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CONSTANT TEMPERATURE MOLECULAR DYNAMICS METHODS

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ABSTRACT: Two basic formulations of the constant temperature molecular dynamics method are presented and some generalizations are discussed. A new extension of the Nosé scheme, a multi-*s*-variable or the Nosé chain method, is proposed.

1. INTRODUCTION

The method of molecular dynamics (MD) is a powerful tool for studying classical many-body systems and has been widely applied in condensed matter physics, material science, and fluid dynamics [1, 2] since it was introduced and set up more then thirty years ago [3-5].

In its traditional formulation MD performs the numerical solution of Newton's equations of motion for a system of particles contained in a fixed cell which is subject to periodic boundary conditions. The total energy of the system is conserved throughout the simulation and time averages represent fairly closely microcanonical ensemble averages. The conditions of constant energy, constant volume and constant number of particles (E, V, N) conditions are, however, not encountered normally in experiments and they are, in fact, very inconvenient for theoretical analysis. Furthermore, in the area of nonequilibrium computer simulations the constant energy (E, V, N) MD approach is unable to create homogeneous steady states [6].

The problem of controlling the temperature instead of the total energy in MD simulations was a real challenge for many years. The earliest method for constant temperature MD is an *ad-hoc* momentum scaling procedure, in which the velocities of the particles are scaled at each time step to maintain the total kinetic energy at a constant value [7]. This approach generates discontinuities in the phase space trajectory and has been used without demonstrated justification. Thus, the ability to perform thermostatted MD simulations in a statistical mechanically rigorous sense remained unsolved for almost 30 years. A significant breakthrough was made in 1980s when several methods for constant temperature MD were proposed. Significant contributions came from papers by Andersen (1980) [8], Hoover et al. (1983) [9] and Evans (1983) [10], Nosé (1984) [11], and Hoover (1985) [12].

Andersen was the first to show that ensembles other than constant energy could be realized in MD. He introduced the constant pressure MD method in which the volume becomes a variable and is allowed to fluctuate in accordance with a fixed pressure. Andersen proposed also a method for constant temperature MD. The method does indeed generate canonical ensemble averages but is based on the stochastic change of the velocities of the particles – effectively is a hybrid of the MD and Monte Carlo methods – and as such limits its usefulness when realistic dynamical trajectories are required.

Hoover et al. and Evans proposed the first deterministic method for thermostatting in molecular dynamics simulations. In this method an additional term proportional to the momentum of the particle, $-\alpha\mathbf{p}$, is added to the forces in the equations of motion. The value of the multiplier, α, changes with time in such a way that the kinetic energy remains constant during the course of simulation [6]. Such modifications or constrained equations of motion generate canonical distribution for the configurational degrees of freedom.

Isothermal, continuous, reversible dynamics capable of mimicking a canonical ensemble in both momentum and position space was proposed by Nosé. In Nosé's formulation the usual $6N$-dimensional phase space $(\mathbf{x}, \mathbf{p})$ of *the real system* is extended by one extra variable and its conjugate momentum. The specific Nosé Hamiltonian guarantees that the equations of motion of the extended system generate averages that are equivalent to canonical averages.

Hoover reformulated and simplified the extended system method. He demonstrated that the $(6N + 2)$ – dimensional phase space of the extended system can be projected on $(6N + 1)$ dimensional phase space and the resulting equations of motion, the Nosé-Hoover equations, generate the canonical distribution.

The papers by Nosé and Hoover established a basic methodology for performing MD at constant temperature. Both approaches has been intensively tested, analyzed and generalized and are of continuing interest because of their supporting role in performing non-equilibrium MD [13, 6].

In this paper some basic generalizations of the original Nosé and Hoover formulations are presented and a new multivariable generalization of the Nosé Hamiltonian is proposed.

