Extended-phase-space isothermal molecular dynamics: Canonical harmonic oscillator

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A modified set of equations is given for the simulation of a canonical ensemble based on the method introduced by Nosé. The equations produce trajectories that are sufficiently chaotic to calculate average properties of a canonical ensemble, even for a small number of degrees of freedom. This important fact is demonstrated by presenting results for a single one-dimensional harmonic oscillator. It is shown that the extended system is chaotic and that the trajectories cover the whole energy surface in phase space.

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I. INTRODUCTION

During the last decade remarkable progress has been achieved in molecular-dynamics simulations of others than the traditional constant energy constant volume ensemble. Alternative simulation methods allow for the control of temperature or pressure rather than energy and volume, and represent canonical ensembles. Andersen [1] originally proposed a method that allows the simulation of an isothermal-isobaric ensemble, where the temperature is maintained constant by a stochastic process. Nosé [2,3] introduced a purely deterministic way of simulating a canonical ensemble in phase space. It is based on an extension of the phase space by one variable (in the case of an isothermal-isobaric ensemble by two) and its conjugated momentum. The additional degree of freedom mimics a heat bath for the physical system. Another formulation of Nosé's method for a constant temperature ensemble was given by Hoover [4]. His equations of motion are closely related to equations previously obtained on the basis of Gauss's principle of least constraint [5,6].

Recently these methods were applied to the one-dimensional harmonic oscillator [4,7,8]. The detailed investigation of the dynamics in the extended phase space shows that Nosé's and Hoover's methods do not generate canonical time averages. Poincaré surfaces of section show regular behavior indicating nonergodicity of the system. However, ergodicity in the extended system is a necessary condition for a canonical ensemble, i.e., the system has to be chaotic. In order to obtain a canonical ensemble Hamilton [8] enforced the virial theorem by extending the Nosé-Hoover equations. This extension introduces a new degree of freedom in the system with an additional undefined parameter. Other extensions of Hoover's non-Hamiltonian method by two degrees of freedom are discussed in [9,10]. In these references also an extension to systems is given, which cannot be described by a set of canonical variables (e.g., systems with classical spins).

In this paper we extend Nosé's original idea and introduce a different coupling to the heat bath. This coupling yields equations of motion which are more nonlinear than in the case of the Nosé-Hoover coupling. As a consequence, the numerical solutions of the equations of motion show chaos in the whole accessible phase space. Averages of time-dependent quantities for such a trajectory correspond to canonical ensemble averages. We also observe mixed regular and stochastic behavior, depending on the initial condition and on a mass parameter. Compared to the method introduced by Hamilton [8], the proposed one involves only one parameter and the phase space is extended by only one degree of freedom. More general extensions of Nosé's method are discussed in detail by Jellinek and Berry [11–13].

In Sec. II we define the Hamiltonian in the scaled variables with the coupling to the heat bath. Furthermore, the equations of motion in scaled and unscaled variables are derived. The implications of the different representations for the virial theorem as well as the effect of different time scalings are discussed. In Sec. III we investigate the harmonic oscillator and present our numerical results in the form of Poincaré surfaces of section. Finally, Sec. IV summarizes our findings.

II. EXTENDED ISOTHERMAL DYNAMICS

A. Virtual variable formulation

Following the idea of Nosé [2] we consider a physical system of N particles with primed coordinates $\mathbf{q}_i'$ and masses m_i. Additionally, unprimed variables $\mathbf{q}_i$ are used for a virtual system. We also introduce the extension of the two systems by one variable s. This extension acts as a heat bath for the N-particle system. The dynamics of the system is considered in the extended phase space of the physical system $\{\mathbf{q}_i',\mathbf{p}_i',s',p_s'\}$ and the virtual system $\{\mathbf{q}_i,\mathbf{p}_i,s,p_s\}$. The connection between the two phase spaces is established by the relations

$$\mathbf{q}_i'=\mathbf{q}_i,\quad \mathbf{p}_i'=\mathbf{p}_i/u(s)\ , \tag{1}$$

$$s'=s,\quad p_s'=p_s/u(s)\ . \tag{2}$$

Nosé used in his calculations $u(s)=s$. We will use

$$u(s)=s^2\ . \tag{3}$$

The equations of motion in the virtual system are obtained from the postulated Hamiltonian

$$H=\sum_i \frac{\mathbf{p}_i^2}{2m_i s^4}+V(\mathbf{q}_i)+\frac{p_s^2}{2Q}+gkT\ln s \ , \tag{4}$$

where we used the new scaling variable $u(s)=s^2$. The potential energy of the particles is denoted by V. The other variables have the usual meaning: Q is the mass associated with the motion of the variable s, k the Boltzmann constant, T the temperature, and g a parameter depending on the number of degrees of freedom of the system which will be calculated exactly later on. Due to the introduced Hamiltonian $\mathbf{q}_i$ and $\mathbf{p}_i$ as well as s and p_s are canonical conjugated variables.

