludes.

2.1 Stochastic Dynamics

The early and successful attempts to describe the dynamics of a mechanical system being in contact with an environment playing a role of the thermostat are based on the concept of the stochastic differential equation [7]. Langevin's equation for the case of one-dimensional motion of a particle mass m in a potential field $V(q)$ provides the characteristic example,

$$m\dot{q} = p, \qquad \dot{p} = -\nabla V(q) - \gamma p + \sqrt{2D} f(t), \tag{1}$$

where the friction coefficient γ and the intensity D of the external random force $f(t)$ are connected by the relation, $D = m\gamma k_{\mathrm{B}}T$; here $f(t)$ is the generalized Gaussian stochastic process, "white noise", with characteristic cumulants $\langle f(t) \rangle = 0$ and $\langle f(t)f(t') \rangle = \delta(t - t')$. The equilibrium solution of the corresponding Fokker–Planck equation,

$$\frac{\partial \rho}{\partial t} = -\frac{p}{m}\frac{\partial \rho}{\partial q} + \frac{\partial}{\partial p}\left[\left(\frac{dV}{dq} + \gamma p\right)\rho\right] + D\frac{\partial^2 \rho}{\partial p^2},$$

is known [7], $\rho_\infty \propto \exp[-(p^2/2m + V(q))/(k_{\mathrm{B}}T)]$.

Langevin's equation (1) is a prototype of the Nosé–Hoover deterministic dynamics (after generalization of the last with the term $\bar{\xi}$ as in (24) it is especially evident). But while the Langevin dynamics generate all the sample trajectories and the corresponding measure, the Nosé–Hoover dynamics produce a single sample trajectory with the correct canonical ensemble statistics when ergodicity holds.

Often details of the dynamics of a system on short time scales are not needed for a dynamical description of the observable variables. However, then the Smoluchowski limit of (1),

$$m\dot{q} = -\tau\nabla V(q) + \sqrt{2mk_{\mathrm{B}}T\tau}\,f(t), \tag{2}$$

where $\tau = \gamma^{-1}$, is an appropriate formulation [7–9]. Only the position variable is involved in this equation. Formally, it is supposed that the momentum variable relaxes to the local equilibrium state. The corresponding Smoluchowski equation has the Boltzmann distribution as the equilibrium solution [7]. Equation (2), without the random perturbation, appears as a dissipative dynamics with $V(q)$ playing a role of the Lyapunov function, $\dot{V} = -\tau(\nabla V(q))^2 \leq 0$. Thus, the full dynamics is a superposition of relaxation to a minimum of the potential and random perturbations that occasionally expel the system outside the vicinity of the minimum. This process equilibrates the system.

2.2 The Nosé–Hoover Dynamics

Consider a system of N particles of mass $m = \{m_k\}_{k=1}^N$ with vectors of coordinate $q = \{\mathbf{q}_k\}_{k=1}^N$ and momentum $p = \{\mathbf{p}_k\}_{k=1}^N$, and the Hamiltonian function $H(q, p) = \sum \mathbf{p}^2/(2m) + V(q)$, where $V(q)$ is the potential function of the system of particles. Here and in what follows $\sum$ means sum over all particles of the system (*e.g.* $\sum \mathbf{p}^2/(2m) \equiv \sum_{k=1}^N \mathbf{p}_k^2/(2m_k)$). Physical space is d-dimensional, d $= 1, 2, 3$, and respectively the system has dN degrees of freedom and 2dN-dimensional phase space $\mathcal{M} = (q, p)$. To simulate the canonical statistics with deterministic dynamics we are in need of non-canonical forces to cool/heat the system and equilibrate the dynamics. The Nosé–Hoover scheme [2–6] is characterized by the simplest form of non-canonical forces, the Rayleigh friction, $-\zeta\mathbf{p}$, and supposes the Gaussian fluctuation of the single thermostat variable ζ at the equilibrium.

Let us emphasize here the following scheme we regularly utilize throughout the paper,

– first, we consider a deformation of the dynamical equations in the phase space $\mathcal{M}$ with a constant parameter (the parameter ζ in this Section). Even if it is obvious that with the constant deformation parameter the equations of motion are too simple to generate the canonical statistics they are a convenient starting point for further discussion;
– then, requiring that the Liouville equation corresponding to these deformed equations of motion has the canonical distribution as a steady state solution we arrive at a condition involving the temperature into dynamics (the condition (4) in this Section). Under this

condition on the dynamic variables the deformation parameter becomes variable (non-constant). This explicit contradiction with original supposition concerning the deformation parameter results in conclusion that the deformed equations of motion together with the obtained temperature control condition cannot generate the canonical statistics;

– finally, to preserve in essential the structure of the Liouville equation corresponding to the dynamical equations with constant deformation parameter and thus allow generation of the canonical statistics, we extend the phase space $\mathcal{M}$ and consider the deformation parameter as an independent variable with its own equation of motion. This results in a dynamical temperature control.

Firstly we consider ζ as a constant, $\zeta \neq 0$, but further it will be endowed with its own equation of motion. Dynamical equations take the form,

$$\dot{\mathbf{q}} = \frac{\mathbf{p}}{m}, \qquad \dot{\mathbf{p}} = -\nabla V(\boldsymbol{q}) - \zeta \mathbf{p}. \tag{3}$$

(Equation (3) reads: $\dot{\mathbf{q}}_k = \mathbf{p}_k/m_k, \dot{\mathbf{p}}_k = -\nabla_{\mathbf{q}_k} V(\boldsymbol{q}) - \zeta \mathbf{p}_k, k = 1, \ldots, N$; in what follows we use the short notation above as it common in literature). Requiring that the Liouville equation corresponding to (3) has the canonical distribution,

$$\rho_\infty \propto \exp\left\{ -\beta \left[\sum \frac{\mathbf{p}^2}{2m} + V(q) \right] \right\},$$

