Canonically modified Nosé-Hoover equation with explicit inclusion of the virial

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The Nosé-Hoover equation has recently been introduced to simulate, in a deterministic and reversible way, the equilibrium properties of a system at constant temperature. However, for many one-dimensional potentials, such as the harmonic oscillator, the Nosé-Hoover scheme is not adequate since the dynamics is not sufficiently ergodic. We present modifications of the Nosé-Hoover equation in which the kinetic energy and the virial are treated in an equivalent manner and which explicitly include the virial within a canonical framework. We show that these modifications can yield an adequate statistical description for one-dimensional potentials such as the double-well and harmonic oscillator.

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Recently, Nosé [1] introduced a purely deterministic and reversible set of equations which model the coupling of a physical system to a heat bath through the action of a virtual coordinate and its conjugate momentum. In this scheme, thermalization can be achieved if the dynamics in the extended phase space is ergodic, so that time averages in the extended system are equivalent to constant-temperature averages in the physical system. A particularly useful form of the Nosé equation was derived by Hoover [2] and it has been shown that the Nosé-Hoover equation adequately thermalizes multidimensional systems. However, it is known [3] that this is not the case for many one-dimensional potentials, such as the harmonic oscillator. This inadequacy has motivated several modifications of the original Nosé-Hoover scheme [4–7]. The successful modifications of Kusnezov, Bulgac, and Baver [4], Winkler [5], and Martyna and Klein [6] thermalize explicitly the kinetic energy of the physical system, so that the equipartition theorem is enforced if the extended phase-space dynamics is ergodic. On the other hand, the virial theorem is another general statement regarding the equilibrium properties of a physical system. It requires the average kinetic energy of the system to be equal to the average virial of the system (which is defined below). The above modifications satisfy the virial theorem as does the Nosé-Hoover scheme, but the virial is not thermalized explicitly. Hamilton [7] considered a modification of the Nosé-Hoover equation which thermalizes explicitly both the kinetic energy and the virial of the physical system. However, this scheme was not set up in a canonical framework. In this paper we consider further generalizations of the Nosé-Hoover equation which treat the kinetic energy and the virial in an equivalent manner within the canonical framework of Jellinek and Berry [8].

In the following, we consider the motion of a point mass under the action of an external one-dimensional potential subjected to a deterministic thermal bath of the Nosé-Hoover form at temperature T. We denote the physical variables—position, momentum, and time—by q', p', and t', respectively. Following the framework of Ref. [8], we let p, q, and t denote the corresponding virtual variables. These are related to the physical variables by $q'=qf(s)$, $p'=p/h(s)$, and $dt'=dt/w(s)$, where $h(s)$, $f(s)$, and $w(s)$ are scaling functions of s, the coordinate associated with the thermal bath. If p_s is the momentum conjugate to s, then $\{q,p,p_s,s\}$ forms a set of canonical variables. The scaling functions used by Nosé were $h(s)=s$, $f(s)=1$, and $w(s)=s$. One can write the Hamiltonian of the system [1,8] in the following manner:

$$\mathcal{H}=\frac{p^2}{2h^2}+V(fq)+\frac{p_s^2}{2Q_1}+g\ln s\ . \tag{1}$$

Here, $V(fq)$ is the external potential, Q_1 is a mass parameter associated with the bath degree of freedom, and g is a number determined by the scaling functions. Without loss of generality, dimensionless units have been used and k_BT has been set equal to 1. Two one-dimensional potentials are considered: the harmonic oscillator $V=q'^2/2$ and the double-well potential $V=(q'^2-1)^2/2$.

We consider general scaling functions of the form $h=s^N$, $f=s^M$, and $w=s^K$. In this case, the canonical equations of motion expressed in terms of the physical variables take the form

$$\dot{q}'=s^{M+K-N}p'+\frac{1}{Q_1}Ms^{K-1}q'p_s\ , \tag{2}$$

$$\dot{p}'=-V's^{M+K-N}-\frac{1}{Q_1}Ns^{K-1}p'p_s\ , \tag{3}$$

$$\dot{s}=s^Kp_s/Q_1\ , \tag{4}$$

$$\dot{p}_s=Ns^{K-1}p'^2-Mq'V's^{K-1}-gs^{K-1}\ , \tag{5}$$

where a dot denotes a derivative with respect to t' and V' is the derivative of the potential with respect to the physical coordinate q'. Note that the factor $q'V'$, which is proportional to the virial of the system, appears explicitly in Eq. (5). However, the virial is not thermalized independently from the kinetic energy. If the system is ergodic, a microcanonical average in the extended phase space is equivalent to a canonical average in the physical phase space for $g=N-M-K+1$. The choice $K=1$ and $M=N-1$ leads to a complete decoupling of the variable s, thus obtaining a generalized Nosé-Hoover equation in which the virial appears explicitly:

$$\dot{q}'=p'+\frac{1}{Q_1}(N-1)q'p_s \ , \tag{6}$$

$$\dot{p}'=-V'-\frac{1}{q_1}Np'p_s \ , \tag{7}$$

$$\dot{p}_s=Np'^2-(N-1)q'V'-1 \ . \tag{8}$$

For $N=1$, the original Nosé-Hoover equation is recovered. For the double-well potential, a numerical integration of Eqs. (6)–(8) (with $N=1$) indicates that the motion is chaotic for a range of parameter values. However, this does not necessarily mean that the canonical distribution is obtained in the physical phase space. In order to examine this, we numerically integrate Eqs. (6)–(8) (with $N=1$) for the double-well potential for a typical chaotic trajectory. In Fig. 1 normalized histogramic distributions of q', p', the virial

$$T_v=q'V'/2=q'^2(q'^2-1) \ ,$$

and the kinetic energy $E_k=p'^2/2$ are presented for a trajectory of duration 10 000 units. The exact thermal distributions are also presented. These are given by

$$P(q')=Z^{-1}\exp[-V(q')] \ , \tag{9}$$

$$P(p')=\frac{1}{\sqrt{2\pi}}\exp(-p'^2/2) \ , \tag{10}$$

$$P(T_v)=\sum_i P(q')\left|\frac{dq'}{dT_v}\right| \ , \tag{11}$$

$$P(E_k)=\frac{1}{\sqrt{\pi E_k}}\exp(-E_k) \ , \tag{12}$$

where $Z=\int_{-\infty}^{\infty}\exp[-V(q')]dq'$ and the summation in Eq. (11) is over the i branches of $q'(T_v)$ bounded by

$$\left|\frac{dq'}{dT_v}\right|=\infty \ .$$

It is seen that, in accord with the results of Ref. [4], the agreement is poor. The histogramic q' distribution shows an enhancement of the $|q'|=1$ peaks which are reflected by excessive values of the T_v distribution near the $T_v=0$ divergence. Also, the q' distribution exhibits secondary extrema for smaller values of $|q'|$. Finally, the p' and E_k distributions show a significant enhancement of the $p'=E_k=0$ maximum.

We wish to treat the kinetic energy and the virial in an equivalent manner and, consequently, the coefficient of these terms in Eq. (8) should be the same, leading us to the choice $N=\frac{1}{2}$. In Fig. 2 similar histogramic distributions are presented for a typical chaotic trajectory. It may be seen that the agreement between the numerical and the exact thermal distributions is good in contrast to