2. THE NOSÉ SCHEME

In the Nosé approach [11, 14] a physical system of N particles with coordinates $\mathbf{q}' = (\mathbf{q}'_1, \mathbf{q}'_2, \dots, \mathbf{q}'_N)$ and momentum $\mathbf{p}' = (\mathbf{p}'_1, \mathbf{p}'_2, \dots, \mathbf{p}'_N)$ in a fixed volume V, and potential energy $U(\mathbf{q}')$ is considered. An additional degree of freedom s is introduced and two phase spaces or systems are defined: the extended virtual system (unprimed variables), $\Gamma \equiv (\mathbf{q}, \mathbf{p}, s, \pi_s)$, and the extended physical system (primed variables), $\Gamma' \equiv (\mathbf{q}', \mathbf{p}', s', \pi'_s)$, where π_s is the conjugate momentum of s. The physical system

$(\mathbf{q}', \mathbf{p}')$ is a subsystem of the extended physical system. The relation between both phase spaces are defined as

$$\mathbf{q}' = \mathbf{q},\ \mathbf{p}' = \mathbf{p}/s,\ s' = s,\ \pi'_s = \pi_s/s,\ dt' = dt/s, \tag{1}$$

and the following Hamiltonian is postulated for the extended virtual system

$$H = \sum_{i=1}^{N} \mathbf{p}_i^2/2ms^2 + U(\mathbf{q}) + \pi_s^2/2Q + gkT\ln s\,. \tag{2}$$

The parameter g is essentially equal to the number of degrees of freedom of the physical system, Q is a parameter which acts as a "mass" for the motion of s, k is the Boltzmann's constant and T is the set temperature. The Hamiltonian equations of motion are

$$\frac{d\mathbf{q}_i}{dt} = \frac{\partial H}{\partial \mathbf{p}_i} = \mathbf{p}_i/ms^2\,, \tag{3}$$

$$\frac{d\mathbf{p}_i}{dt} = -\frac{\partial H}{\partial \mathbf{q}_i} = -\frac{\partial U}{\partial \mathbf{q}_i}\,, \tag{4}$$

$$\frac{ds}{dt} = \frac{\partial H}{\partial \pi_s} = \pi_s/Q\,, \tag{5}$$

$$\frac{d\pi_s}{dt} = -\frac{\partial H}{\partial s} = \left(\sum_i \mathbf{p}_i^2/ms^2 - gkT\right)\Big/s\,. \tag{6}$$

In the extended virtual system the total energy is conserved and we have a similar situation to the traditional (E, V, N) microcanonical MD, i.e., assuming the quasiergodic hypothesis, the time averages along the trajectory determined by Eqs. (3-6) are exactly those in the microcanonical ensemble with the partition function

$$Z_\mu = \int d\pi_s \int ds \int d\mathbf{p} \int d\mathbf{q}\,\delta(H - E)\,. \tag{7}$$

The essence of the Nosé approach is a simple relation between the microcanonical partition function of the extended virtual system and the canonical partition function of the physical system,

$$Z_\mu = C \int d\mathbf{p}' \int d\mathbf{q}' \exp[-H_0(\mathbf{p}', \mathbf{q}')/kT]\,, \tag{8}$$

were $H_0 = \sum \mathbf{p}'^2_i/2m + U(\mathbf{q}')$ and C is a constant factor. This relation ensures that the averages of any quantity expressed as function of $\mathbf{p}_i/s$, $\mathbf{q}_i$ along the trajectory determined by Eqs. (3-6) are exactly those in the canonical ensemble:

$$\lim_{t\to\infty} \frac{1}{t} \int_0^t A(\mathbf{p}/s, \mathbf{q}\rangle_\mu = \langle A(\mathbf{p}', \mathbf{q}'\rangle_c\,. \tag{9}$$

$\langle\ldots\rangle_\mu$ and $\langle\ldots\rangle_c$ denote the microcanonical ensemble average in the extended virtual system and the canonical ensemble in the physical system, respectively. The Hamiltonian dynamics in the extended virtual space (Eqs. 3-6) generates fluctuations of the kinetic and potential energy in the physical system in accordance with the canonical distribution of ($\mathbf{p}'$, $\mathbf{q}'$) at the fixed temperature T.