(where $\beta \equiv 1/(k_B T)$, k_B denotes the Boltzmann constant and T is the temperature), as a steady state solution, we obtain the following condition,

$$\sum \frac{\mathbf{p}^2}{m} = \mathrm{d}N k_B T. \tag{4}$$

It means that the total kinetic energy is constant and equal to equilibrium value according to the equipartition theorem. In other word, with set (3) and condition (4) we arrive at the so-called Gaussian isokinetic thermostat [3]. This thermostat does not extend system phase space $\mathcal{M}$. Nonholonomic condition (4) provides for the temperature control and requires nonconstant ζ (in contradiction with the original supposition). The Gaussian isokinetic thermostat does not generate the canonical statistics. To preserve in essential the structure of (3) and the corresponding Liouville equation with constant ζ we need extend the phase space $\mathcal{M}$ and consider ζ as an independent variable.

The Nosé–Hoover method is based on the idea of extended dynamics. When variable ζ is endowed with its own equation of motion,

$$\dot{\zeta} = g(\boldsymbol{q}, \boldsymbol{p}), \tag{5}$$

then set (3) and (5) represents an autonomous system, and variable ζ simulates the thermostat in such a way that (4) takes place only after time averaging. Thus the kinetic energy is allowed to dynamically fluctuate around its equilibrium value. More precisely, the Liouville equation corresponding to set (3) and (5) has a steady states solution of the form

$$\rho_\infty \propto \exp\left\{ -\beta \left[\sum \mathbf{p}^2/(2m) + V(\boldsymbol{q}) + \Phi(\zeta) \right] \right\}$$

only if

$$\Phi(\zeta) = \frac{1}{2} Q \zeta^2, \qquad g = \frac{1}{Q} \left(\sum \frac{\mathbf{p}^2}{m} - \mathrm{d}N k_B T \right), \tag{6}$$

where Q is a constant. Thus the function g is fixed up to a constant multiplier. The parameter $Q \equiv \mathrm{d}Nk_{\mathrm{B}}T\tau_{\mathrm{p}}^2$ appears as a characteristic time scale τ_{p}. After the time averaging,

$$\overline{(\cdots)} = \lim_{\Theta \to \infty} \frac{1}{\Theta} \int_0^{\Theta} dt\,(\cdots),$$

assuming the motion is bounded, (5) leads to relation

$$\overline{\left(\sum \frac{\mathbf{p}^2}{m} \right)} = \mathrm{d}Nk_{\mathrm{B}}T$$

that is in agreement with the equipartition theorem.

To conclude this section we note that the Nosé–Hoover extended dynamics allows Hamiltonian reformulation. Consider balance of the mechanical work along trajectories of (3–5),

$$\sum -\nabla V \cdot d\mathbf{q} = d\left(\sum \frac{\mathbf{p}^2}{2m} + \frac{1}{2}Q\zeta^2 \right) + \mathrm{d}Nk_{\mathrm{B}}T\zeta\,dt.$$

To obtain an exact differential equation, it is necessary to set

$$\zeta\,dt = d\lambda.$$

In that case the following first integral is apparent,

$$I_{\mathrm{NH}} = \sum \frac{\mathbf{p}^2}{2m} + V(\boldsymbol{q}) + \frac{1}{2}Q\zeta^2 + \mathrm{d}Nk_{\mathrm{B}}T\lambda. \tag{7}$$

Since the origin of the redundant variable λ is arbitrary, it is always possible for an arbitrary fixed trajectory to set $I_{\mathrm{NH}} = 0$. Integral of motion (7) is apparent starting point for the Hamiltonian reformulation of the Nosé–Hoover dynamics [14, 18]. The Hamiltonian function has the form,

$$\mathcal{H}(\boldsymbol{q}, \lambda; \boldsymbol{u}, \psi) = e^{-\lambda} \sum \frac{\mathbf{u}^2}{2m} + e^{\lambda} V(\boldsymbol{q}) + e^{-\lambda} \frac{1}{2Q}\psi^2 + e^{\lambda}\mathrm{d}Nk_{\mathrm{B}}T\lambda,$$

where the canonical variables, $\boldsymbol{u} = \{\mathbf{u_k}\}_{k=1}^N$ and ψ, are connected with the Nosé–Hoover dynamical variables, $\boldsymbol{p}$ and ζ, by the relations

$$\boldsymbol{u} = \exp(\lambda)\boldsymbol{p}, \qquad \psi = \exp(\lambda)Q\zeta.$$

Equations of motion,

$$\dot{\mathbf{q}} = \nabla_{\mathbf{u}}\mathcal{H}, \qquad \dot{\mathbf{u}} = -\nabla_{\mathbf{q}}\mathcal{H}, \qquad \dot{\lambda} = \nabla_{\psi}\mathcal{H}, \quad \dot{\psi} = -\nabla_{\lambda}\mathcal{H},$$

coincide with the Nosé–Hoover thermostat equations (3–5) on the level set

$$I_{\mathrm{NH}} = 0.$$

2.3 The Virial Theorem and Virial Thermostat

The virial theorem is proved in classical as well as statistical mechanics [19–21]. This theorem has a great generality since it does not require even ergodicity of motion. This means that the temperature control below is valid when the Nosé–Hoover thermostat is valid. There is a difference of kind between the kinetic temperature and virial temperature control in the time scale of thermostatting dynamics. The virial in connection with the Nosé–Hoover thermostat first appears in [12, 13] in the context of the harmonic oscillator. In this section we consider a more general case.