The equations of motion for the extended system in the virtual phase space are given by Hamilton's equations:

$$\frac{d\mathbf{q}_i}{dt}=\frac{\mathbf{p}_i}{m_i s^4} \ , \tag{5}$$

$$\frac{d\mathbf{p}_i}{dt}=\mathbf{F}_i \ , \tag{6}$$

$$\frac{ds}{dt}=\frac{p_s}{Q} \ , \tag{7}$$

$$\frac{dp_s}{dt}=\frac{1}{s}\left[\sum_i \frac{2\mathbf{p}_i^2}{m_i s^4}-gkT\right] , \tag{8}$$

where $\mathbf{F}_i$ denotes the force on particle i derived from the potential V. These equations are different from the ones originally obtained by Nosé in the coupling term s^{-4}.

The second-order equations of motion for $\mathbf{q}_i$ and s are given by

$$\frac{d}{dt}\left[m_i s^4\frac{d\mathbf{q}_i}{dt}\right]=\mathbf{F}_i \ , \tag{9}$$

$$\frac{d}{dt}\left[Q\frac{ds}{dt}\right]=\frac{1}{s}\left[\sum_i \frac{2\mathbf{p}_i^2}{m_i s^4}-gkT\right] . \tag{10}$$

Multiplication of Eq. (9) by $\mathbf{q}_i$ and summation over all particles i yields

$$\frac{d}{dt}\left[\sum_i m_i s^4\mathbf{q}_i\frac{d\mathbf{q}_i}{dt}\right]=\sum_i m_i s^4\left[\frac{d\mathbf{q}_i}{dt}\right]^2+\sum_i \mathbf{F}_i\mathbf{q}_i \ . \tag{11}$$

The time average of the left-hand side of this equation vanishes for bounded systems. Thus we obtain for the physical variables

$$\left\langle\sum_i \frac{(\mathbf{p}_i')^2}{m_i}\right\rangle_t+\left\langle\sum_i \mathbf{F}_i'\mathbf{q}_i'\right\rangle_t=0 \ , \tag{12}$$

i.e., the virial theorem is satisfied in the phase space of the virtual variables. This is no longer the case in the space of the physical variables, as we will show later. The multiplication of Eq. (10) by s and averaging over time yields

$$\left\langle\frac{p_s^2}{Q}\right\rangle_t+\left\langle\sum_i \frac{2(\mathbf{p}_i')^2}{m_i}\right\rangle_t=gkT \ , \tag{13}$$

if s is bounded. When the time averages can be replaced by canonical ensemble averages, g is given by $g=2f+1$, where f is the number of degrees of freedom of the N-particle system. (In the case of a three-dimensional system $f=3N$.) Since Eq. (13) includes the average of the square of the momentum p_s, the time average of the kinetic energy of the particles is not necessarily equivalent to the ensemble average, if the extended system is nonergodic on the energy hypersurface. However, the virial theorem is satisfied regardless of whether the system is ergodic or not. This might not be important for systems with a large number of degrees of freedom, however, it is very important for systems with a small number of degrees of freedom.

Similar to the extended system of Nosé, for any function $A(\{\mathbf{q}_i'\},\{\mathbf{p}_i'\})=A(\{\mathbf{q}_i\},\{\mathbf{p}_i/s^2\})$ we find that microcanonical ensemble averages (index m) in the extended virtual system are equal to canonical ensemble averages (index c) in the physical system

$$\langle A(\{\mathbf{q}_i'\},\{\mathbf{p}_i'\})\rangle_c=\langle A(\{\mathbf{q}\},\{\mathbf{p}/s^2\})\rangle_m \ , \tag{14}$$

if the factor g is appropriately chosen. As we showed in Eq. (13), with the scaling function (3) the relation (14) holds for $g=2f+1$. Since the calculations are completely similar to the original ones by Nosé, we will not present them here in detail. They can be found in [2,11]. If the equations of motion (5)–(8) generate an ergodic dynamics in the extended phase space, the time average of any physical quantity $A(\{\mathbf{q}_i'(t)\},\{\mathbf{p}_i'(t)\})=A(\{\mathbf{q}_i(t)\},\{\mathbf{p}_i(t)/s^2\})$ will be equal to the canonical ensemble average of this quantity.