3. THE HOOVER SCHEME

The equations of motion in the extended virtual space can be formally transformed, by the relations (1), into the equations of motion in the extended physical space

$$\frac{d\mathbf{q}_i}{dt'} = \mathbf{p}_i/m\,, \tag{10}$$

$$\frac{d\mathbf{p}_i}{dt'} = -\frac{\partial U}{\partial \mathbf{q}_i'} - s'\pi_s\mathbf{p}_i'/Q\,, \tag{11}$$

$$\frac{ds'}{dt'} = s'^2\pi_s/Q\,, \tag{12}$$

$$\frac{d\pi_s}{dt'} = \left(\sum_i \mathbf{p}'^2/ms'^2 - gkT\right)/s' - s'\pi_s'^2/Q\,. \tag{13}$$

A conserved quantity of this system is

$$H' = \sum_i \mathbf{p}_i'^2/2m + s'^2\pi_s'^2/2Q + gkT\ln s'\,, \tag{14}$$

which is not a hamiltonian and Eqs. (10-13) are no longer canonical equations of motion. Hoover pointed out that, for the thermostatting mechanism, only the product of s' and π'_s is significant. Defining $\zeta = s'\pi'_s/Q$ he transformed Eqs. (10-13) into a closed set of equations in ($\mathbf{p}'$, $\mathbf{q}'$, ζ) space

$$\frac{d\mathbf{q}_i'}{dt'} = \mathbf{p}_i'/m\,, \tag{15}$$

$$\frac{d\mathbf{p}_i'}{dt'} = -\frac{\partial U}{\partial \mathbf{q}_i'} - \zeta\mathbf{p}_i'\,, \tag{16}$$

$$\frac{d\zeta}{dt'} = \left(\sum_i \mathbf{p}'^2_i/m - gkT\right)/Q\,. \tag{17}$$

with the subsidiary equation for s'

$$\frac{ds'}{dt'} = s'\zeta\,, \tag{18}$$

which is not needed to compute the trajectories of the N interacting particles. The set of dynamic equations Eqs. (15-17) defines the so called Nosé-Hoover dynamics. It generates the canonical distribution of the physical phase space variables [12].

The Nosé and Hoover schemes have essentially solved the problem of performing equilibrium MD at constant temperature and both approaches have become standard tools in MD simulation.

The time scaling necessary in the Nosé scheme makes the calculations more cumbersome comparing to the Hoover scheme. The Nosé scheme is, however, the Hamiltonian based approach what can have some advantages from a theoretical point of view [15].

There is no simple and obvious meaning for the extended variables s and ζ which provide a coupling to the thermal bath. Formally, s can be considered to be a time or particle mass scaling parameter. Because of apparent similarities between the Nosé-Hoover and the constrained dynamics, ζ is treated as a friction-like variable (which can be positive as well as negative). There are some indications that the extended variables can be related to the thermodynamic functions [16, 17].

The value of the parameter Q does influence the dynamics in the both schemes. The parameter Q controls the speed of the response of the thermostat (determine the rateof fluctuations for the kinetic energy, see e.g., Eq. 17). It can be related to a characteristic time of the system (typically the average time between atomic collision) and its value, compared to this characteristic time, should be neither too big nor too small [18].

4. THE GENERALIZATIONS OF THE ISOTHERMAL DYNAMICS

Equilibrium correlation functions computed by Nosé-Hoover and Newtonian dynamics are equivalent in the thermodynamic limit [19] but, in general, calculations of dynamic properties generally show some differences. Furthermore, for small or stiff systems the isothermal dynamics is often not ergodic and the correct distributions are not generated. These problems have led to various generalizations of the Nosé and Hoover schemes.

In 1988 Jellinek and Berry [20] demonstrated that Nosé dynamics Eqs. (3-6) is not unique. In fact, there exist many inequivalent dynamics which generate the same static canonical ensemble averages. Those different dynamics are defined by the generalized Nosé hamiltonian,

$$H = \sum_i \mathbf{p}_i^2/2mh_i^2(s) + U(f(s)\mathbf{q}) + \pi_s^2/2u(s)Q + kTv(s)\,, \tag{19}$$

where $h_i(s)$, $f(s)$, $u(s)$, and $v(s)$ are real nonvanishing differentiable functions of s. For $h(s) = s$, $f(s) = 1$, $u(s) = 1$, $v(s) = glns$ the original Nosé hamiltonian is recovered. The generalized Hamiltonian opens the possibility of searching for a dynamics which is able to mimic adequately not only the equilibrium but also the time dependent properties of a particular physical system.

To our knowledge this new possibility has been not been exploited yet. We are aware of only a few applications of the generalized isothermal dynamics [21, 22].