Consider a system of N particles as above. The quantity $\mathcal{V}(\boldsymbol{q})$,

$$\mathcal{V}(\boldsymbol{q}) = \sum \mathbf{q} \cdot \nabla V(\boldsymbol{q}),$$

defines the virial of the forces in the configuration q (in short, the virial). The virial theorem (Clausius) states the following relation of the time averages,

$$\overline{\left(\sum \frac{\mathbf{p}^2}{m}\right)} = \overline{\mathcal{V}(\boldsymbol{q})}. \tag{8}$$

The same relation is valid for the equilibrium averages in the canonical ensemble as well. The immediate corollary of this relation,

$$\overline{\mathcal{V}(\boldsymbol{q})} = \mathrm{d}Nk_\mathrm{B}T, \tag{9}$$

clearly suggests the virial $\mathcal{V}(\boldsymbol{q})$ for the temperature control in a thermostat similar to the Nosé–Hoover one.

The virial $\mathcal{V}(\boldsymbol{q})$ of a system in a volume v can be expressed as sum of the virial of internal forces, $\mathcal{V}_\mathrm{int}(\boldsymbol{q})$, and the virial of external forces on the boundary of the volume v, $\mathcal{V}_{ext}(\boldsymbol{q})$. In result we arrive at the following relation,

$$\overline{\mathcal{V}_\mathrm{int}(\boldsymbol{q})} + \mathrm{d}Pv = \mathrm{d}Nk_\mathrm{B}T, \tag{10}$$

where P is the pressure (the second theorem of Clausius; we refer to [20, 21] for details). In the case of free particles, $\overline{\mathcal{V}_\mathrm{int}(\boldsymbol{q})} = 0$, and relation (10) is the ideal gas equation ($Pv = Nk_\mathrm{B}T$). Relation (10) is useful when the pressure control is required.

Analogues of the Gaussian isokinetic thermostat and the Nosé–Hoover thermostat but under the temperature control provided by the virial instead of the kinetic energy can be formulated in the following manner. First, in the same situation as in Sect. 2.2, consider deformation of the Hamiltonian system,

$$\dot{\mathbf{q}} = \frac{\mathbf{p}}{m}, \qquad \dot{\mathbf{p}} = -\nabla V(\boldsymbol{q}),$$

with a scalar parameter $\eta = \mathrm{const}$ such that the Liouville equation corresponding to the deformed dynamics has the canonical distribution,

$$\rho_\infty \propto \exp\left\{-\beta\left[\sum \mathbf{p}^2/(2m) + V(\boldsymbol{q})\right]\right\},$$

as a steady state solution under condition

$$\mathcal{V}(\boldsymbol{q}) = \mathrm{d}Nk_\mathrm{B}T. \tag{11}$$

Since the virial contains gradients of $V(\boldsymbol{q})$ the requirements above define the following deformed equations of motion,

$$\dot{\mathbf{q}} = \frac{\mathbf{p}}{m} + \eta\mathbf{q}, \qquad \dot{\mathbf{p}} = -\boldsymbol{\nabla}V(\boldsymbol{q}). \tag{12}$$

It can be verified by direct calculation that the Liouville equation corresponding to (12) has the canonical distribution as a steady state solution only if (11) is valid. In other words, the virial is a constant equal to equilibrium average value (9). By analogy with the isokinetic thermostat we denote (12) together with condition (11) as the isovirial thermostat. The isovirial thermostat does not extend system phase space $\mathcal{M}$. Condition (4) provides for the temperature control and requires nonconstant η (in contradiction with the original supposition). The isovirial thermostat does not generate the canonical statistics. To preserve in essential the structure of (12) and the corresponding Liouville equation with constant η we need extend the phase space $\mathcal{M}$ and consider η as an independent variable.

Now we endow η with its own equation of motion as in the Nosé–Hoover dynamics and consider the following extended dynamics,

$$\dot{\mathbf{q}} = \frac{\mathbf{p}}{m} + \eta\mathbf{q}, \qquad \dot{\mathbf{p}} = -\boldsymbol{\nabla}V(\boldsymbol{q}), \qquad \dot{\eta} = h(\boldsymbol{q}, \boldsymbol{p}). \tag{13}$$

The Liouville equation corresponding to system (13) has a steady state solution of the form,

$$\rho_\infty \propto \exp\left\{-\beta\left[\sum \mathbf{p}^2/(2m) + V(\boldsymbol{q}) + \Psi(\eta)\right]\right\},$$

only if

$$\Psi(\eta) = \frac{1}{2}Q\eta^2, \qquad h = \frac{1}{Q}(\mathrm{d}Nk_\mathrm{B}T - \mathcal{V}(\boldsymbol{q})), \tag{14}$$

where Q is a constant. Thus function h is fixed up to a constant multiplier. Parameter $Q \equiv \mathrm{d}Nk_\mathrm{B}T\tau_\mathrm{q}^2$ appears as a characteristic time scale τ_q. It should be observed here that time scales τ_q and τ_p (Sect. 2.2) are possibly different.

Remark: The virial theorem has no relation to time scales τ_p (see below (6)) and τ_q. Characteristic scales for time averaging of left-hand side and right-hand side of (8) are possibly different. Since the temperature control based on the virial is configurational we can *a priori* expect that the corresponding dynamics relates to slower processes then the Nosé–Hoover dynamics. However this point requires a special investigation, for example, to make a comparison of autocorrelation functions of the Nosé–Hoover and the virial thermostatting dynamics. We do not discuss this problem here.