B. Physical variable formulation

The equations of motion (5)–(8) can be transformed into equations of motion for the physical variables $\{\mathbf{q}_i',\mathbf{p}_i'\}$. As shown by Nosé [2] and Jellinek [11] this can be done not only by the scaling transformation of Eqs. (1) and (2); additionally a scaling of time is possible. If we use the scaling of time suggested by Nosé:

$$t'=\int^t dt\frac{1}{s} \ , \tag{15}$$

we obtain the following equations of motion for the physical variables:

$$\frac{d\mathbf{q}_i'}{dt'}=\frac{\mathbf{p}_i'}{m_i s} \ , \tag{16}$$

$$\frac{d\mathbf{p}_i'}{dt'}=\frac{\mathbf{F}_i'}{s}-\frac{2s^2p_s'\mathbf{p}_i'}{Q} \ , \tag{17}$$

$$\frac{ds}{dt'}=s^3\frac{p_s'}{Q} \ , \tag{18}$$

$$\frac{dp_s'}{dt'}=\frac{1}{s^2}\left[\sum_i \frac{2(\mathbf{p}_i')^2}{m_i}-\tilde{g}kT\right]-\frac{2(p_s')^2s^2}{Q} \ . \tag{19}$$

In order to obtain time averages that are equal to canonical ensemble averages the factor g of the scaled equations has to be replaced by another factor ($\tilde{g}$) [2,11]. Although these equations are no longer canonical equations, the energy

$$H'=\sum_i \frac{(\mathbf{p}_i')^2}{2m_i}+V(\mathbf{q}_i')+\frac{s^4(p_s')^2}{2Q}+\bar{g}kT\ln s \tag{20}$$

is still conserved. Compared to the equations derived by Nosé [Eqs. (2.19)–(2.22) of Ref. [2]], the new equations of motion are more nonlinear. The heat bath variable s is coupled to all other variables.

The Lagrangian forms of the equations of motion are

$$\frac{d}{dt'}\left[m_i s^2\frac{d\mathbf{q}_i'}{dt'}\right]=\mathbf{F}_i'-m_i\frac{ds}{dt'}s\frac{d\mathbf{q}_i'}{dt'}\ , \tag{21}$$

$$\frac{d}{dt'}\left[\frac{Q}{s}\frac{ds}{dt'}\right]=\sum_i\frac{2(\mathbf{p}_i')^2}{m_i}-\bar{g}kT\ . \tag{22}$$

Multiplication of Eq. (21) by $\mathbf{q}_i'$, summation over all particles, and averaging over time (t') yields for a bounded system

$$\left\langle\sum_i\frac{(\mathbf{p}_i')^2}{m_i}\right\rangle_{t'}+\left\langle\sum_i\mathbf{F}_i'\mathbf{q}_i'\right\rangle_{t'}=\left\langle\sum_i m_i\frac{d\mathbf{q}_i'}{dt'}\frac{ds}{dt'}\mathbf{q}_i's\right\rangle_{t'}\ . \tag{23}$$

Averaging of Eq. (22) over time gives

$$\left\langle\sum_i\frac{(\mathbf{p}_i')^2}{2m_i}\right\rangle_{t'}=\frac{\bar{g}}{4}kT\ . \tag{24}$$

From Eq. (24) we find that the average of the kinetic energy is always equal to the desired value in this formulation as long as $\bar{g}$ is chosen to be $\bar{g}=2f$. However, this does not show that the principle of equipartition of energy holds. The system is not necessarily ergodic, even if the mean of the kinetic energy assumes the given value. The virial theorem in the physical variable formulation is only satisfied if the right-hand side of Eq. (23) vanishes. In general, that happens if the system is mixing. Simple ergodicity might not be sufficient. For example, in a physical system with one degree of freedom the time average of the right-hand side of Eq. (23) is usually different from zero even in a nonmixing ergodic system, if there is a defined phase relation between the space coordinate and s. Thus the validity of the virial theorem is an indication of global chaotic motion in the system and the principle of equipartition of energy holds. On the other hand, in the virtual variable system a chaotic motion leads to a correct thermalization of all degrees of freedom, and the virial is equal to the thermal average of the kinetic energy ($\langle\sum_i\mathbf{F}_i'\mathbf{q}_i'\rangle_t=-fkT$). As a consequence, this relation is a test for ergodic behavior of a system in both the virtual and physical variable description.