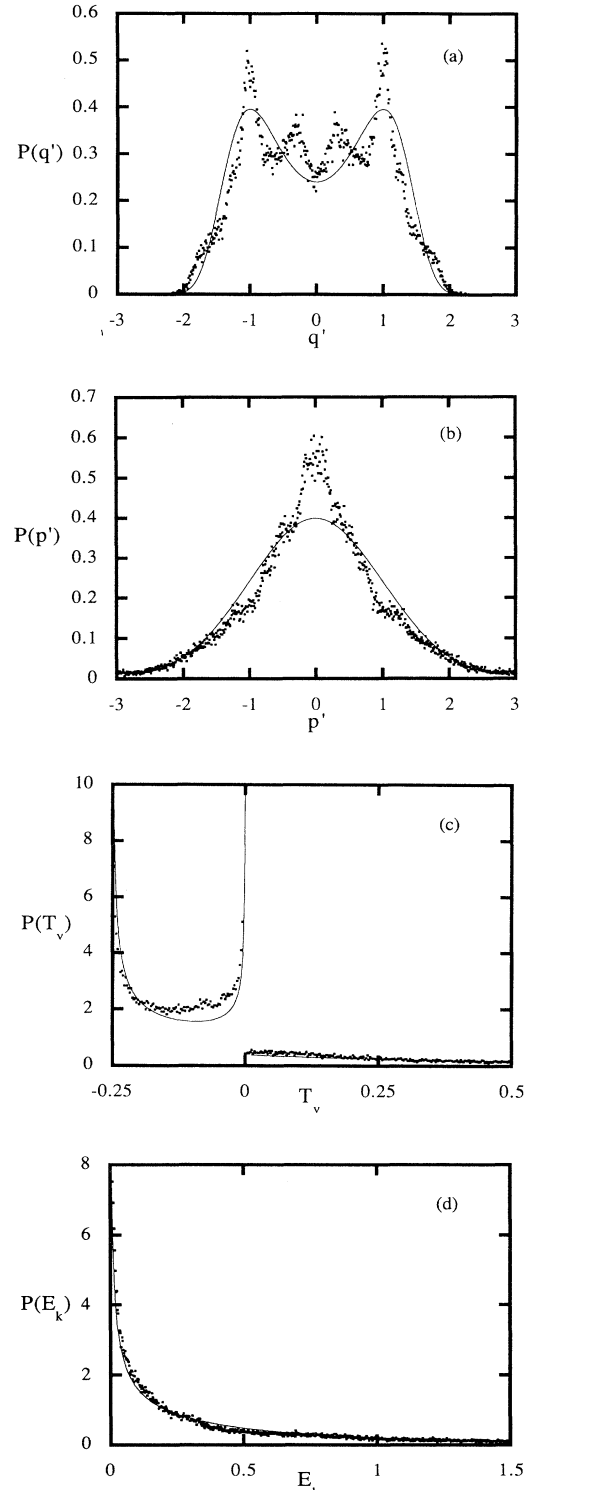

FIG. 1. Normalized distributions P of (a) q', (b) p', (c) T_v, and (d) E_k for the double-well potential using the Nosé-Hoover equation. The initial conditions are $q'(0)=0.25$, $p'(0)=0$, $p_s(0)=0$, and the mass of the bath degree of freedom is $Q_1=1.0$. The trajectory run is 10 000 time units and the sampling time is 0.1. The bin size is 0.01 for (a) and (b) and 0.0025 for (c) and (d). The continuous curves gives the exact thermal distributions of Eqs. (9)–(12).