Equation (13) after time averaging leads to the expected relation,

$$\overline{\mathcal{V}(\boldsymbol{q})} = \mathrm{d}Nk_\mathrm{B}T.$$

The virial thermostatting dynamics allows Hamiltonian reformulation. Consider balance of the mechanical work along trajectories.

$$\sum -\boldsymbol{\nabla}V \cdot d\mathbf{q} = d\left(\sum \frac{\mathbf{p}^2}{2m} + \frac{1}{2}Q\eta^2\right) - \mathrm{d}Nk_\mathrm{B}T\eta dt.$$

To obtain an exact differential equation, it is necessary to set

$$\eta dt = d\mu.$$

In that case, we obtain the following integral of motion,

$$I_V = \sum \frac{\mathbf{p}^2}{2m} + V(\boldsymbol{q}) + \frac{1}{2} Q \eta^2 + \mathrm{d} N k_B T \mu. \qquad (15)$$

Since the origin of the redundant variable μ is arbitrary, it is always possible for an arbitrary fixed trajectory to set $I_V = 0$. The integral of motion (15) is apparent starting point for the Hamiltonian reformulation of the virial thermostatting dynamics (13). The Hamiltonian function has the form [14],

$$\mathcal{H}(\boldsymbol{k}, \lambda_\eta; \boldsymbol{p}, \varphi) = e^{-\mu} \sum \frac{\mathbf{p}^2}{2m} + e^{-\mu} V(e^\mu \boldsymbol{k}) + e^\mu \frac{1}{2Q} \varphi^2 - e^{-\mu} \mathrm{d} N k_\mathbf{B} T \mu,$$

where the canonical variables, $\boldsymbol{k} = \{\mathbf{k}_i\}_{i=1}^N$ and φ, are connected with corresponding dynamical variables, $\boldsymbol{q}$ and η, by the relations,

$$\boldsymbol{k} = e^\mu \boldsymbol{q}, \qquad \varphi = e^{-\mu} Q \eta.$$

Canonical equations of motion,

$$\dot{\mathbf{k}} = \nabla_\mathbf{p} \mathcal{H}, \qquad \dot{\mathbf{p}} = -\nabla_\mathbf{k} \mathcal{H}, \qquad \dot{\mu} = \nabla_\varphi \mathcal{H}, \qquad \dot{\varphi} = -\nabla_\mu \mathcal{H},$$

coincide with the virial thermostat equations (13) on the level set

$$I_V = 0.$$

To conclude this section we point out that the virial thermostat is very suggestive of a configurational thermostat scheme. Namely, consider dynamical system (13). Since equation for thermostat variable η (14) does not explicitly include momenta variables p and the virial has rate of converging to equilibrium value supposedly different from kinetic energy then it is possible to postulate that momentum variables are relaxed, similar to overdamped regime, to

$$\mathbf{p} = -\tau \nabla V(\boldsymbol{q}),$$

where $\tau = \mathrm{const}$ is a relaxation time, and arrive at the following configurational dynamics,

$$\dot{\mathbf{q}} = -\tau \frac{1}{m} \nabla V(\boldsymbol{q}) + \eta \mathbf{q}, \qquad \dot{\eta} = \frac{1}{Q} (\mathrm{d} N k_B T - \mathcal{V}(\boldsymbol{q})). \qquad (16)$$

Since the Liouville equation corresponding to this system has under certain condition (see Sect. 3) the Boltzmann distribution as a steady state solution we can consider (16) as a first step toward a deterministic fully configurational thermostat. This problem is considered in more general context in Sect. 3.

2.4 Stimulated Nosé–Hoover Dynamics

The Nosé–Hoover chain method [15] is often used in practice, *e.g.* [1]. It is based on observation that variable ζ generates the Gaussian statistics as well as variables $\boldsymbol{p}$. This observation immediately suggests to thermostat variable ζ by new thermostat variable ζ_1 in a same

manner and so on, and thus stimulate the equilibrium statistics of the thermostat [15]. The
Nosé–Hoover chain of the full length of M has the form,

$$\dot{\mathbf{q}} = \frac{\mathbf{p}}{m}, \qquad \dot{\mathbf{p}} = -\nabla V(\boldsymbol{q}) - \zeta \mathbf{p},$$

$$\dot{\zeta} = g - \zeta_1 \zeta, \qquad \dot{\zeta}_i = \frac{1}{Q_i}(Q_{i-1}\zeta_{i-1}^2 - k_{\mathrm{B}}T) - \zeta_{i+1}\zeta_i,$$

where $i = 1, \ldots, \mathrm{M}$, $\zeta_0 = \zeta$, $\zeta_{\mathrm{M}+1} \equiv 0$; $\{Q_i\}$ are constant parameters. In that case

$$\rho_\infty \propto \exp\left\{-\beta\left[\sum \frac{\mathbf{p}^2}{2m} + V(\boldsymbol{q}) + \frac{1}{2}Q\zeta^2 + \sum_{i=1}^{\mathrm{M}} \frac{1}{2}Q_i\zeta_i^2\right]\right\}.$$

The corresponding integral of motion has the following form,

$$I_{\mathrm{NHchain}} = \sum \frac{\mathbf{p}^2}{2m} + V(\boldsymbol{q}) + \frac{1}{2}Q\zeta^2 + \sum_{(i)} \frac{1}{2}Q_i\zeta_i^2 + k_{\mathrm{B}}T\lambda,$$

where the redundant variable λ satisfies equation

$$\dot{\lambda} = \mathrm{d}N\zeta + \sum_{(i)} \zeta_i.$$

Since the Nosé–Hoover chain method is based on forcing the Gaussian statistics of the
thermostat variable(s) and thus speed up the system to generate the equilibrium canonical
statistics, we can propose a stochastic stimulation scheme as an alternative to the chain
method. The stochastic stimulation scheme becomes apparent when it is considered that
linear transformation of a Gaussian random process is another Gaussian random process
[7]. We propose the following set of dynamical equations instead of the Nosé–Hoover chain
thermostatting dynamics,

$$\dot{\mathbf{q}} = \frac{\mathbf{p}}{m}, \qquad \dot{\mathbf{p}} = -\nabla V(\boldsymbol{q}) - \zeta \mathbf{p}, \qquad \dot{\zeta} = g(\boldsymbol{p}) - \gamma\zeta + f(t), \qquad (17)$$

where $f(t)$ is a generalized Gaussian random process ("white noise"), completely charac-
terized by the first two cumulants,

$$\langle f(t)\rangle = 0, \qquad \langle f(t)f(t')\rangle = 2D\delta(t - t').$$

Thus the governing thermostatting equation (variable ζ) is the stochastic differential equa-
tion. In contrast to the Langevin method [7] the only thermostat variable ζ is subject to
stochastic perturbation but the dynamical variables (q, p) are not directly stochastically per-
turbed. The advantage over the chain method of the stochastic stimulation method above
consists in ensuring the ergodicity of the thermostat [22].