Recently, Winkler argue that the case $h(s) = s^2, f(s) = 1, u(s) = 1, v(s) = g\ln s$, gives a better mixing of phase space trajectories in a system with a small number of degrees of freedom. The reason for a small number of applications of the generalized isothermal dynamics probably is its complexity and the fact that, in practice, the generalized hamiltonian is not so general as is suggested by its definition. First of all, the scaling of the position coordinates is purely formal as, in fact, the only possible choice is $f(s) =$ constant [23]. The choice for $v(s)$ is limited and strongly related to the form of the function $h(s)$. Also the $u(s)$-scaling of π_s has probably only a minor effect on the main features of the dynamics. Thus, we consider that the essential extension of the original Nosé scheme is the replacement of the variable s by its functions $h_i(s)$.

The first generalization of the Hoover scheme was due to Nosé himself [24]. His main idea was to perform a separate temperature control for different degrees of freedom, e.g., different for translation and molecular rotation. The separate temperature control can be advantageous in carrying out calculations on a system that has more than one typical time scale. In such systems, the use of many temperature control variables, ζ_j, may provide a more quick global equilibration. The proposed generalized equations (see Eqs. 15-17) are,

$$\frac{d\mathbf{q}'_i}{dt'} = \mathbf{p}'_i/m, \tag{20}$$

$$\frac{d\mathbf{p}'_i}{dt'} = -\frac{\partial U}{\partial \mathbf{q}'_i} - \zeta_j \mathbf{p}'_i \tag{21}$$

$$\frac{d\zeta_j}{dt'} = \left(\sum_i \mathbf{p}'^2_i/m - g_j kT \right) / Q_j . \tag{22}$$

The constants g_j and Q_j have similar meaning as above.

Hoover [25] suggested that the canonical ensemble can be mimicked by a specific set of non-Hamiltonian dynamics in which the thermostatting force, $\zeta\mathbf{p}$, can be generalized to a combination of different friction coefficients and powers of particle momentum, $\sum \zeta_n \mathbf{p}^n$.

A different dynamics, the Nosé-Hoover chain method, has been proposed by Martyna and Klein [26]. They also introduced a set of different friction coefficients, but in this case the aim was to provide a thermostatting mechanism also for the extended variable, ζ. The Nosé-Hoover chain method is defined by the following equations of motion,

$$\frac{d\mathbf{q}'_i}{dt'} = \mathbf{p}'_i/m, \tag{23}$$

$$\frac{d\mathbf{p}'_i}{dt'} = -\frac{\partial U}{\partial \mathbf{q}'_i} - \mathbf{p}'_i \zeta_1 / Q_1 , \tag{24}$$

$$\frac{d\zeta_1}{dt'} = \left(\sum_i \mathbf{p}'^2_i/m - gkT \right) - \zeta_1 \zeta_2 / Q_2 , \tag{25}$$

$$\frac{d\zeta_j}{dt'} = (\zeta^2_{j-1}/Q_{j-1} - kT) - \zeta_j \zeta_{j+1}/Q_{j+1} , \tag{26}$$

$$\frac{d\zeta_M}{dt'} = (\zeta^2_{M-1}/Q_{M-1} - kT) . \tag{27}$$

It was argued [26, 27] that the above set of equations is able to give a more correct (canonical) distribution for small or stiff cases.

The fourth generalization of the Hoover scheme is due to Bulgac and Kusnezov [28]. They proposed a very general set of equations in which the thermostatting force is added to both equations for momentum and position.

$$\frac{d\mathbf{q}'_i}{dt'} = \frac{\partial H}{\partial \mathbf{p}'_i} - h_2(\xi)\mathbf{F}_i(\mathbf{p}',\mathbf{q}') \tag{28}$$

$$\frac{d\mathbf{p}'_i}{dt'} = -\frac{\partial H}{\partial \mathbf{q}'_i} - h_1(\zeta)\mathbf{G}_i(\mathbf{p}',\mathbf{q}') \tag{29}$$

$$\frac{d\zeta}{dt'} = \frac{\partial H}{\partial \mathbf{p}'_i}\mathbf{G}_i - kT\frac{\partial \mathbf{G}_i}{\partial \mathbf{p}'_i} \tag{30}$$

$$\frac{d\xi}{dt'} = \frac{\partial H}{\partial \mathbf{q}'_i}\mathbf{F}_i - kT\frac{\partial \mathbf{F}_i}{\partial \mathbf{q}'_i} \tag{31}$$

where $\mathbf{F}$, $\mathbf{G}$, h_1, h_2 are arbitrary functions and the equations can be extended to an arbitrary number of the friction-like variables. Most of generalizations of the Hoover scheme can be derived from the above equations [26].