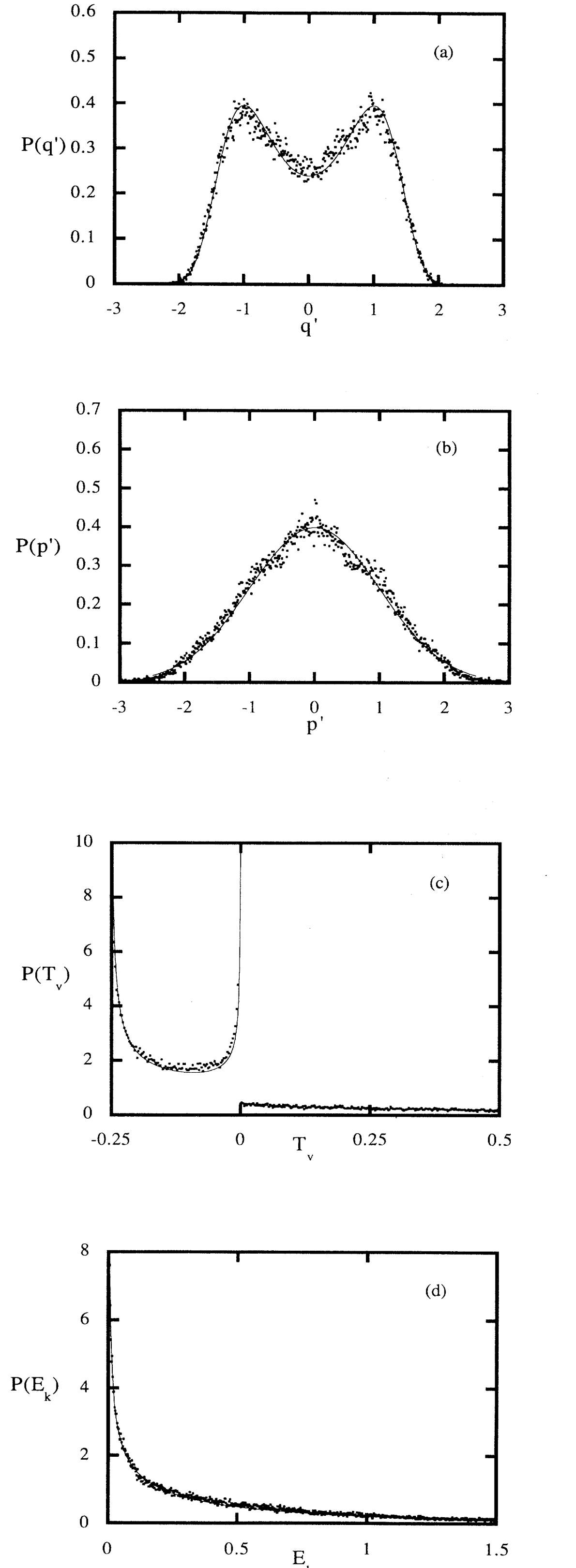

FIG. 2. Same as Fig. 1, but using Eqs. (6)–(8) with $N=\frac{1}{2}$. The initial conditions are $q'(0)=1$, $p'(0)=0$, $p_s(0)=0$, and the mass of the bath degree of freedom is $Q_1=1.0$.

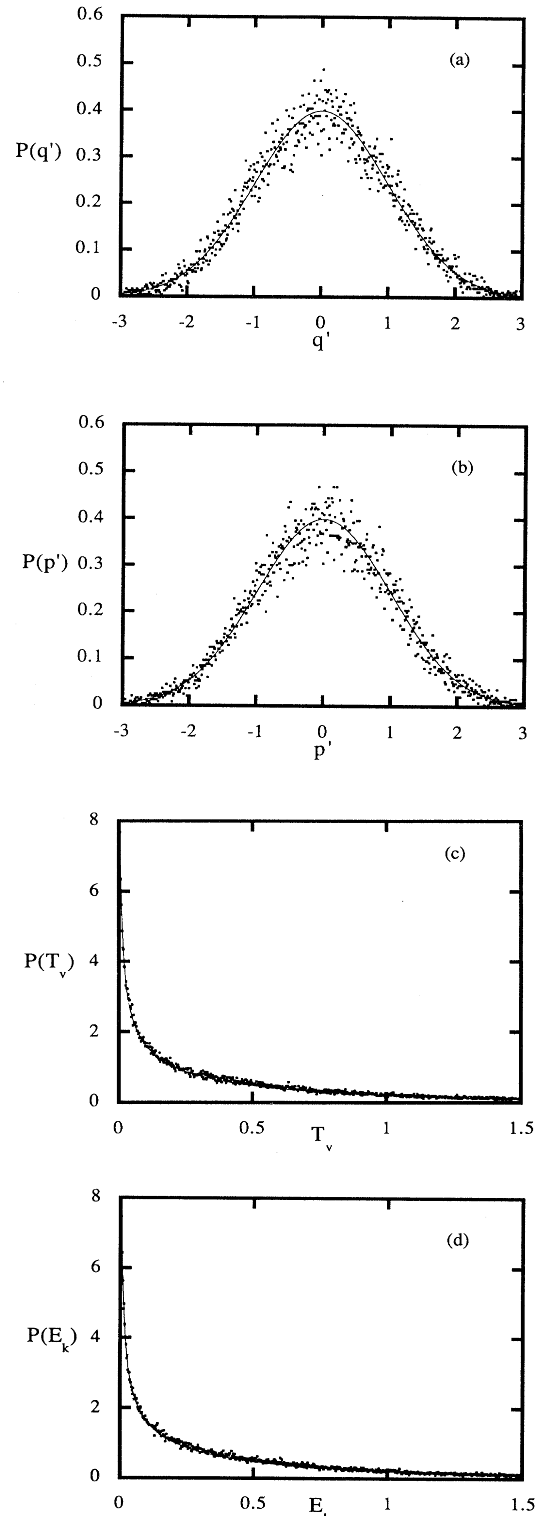

FIG. 3. Same as Fig. 1, but using Eqs. (14)–(19) for the harmonic oscillator. The initial conditions are $q'(0)=p_s(0)=p_u(0)=0$, $p'(0)=s(0)=u(0)=1.0$, and the masses of the bath degrees of freedom are $Q_1=Q_2=1.0$. The standard deviations of the q', p', T_v, E_k distributions with the exact values (in parentheses) are, respectively; 0.9995 (1.0), 1.0007 (1.0), 0.7055 (0.7071), and 0.7042 (0.7071).

the Nosé-Hoover system. We believe that Eqs. (6)–(8) will provide canonical distributions for other anharmonic potentials and for multidimensional systems. Unfortunately, for the harmonic potential, it may be shown that Eqs. (6)–(8) are integrable. Other variants of the general equations (2)–(5) for which the coefficients of the virial and of the kinetic energy are again identical (i.e., $M=-N$) could be considered. However, for the harmonic oscillator, it is again possible to show that the motion is integrable.