The Liouville equation corresponding to (17) after averaging over all realizations of the
random process $f(t)$ takes form of the Fokker–Planck equation,

$$\frac{\partial\rho}{\partial t} = \sum\left[-\frac{\mathbf{p}}{m}\cdot\nabla_{\mathbf{q}}\rho + \nabla_{\mathbf{q}}V\cdot\nabla_{\mathbf{p}}\rho + \zeta\nabla_{\mathbf{p}}\cdot(\mathbf{p}\rho)\right]$$

$$- g(p)\frac{\partial\rho}{\partial\zeta} + \gamma\frac{\partial}{\partial\zeta}(\zeta\rho) - D\frac{\partial^2\rho}{\partial\zeta^2}. \qquad (18)$$

It only remains to prove that this equation has the steady state solution ρ_∞,

$$\rho_\infty \propto \exp\left\{-\beta\left[\sum \frac{\mathbf{p}^2}{2m} + V(\boldsymbol{q}) + \frac{1}{2}Q\zeta^2\right]\right\}.$$

Substitution of ρ_∞ into (18) leads to the following conditions,

$$D = \frac{\gamma}{Q}k_B T,$$

$$g(\boldsymbol{p}) = \frac{1}{Q}\left[\sum \frac{\mathbf{p}^2}{m} - \mathrm{d}Nk_B T\right].$$

The last expression for the function g is the same as (6) for the analogous function in the Nosé–Hoover chain method. The first equation is an analogue of the fluctuation-dissipation relation.

3 Configurational Thermostat

It is reasonable, in the spirit of deterministic thermostat methods, to conjecture that it is possible to use the relaxation time τ for thermostatting configurational degrees of freedom when momentum variables are still relaxed in their local equilibrium state. Of course, in this case the sign of τ is not fixed and V loses its meaning as a Lyapunov function. In a sense, it means that time can go back as well as forward.

First, consider the simple dynamical equations for $\mathrm{d}N$ degrees of freedom,

$$m\dot{\mathbf{q}} = -\tau\nabla V(\boldsymbol{q}), \tag{19}$$

where τ is a constant, but by analogy with Nosé–Hoover will be endowed with its own equation of motion below. Short notation as in Sect. 2 is used in (19) and in what follows; (19) reads as $m_k\dot{\mathbf{q}}_k = -\tau\nabla_{\mathbf{q}_k}V(\boldsymbol{q})$, $k = 1, \ldots, N$. By the change of variables, $\mathbf{x} = \sqrt{m}\mathbf{q}$, it is possible to exclude all masses from the formulae in what follows, but we prefer to save the physical notation. Requiring that the corresponding Liouville equation has the Boltzmann distribution, $\rho_\infty \propto \exp[-V(\boldsymbol{q})/(k_B T)]$, as a steady state solution, we arrive at the condition that involves the temperature in the dynamics,

$$\sum \frac{1}{m}\left[\Delta V(\boldsymbol{q}) - \frac{1}{k_B T}(\nabla V(\boldsymbol{q}))^2\right] = 0. \tag{20}$$

After time averaging, (20) appears as the definition of the recently introduced so-called configurational temperature [10, 11]. Currently it is used in molecular dynamics simulations [23, 24]. In a more general context, in the case of a presupposed anisotropy in the system, let us assume that τ in (19) is a matrix, $\tau \to \Gamma$. Then the dynamics take the form, $m\dot{\mathbf{q}} = -\Gamma\nabla V(\boldsymbol{q})$, and the condition that involves the temperature in the dynamics is

$$\sum \frac{1}{m}\left[(\nabla, \Gamma\nabla)V(\boldsymbol{q}) - \frac{1}{k_B T}(\nabla V(\boldsymbol{q}), \Gamma\nabla V(\boldsymbol{q}))\right] = 0.$$

Note that this condition involves the presupposed time scales in the dynamical temperature control. Conventional Nosé–Hoover methods do not allow such a generalization. In what

follows we also consider τ as a scalar. On the other hand, it is useful to keep in mind the possibility of the generalization.

We now attempt to generate statistics as in the Nosé–Hoover scheme by making τ an independent variable in (19). It is easily seen that this is too simple. At an equilibrium point $\nabla V = 0$, that is, all forces are zero, the evolution comes to a halt and no longer fluctuates, irrespective of the time dependence of τ. For initial conditions with nonzero forces (19) after a (positive or negative) change of time variable, it is a gradient flow as defined in [25], and it is easy to show that all trajectories move along paths in q with equilibrium points at either end. In short, the system is not ergodic. Note also that (20) is singular when $\nabla V = 0$.