The above four generalizations of the Hoover scheme are not derived from a hamiltonian. The proof, that the equations (in each case) give the canonical distribution is based on the conservation of the probability distribution function. Thus, the proof is necessary but not sufficient for a general system. It is valid only for ergodic systems and does not guarantee that the correct limiting distribution will be generated [15].

5. THE NOSÉ CHAIN METHOD

The generalizations of the Hoover scheme are mainly based on introducing additional extended variables (friction-like variables). We propose a similar extension for the Nosé scheme by introducing the following multi-s-variable Hamiltonian,

$$H = \sum_{i=1}^{N} (\mathbf{p}_i^2/2ms_1^2 + U(\mathbf{q})) + \sum_{j=1}^{M} (\pi_j^2/2Q_j s_{j+1}^2 + g_j kT \ln s_j) + \\ + \pi_{M+1}^2/2Q_{M+1} + g_{M+1} kT \ln s_{M+1} . \tag{32}$$

The Hamiltonian is defined in the $6N + 2(M + 1)$ dimensional phase space and for $M = 0$ reduces to the original Nosé hamiltonian (2). Q_j and g_j are constants. Following Nosé's arguments [11, 14], one can readily show that the microcanonical partition function of the extended virtual system defined by the hamiltonian (32) is proportional to the canonical partition function of the physical system. Consequently, the average of some static quantity which is an arbitrary function of $\mathbf{p}/s_1$ and $\mathbf{q}$ in the extended virtual system is exactly the same as in the canonical ensemble. The equations of motion in the multi-s-variable formulation are

$$\frac{d\mathbf{q}_i}{dt} = \frac{\partial H}{\partial \mathbf{p}_i} = \mathbf{p}_i/ms_1^2 , \tag{33}$$

$$\frac{d\mathbf{p}_i}{dt} = -\frac{\partial H}{\partial \mathbf{q}_i} = -\frac{\partial U}{\partial \mathbf{q}_i} , \tag{34}$$

$$\frac{ds_1}{dt} = \frac{\partial H}{\partial \pi_1} = \pi_1/Q_1 s_2^2 , \tag{35}$$

$$\frac{d\pi_1}{dt} = -\frac{\partial H}{\partial s_1} = \left(\sum_i \mathbf{p}_i^2/ms_1^2 - g_1 kT \right) / s_1 . \tag{36}$$

$$\frac{ds_j}{dt} = \frac{\partial H}{\partial \pi_j} = \pi_j/Q_j s_{j+1}^2 , \tag{37}$$

$$\frac{d\pi_j}{dt} = -\frac{\partial H}{\partial s_j} = (\pi_{j-1}^2/Q_{j-1} s_j^2 - g_j kT)/s_j . \tag{38}$$

$$\frac{ds_{M+1}}{dt} = \frac{\partial H}{\partial \pi_{M+1}} = \pi_{M+1}/Q_{M+1} , \tag{39}$$

$$\frac{d\pi_{M+1}}{dt} = -\frac{\partial H}{\partial s_{M+1}} = (\pi_M^2/Q_M s_{M+1}^2 - g_{M+1} kT)/s_{M+1} . \tag{40}$$

The above set of equations strongly resembles the Nosé-Hoover chain method and we call it the Nosé chain method. Obviously, it can be further generalized along the line proposed by Jellinek and Berry, e.g., the set of s-variables, $\{s_j\}$, can be replaced by the set of their functions, $\{h_j(s_j)\}$.

6. CONCLUSIONS

In this work we have discussed some recently proposed constant temperature molecular dynamics methods. It has been pointed out that the main progress in this field is based on various generalizations of the original Nosé and Hoover schemes.

Also the Nosé chain method, based on the Nosé scheme has been proposed. The method, as for the Nosé-Hoover chain method, is expected to help establish ergodic conditions. Thus, the chain dynamics should be quite useful for cases where the other approaches fail, e.g., for small or stiff systems. Computationally the method is relatively inexpensive as the extra s-variables form only a single one dimensional chain.

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