A further modification of the Nosé-Hoover equation may be obtained by explicitly thermalizing the virial independently from the kinetic energy, as in Ref. [7]. In order to do so, we introduce a second thermal bath coordinate u and its conjugate momentum p_u. We extend the Hamiltonian of Eq. (1) in the following manner:

$$\mathcal{H}=\frac{p^2}{2h^2}+V(fq)+\frac{p_s^2}{2Q_1}+\frac{p_u^2}{2Q_2}+g\ln s+ju \ , \quad (13)$$

where we have introduced a mass parameter Q_2 associated with the second bath degree of freedom and j is an arbitrary parameter. In Eq. (13) we extend the scaling functions to $h=s^a u^b$, $f=s^c u^d$, and $w=s^k u^l$. If the system is ergodic, a microcanonical average in the extended phase space is equivalent to a canonical average in the physical phase space for $g=a-c-k+1$ and for $b-l-d>-1$. This last condition guarantees the convergence of the u contribution to the partition function. The special case $a=k=1$, $b=d=\frac{1}{3}$ and $l=0$ constitutes the well-known constant-temperature–constant-pressure method [1] for which j corresponds to the externally set pressure and u is the volume.

In the following, we take j equal to unity and we consider the scaling $a=1$, $b=c=0$, $d=-1$, and $k=l=1$. The resulting system of six canonical equations of motion then simplifies and takes a symmetrical form. Expressed in terms of the physical variables, they are

$$\dot{q}'=p'-\frac{1}{Q_2}sq'p_u \ , \quad (14)$$

$$\dot{p}'=-V'-\frac{1}{Q_1}up'p_s \ , \quad (15)$$

$$\dot{s}=sup_s/Q_1 \ , \quad (16)$$

$$\dot{u}=sup_u/Q_2 \ , \quad (17)$$

$$\dot{p}_s=u(p'^2-1) \ , \quad (18)$$

$$\dot{p}_u=s(q'V'-u) \ . \quad (19)$$

With the Hamiltonian of Eq. (13), the u contribution to the probability density is proportional to $\exp(-u)$, so that the canonical average $\langle u\rangle=1$. It is then easily seen from Eqs. (18) and (19) that the kinetic energy and the virial are independently thermalized by the dynamics of the bath variables [9]. This set of equations implements in a canonical way the objective of Ref. [7].

In Fig. 3 we compare the normalized histogramic distributions of q', p', T_v, and E_k for the harmonic oscillator with the exact thermal distributions for a typical chaotic trajectory of duration 10 000 units. It is seen that there is very good agreement between the numerical and exact thermal distributions. Moreover, the distributions of both q', p' and T_v, E_k are in agreement with each other, as they should be. In contrast, for the Nosé-Hoover equation, the thermal distribution is not obtained for the harmonic oscillator, even for a chaotic trajectory, as shown in Ref. [4].

In conclusion, we have generalized the Nosé-Hoover equation to a set of equations which are canonical in the extended phase space and which treat the kinetic energy and the virial on an equivalent basis. In Eqs. (14)–(19), these quantities are thermalized independently by the action of two bath variables. We have shown that these equations can adequately thermalize the one-dimensional harmonic oscillator, in contrast to the original Nosé-Hoover scheme. In Eqs. (2)–(5) (with $M=-N$) and Eqs. (6)–(8) (with $N=\frac{1}{2}$), it is rather the sum of the kinetic energy and the virial which is explicitly thermalized. As there is only one bath variable, these sets of equations are smaller and although they are integrable for the harmonic oscillator, they can adequately thermalize the one-dimensional double-well potential, in contrast to the original Nosé-Hoover scheme. We believe that the smaller sets [Eqs. (2)–(8)] may prove useful for other anharmonic one-dimensional potentials and for multidimensional systems.

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[9] The Hamiltonian (13) can be easily generalized by writing u^m instead of the linear term u. Equation (19) is then changed to $\dot{p}_u=s(q'V'-mu^m)$. With the u contribution to the probability density proportional to $\exp(-u^m)$, one has $\langle mu^m\rangle=1$ so that the virial is still thermalized.