The way to overcome this difficulty is suggested by the Smoluchowski stochastic equation. In this equation the ergodic motion is ensured by the random forcing. Hence, we need to add a deterministic analogue of the random force term in (2). Let us consider, instead of (19), the dynamical equations,

$$m\dot{\mathbf{q}} = -\tau \nabla V(\boldsymbol{q}) + \boldsymbol{\xi}, \tag{21}$$

where $\boldsymbol{\xi}$ are constant vectors, but they will be endowed with their own equation of motion below. Requiring that the Liouville equation corresponding to (21) has the Boltzmann distribution as a steady state solution, together with temperature control condition (20) we arrive at the condition

$$\sum \frac{1}{m} \boldsymbol{\xi} \cdot \nabla V(\boldsymbol{q}) = 0. \tag{22}$$

To detail the nature of vectors $\boldsymbol{\xi}$, three principal cases are possible: (a) All $\boldsymbol{\xi} = \{\boldsymbol{\xi}_i\}_{i=1}^N$, where N is number of particle in the system, can be varied independently; (b) All $\boldsymbol{\xi}_i = \boldsymbol{\xi}$ are varied identically; (c) There exist a preferred direction, $\mathbf{e}$, where $\mathbf{e}$ is a constant unit vector of physical (*i.e.* three dimensional) space, and only one variable, ξ, $\boldsymbol{\xi} = \xi \mathbf{e}$, is varied. Varying $\boldsymbol{\xi}$ in (22) according to cases (a), (b) and (c) we correspondingly obtain the following particular conditions,

$$\text{(a)} \quad \nabla V(\boldsymbol{q}) = 0, \qquad \text{(b)} \quad \sum \frac{1}{m} \nabla V(\boldsymbol{q}) = 0, \qquad \text{(c)} \quad \sum \frac{1}{m} \mathbf{e} \cdot \nabla V(\boldsymbol{q}) = 0. \tag{23}$$

These conditions do not involve temperature but the thermalized forces acting in the system. All of them, as well as a their combination, are candidates for simulating the deterministic analogue of the random force, chosen according to the problem under consideration. For example, in respect of the Peyrard–Bishop dynamical model of the DNA molecule [1], case (c) appears to be appropriate.

The physical sense of the conditions above are the following.

Case (a): the force acting on a particle in the system equals zero (static equilibrium of forces). In that case dynamical equations (21) degenerate to triviality, $\boldsymbol{\xi} = 0$ and the temperature control condition takes a sense only if the temperature $T = 0$. But when $\boldsymbol{\xi}$ are endowed with their own equations of motion and conditions (a) take place only after time averaging then dynamics (21) is robust and $\boldsymbol{\xi}$ provide a shaking of the system around the configuration of the mechanical equilibrium of the system.

Case (b): the static equilibrium of forces is not required but the total force acting on the system equals zero (stability of the system). In that case when $\boldsymbol{\xi}$ is endowed with its own equation of motion, it provides a shaking of the system around its center of inertia.

Case (c): stability of the system in the direction $\mathbf{e}$. When ξ is endowed with its own equation of motion, it provides a shaking of the system along the direction $\mathbf{e}$.

In all cases the time scale of such a shaking is still a parameter of the theory.

It is practical to remark, in consideration of the virial thermostat scheme of Sect. 2.3, that a thermostatting dynamics more general than (21) is possible. Consider dynamical equations of the form

$$m\dot{\mathbf{q}} = -\tau \nabla V(\mathbf{q}) + \eta m \mathbf{q} + \boldsymbol{\xi}, \tag{24}$$

where the term $\eta m \mathbf{q}$ is suggested by the virial thermostatting scheme. Requiring that the Liouville equation corresponding (24) has the Boltzmann distribution as a steady state solution we obtain together with (20) and 22) the following condition on the virial function,

$$dNk_{\mathrm{B}}T - \sum \mathbf{q} \cdot \nabla V = 0. \tag{25}$$

In this case a double temperature control is provided. The η term is not a mandatory temperature control for our configurational thermostat. We could consider only the τ term by a trivial modification of (24) and subsequent equations but consider a more general equations of the form (24). The reason is that the virial function involves the pressure in the dynamics and this is important for biologically oriented models. For the sake of definiteness and keeping in mind a future application we here fix case (c). When ξ is endowed with its own equation of motion, it provides a shaking of the system along the direction $\mathbf{e}$.

Now we have three parameters which we group together as a 3-vector $\boldsymbol{\alpha} = (\tau, \eta, \xi)^{\mathrm{T}}$. As in (20), (22) and (25) we find a stationary solution of the Liouville equation of the form

$$\rho_\infty \propto \exp[-(V(\mathbf{q}) + \boldsymbol{\alpha}^{\mathrm{T}} \mathsf{Q} \boldsymbol{\alpha}/2)/(k_{\mathrm{B}}T)]$$

where Q is a positive definite real symmetric matrix. It is, of course, not possible to justify consistently that parameters $\boldsymbol{\alpha}$ have a Gaussian distribution at equilibrium. It is just a reasonable assumption that leads to the simplest form of self-consistent thermostat dynamics. Intuitively, we can justify the Gaussian character of the parameters at equilibrium by the limiting theorems of probability theory. Note that when multiple thermostats are present, they are usually assumed to be uncoupled (diagonal Q); mathematically it is not required and we do not feel that this is physically necessary, thus we consider that the more general case of coupled thermostats may be useful. For comparison with the uncoupled case we define $\tilde{\mathsf{Q}} = \mathrm{diag}(Q_{\tau\tau}, Q_{\eta\eta}, Q_{\xi\xi})$ to be the matrix with only the diagonal components of Q. Instead of (20), (23) and (25) we obtain

$$\tilde{\mathsf{Q}}\boldsymbol{g} \equiv \begin{pmatrix} \sum \frac{1}{m}[(\nabla V)^2 - k_{\mathrm{B}}T\,\Delta V] \\ dNk_{\mathrm{B}}T - \sum \mathbf{q} \cdot \nabla V \\ -\sum \frac{1}{m}\mathbf{e} \cdot \nabla V \end{pmatrix} = 0, \tag{26}$$

which now defines $\boldsymbol{g}$. It should be remembered (see Sects. 2.2 and 2.3) that conditions $\tilde{\mathsf{Q}}\boldsymbol{g} = 0$ are inconsistent with the initial supposition of $\boldsymbol{\alpha} = \mathrm{const}$.

Let us realize the main conjecture the configurational thermostat scheme and allow the components of $\boldsymbol{\alpha}$ to fluctuate so that (26) holds only after time averaging. Thus we extend the original phase space $\mathcal{M}$. We write

$$\dot{\boldsymbol{\alpha}} = \boldsymbol{G} \tag{27}$$

where $\boldsymbol{G}$ is as yet an undetermined vector of functions. Now requiring the same condition for the solution of the Liouville equation corresponding to system (24) and (27), we find that

the only solution is

$$G = Q^{-1}\tilde{Q}g. \tag{28}$$

Thus the only undetermined parameters of our thermostatting scheme are the components of the positive definite real symmetric matrix Q, and in the uncoupled case $\tilde{Q} = Q$ we have $G = g$. In this uncoupled case dynamics takes the simple form,

$$m_k \dot{\mathbf{q}}_k = -\tau \boldsymbol{\nabla}_{\mathbf{q}_k} V(\boldsymbol{q}) + \eta m_k \mathbf{q}_k + \boldsymbol{\xi},$$

$$\dot{\tau} = \frac{1}{Q_{\tau\tau}} \sum_{k=1}^{N} \frac{1}{m_k} [(\boldsymbol{\nabla}_{\mathbf{q}_k} V)^2 - k_{\mathrm{B}} T \Delta_{\mathbf{q}_k} V],$$

$$\dot{\eta} = \frac{1}{Q_{\eta\eta}} \left(\mathrm{d}N k_{\mathrm{B}} T - \sum_{k=1}^{N} \mathbf{q_k} \cdot \boldsymbol{\nabla}_{\mathbf{q}_k} V \right),$$

$$\dot{\boldsymbol{\xi}} = -\frac{1}{Q_{\xi\xi}} \sum_{k=1}^{N} \frac{1}{m_k} \mathbf{e} \cdot \boldsymbol{\nabla}_{\mathbf{q}_k} V.$$

Parameters $Q_{\tau\tau}$, $Q_{\eta\eta}$, $Q_{\xi\xi}$ define time scales that are in general different.

We can now ask whether the addition of new variables η and/or ξ will remove the lack of ergodicity implied by the potential flow argument applying to (19). A partial answer is provided by the Frobenius theorem of differential geometry [26], which in our case states that an integral surface exists (hence the dynamics are definitely not ergodic) if a vector space containing the terms in the equation for $\mathbf{q}$ but smaller than the full phase space is closed under Lie brackets. For realistic potentials (not the harmonic oscillator) this is very unlikely since multiple derivatives of V are almost always linearly independent. If the theorem does not apply we are in the same situation as for nonthermostatted nonintegrable many particle systems, which are often assumed to be ergodic, at least for practical purposes.

Since under the transformation $t \to -t$, $\boldsymbol{\alpha} \to -\boldsymbol{\alpha}$ the equations of motion (24) and (27) are still unchanged, they are time reversible.

To find a mechanically important integral of motion of system (24), we need to add a redundant variable. Indeed, consider the balance of the mechanical work along trajectories of (24) and (27),

$$\sum -\boldsymbol{\nabla} V \cdot d\mathbf{q} = d(\boldsymbol{\alpha}^{\mathrm{T}} Q \boldsymbol{\alpha}/2) + k_{\mathrm{B}} T \left(\sum \frac{\Delta V}{m} \tau - \mathrm{d}N\eta \right) dt.$$

To obtain an exact differential equation, it is necessary to set

$$\left(\sum \frac{\Delta V}{m} \tau - \mathrm{d}N\eta \right) dt = d\theta.$$

In that case, the following integral of motion is apparent,

$$I_{\mathrm{S}} = V(\boldsymbol{q}) + \boldsymbol{\alpha}^{\mathrm{T}} Q \boldsymbol{\alpha}/2 + k_{\mathrm{B}} T \theta.$$

Since the origin of the redundant variable θ is arbitrary, it is always possible for an arbitrary fixed trajectory to set $I_{\mathrm{S}} = 0$. This integral of motion is apparent control parameter in numerical simulations. Besides, it clearly relates to the equilibrium distribution ρ_{∞} and thus can be considered as a first step to reformulation of (24) and (27) in terms of a free energy

functional. Recall that the corresponding Nosé–Hoover integral of motion, Sect. 2.2, as well as the virial scheme integral of motion, Sect. 2.3, both are given by their Hamiltonian—no Hamiltonian is possible here since the momentum does not appear explicitly.

4 Stimulated Configurational Thermostats

Since the configurational dynamics above result in the Gaussian equilibrium fluctuation of thermostat variables, the latter admits reinforcing by a chain of equations analogous to the Nose–Hoover chain thermostat [15]. The chain method consists in including a subsidiary sequence of dynamical variables, $\{\boldsymbol{\alpha}_i\}$, into a thermostat scheme such that asymptotically, in the equilibrium distribution, they are independent Gaussian variables,

$$\rho_\infty \propto \exp\left[-\left(V(\boldsymbol{q}) + \frac{1}{2}\boldsymbol{\alpha}^\mathrm{T}\mathsf{Q}\boldsymbol{\alpha} + \sum_{(i)} \frac{1}{2}\boldsymbol{\alpha}_i^\mathrm{T}\mathsf{Q}_i\boldsymbol{\alpha}_i\right)\Big/(k_\mathrm{B}T)\right].$$

The corresponding dynamics are not unique. We have obtained a clear method for generalizing the chain, but since this does not directly relate to our main topic we do not discuss the details. Instead we cite the example of the chain rule that has been used in our test simulation,

$$m\dot{\mathbf{q}} = -\tau\boldsymbol{\nabla}V(\boldsymbol{q}) + \xi\boldsymbol{e}, \dot{\tau} = g_\tau + \tau_1\tau,$$
$$\dot{\tau}_i = \frac{1}{Q_{\tau_i}}(k_\mathrm{B}T - Q_{\tau_{i-1}}\tau_{i-1}^2) + \tau_{i+1}\tau_i, \dot{\xi} = g_\xi, \tag{29}$$

where $i = 1, \ldots, \mathrm{M}, : \tau_0 = \tau, : \tau_{\mathrm{M}+1} \equiv 0$. It is a simple chain of total length M.

It should also be noted that in spite of its popularity, the effectiveness of the chain method for computing non-equilibrium properties has been questioned [5, 27].

It is possible to stimulate the Gaussian fluctuation of the thermostat variables by the process of Brownian motion. This scheme has the advantage of ensuring the ergodicity property. The stimulation, similar to the chain one, may be done in a few ways, applying to one or more of the variables τ, η and ξ (see Sect. (2.4) for the prototype). In general we have

$$m\dot{\mathbf{q}} = -\tau\boldsymbol{\nabla}V(\boldsymbol{q}) + \eta m\mathbf{q} + \xi\boldsymbol{e}, \qquad \dot{\boldsymbol{\alpha}} = \boldsymbol{G} - \Lambda\boldsymbol{\alpha} + \sqrt{2\mathsf{D}}\boldsymbol{f}(t), \tag{30}$$

where now Λ and $\sqrt{2\mathsf{D}}$ are positive definite real symmetric matrices, and $\boldsymbol{f}(t)$ is a vector of independent white noise components. The Liouville equation corresponding to (30), averaged over all the realizations of $\boldsymbol{f}(t)$, has the form of the Fokker–Planck equation (similar to (18)) and the Boltzmann distribution as a steady state solution only if

$$k_\mathrm{B}T\Lambda = \mathsf{DQ}.$$

We consider that the most physical case is when the noise is used only for temperature control, that is, for τ and η only. We do not establish extreme generality here because our main aim is the presentation of the idea of the *deterministic* fully configurational thermostat. The effectiveness of (30) for systems far from equilibrium is not clear.
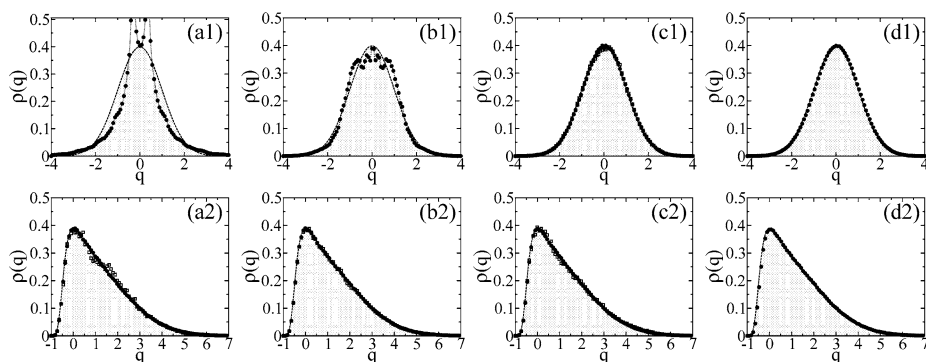
Fig. 1 Probability distributions of position variable (shown on background of exact analytical distribution) of the harmonic (1) and Morse (2) oscillator. Probability densities are calculated as normalized sojourn distributions. Correspondingly, thermostat is: (**a1**)–(**a2**) non-stimulated and uncorrelated (see (24), $\dot{\tau} = g_\tau$, $\eta \equiv 0$, $\dot{\xi} = g_\xi$); (**b1**)–(**b2**) non-stimulated and uncorrelated but under double temperature control (see (24), $\dot{\tau} = g_\tau$, $\dot{\eta} = g_\eta$, $\dot{\xi} = g_\xi$); (**c1**)–(**c2**) uncorrelated but stimulated by the chain rule (see (29), M = 1); (**d1**)–(**d2**) stimulated by stochastic process (see (30), $\eta \equiv 0$, $D = 1$). All simulations are performed at $Q_\tau = Q_\xi = 1$, $Q_\eta = 0.1$ for $t = 10^4$ (*squares*) and $t = 10^6$ (*black circles*)

5 Test Numerical Simulations

The harmonic oscillator is both a simple and an important physical system. At the same time, it reveals the ergodicity problem in the canonical ensemble simulation. For this reason, it is important to test the configurational thermostat method capable of generating the Boltzmann distribution for a single harmonic oscillator in one dimension, $V(q) = q^2/2$. Then it is reasonable to simulate another one-dimensional system, 'good' from the point of view of the Frobenius theorem, and to compare results. We choose for this purpose the Morse oscillator, $V(q) = V_0(1 - \exp(-aq))^2 + kq^2/2$. Simulations are performed using global parameters $m = 1$ and $k_B T = 1$, and the Morse potential parameters $V_0 = 0.25$, $a = 2$, k = 0.25. Figure 1 shows the probability distribution of the position variable calculated with the four simplest configurational thermostats. Note the effectiveness of the double temperature control. The ability of the configurational thermostat to reproduce the correct distribution function, $\rho(q)$, even with absolute minimum of this thermostat capacity, demonstrates its great potential for application.

6 Conclusion

An innovative constant temperature thermostat, the configurational thermostat, exclusively involving dynamics of the configurational variables has been introduced. It poses the general problem of the derivation of a thermostatting dynamics for slow dynamical variables and outlines at least one way of the solution. For practical purposes, the new thermostatting scheme can easily be combined with complementary temperature control via dynamical fluctuation of the virial function. This combination helps to enhance the efficiency of the thermostat temperature control as well as to implement pressure control into the dynamics. It is also relevant to emphasize the appearance of the dynamically fluctuated forces and correlated temperature control in the presented thermostatting scheme. We finally remark that the proposed method is applicable to thermostatting such macro/meso-scale models as the reaction-diffusion dynamical equations.

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