Since the virial theorem holds in the virtual phase space [Eq. (12)], we obtain a similar relation for the equations (16)–(19) by transforming the time in Eq. (12) according to Eq. (15):

$$\left\langle s\sum_i\frac{(\mathbf{p}_i')^2}{m_i}\right\rangle_{t'}+\left\langle s\sum_i\mathbf{F}_i'\mathbf{q}_i'\right\rangle_{t'}=0\ . \tag{25}$$

If the fluctuations of s are small, the deviation from the virial will be small. In this case, it is difficult to distinguish ergodic from nonergodic trajectories by the virial theorem in a numerical solution of the equations of motion. Nevertheless, the virial theorem is not exactly fulfilled by nonergodic trajectories.

In the previous calculations we used the time scaling of Eq. (15). As discussed by Jellinek [11] many other scalings are possible. In order to obtain a set of equations more similar to the Nosé-Hoover equations, we use the time scaling

$$t'=\int^t dt\frac{1}{s^2}\ . \tag{26}$$

The equations of motion are then given by

$$\frac{d\mathbf{q}_i'}{dt'}=\frac{\mathbf{p}_i'}{m_i}\ , \tag{27}$$

$$\frac{d\mathbf{p}_i'}{dt'}=\mathbf{F}_i'-\frac{2s^3p_s'\mathbf{p}_i'}{Q}\ , \tag{28}$$

$$\frac{ds}{dt'}=s^4\frac{p_s'}{Q}\ , \tag{29}$$

$$\frac{dp_s'}{dt'}=\frac{1}{s}\left[\sum_i\frac{2(\mathbf{p}_i')^2}{m_i}-\bar{g}kT\right]-\frac{2(p_s')^2s^3}{Q}\ . \tag{30}$$

Now the original value of g has changed to $\bar{g}=2f-1$. This is a consequence of weighting the distribution function in phase space by time scaling [11]. Again, a comparison with Nosé's original equations shows that our equations are more nonlinear. In this formulation of the equations of motion neither the virial theorem nor the mean of the kinetic energy are automatically fulfilled. Here we find conditions similar to Eqs. (13) and (23).

The introduction of a variable $\zeta=(1/s)(ds/dt')$ in Nosé's original formulation leads to the Nosé-Hoover equations [2,4,7,11]. For our scaling [Eq. (3)] we find

$$\frac{d\mathbf{q}_i'}{dt'}=\frac{\mathbf{p}_i'}{m_i}\ , \tag{31}$$

$$\frac{d\mathbf{p}_i'}{dt'}=\mathbf{F}_i'-2\zeta\mathbf{p}_i'\ , \tag{32}$$

$$\frac{ds}{dt'}=s\zeta\ , \tag{33}$$

$$\frac{d\zeta}{dt'}=\frac{s^2}{Q}\left[\sum_i\frac{2(\mathbf{p}_i')^2}{m_i}-\bar{g}kT\right]+\zeta^2\ . \tag{34}$$

Aside from the factor 2, Eqs. (31) and (32) are equal to Hoover's original equations [Eqs. (6) or Ref. [4]]. In contrast to the Nosé case, in our set of equations of motion the variable s is not decoupled from the other variables. The equation of motion for ζ contains s and ζ itself in nonlinear form.

The two sets of equations of motion, (16)–(19) and (27)–(30), yield trajectories in the phase space of the physical variables $\{\mathbf{q}_i',\mathbf{p}_i'\}$. However, the generated dynamics is different because of the different values of $\bar{g}$ and $\bar{g}$. Aside from these factors, the latter set of equations is obtained from the former by a time scaling. Thus for $\bar{g}=\bar{g}$ the same trajectory in phase space is obtained. But the rate at which it is traversed is altered. Since $\bar{g}$ and $\bar{g}$ are different, it is not obvious which of the sets of equations of motion generates the correct time behavior. Al-

though the force in Eq. (21) is scaled by s^2, and the additional s, ds/dt'-dependent term is small in the thermodynamic limit, Eqs. (16)–(19) can produce the correct dynamics, if $s \approx 1$. Hence the question of which of the sets of equations of motion gives the correct dynamical behavior for a specific system needs to be investigated in more detail. The dependence on the ratio $H'/\bar{g}kT$ is especially important, because this determines the size of s. We think that the accurate dynamics is obtained if the conditions $s \approx 1$, $p_s' \approx 0$ are fulfilled. However, static quantities can be obtained from either of the three different sets of equations.

Since our equations of motion are more nonlinear we can hope to obtain a sufficiently chaotic motion for a fully statistical description, even for systems with a small number of degrees of freedom. In the next section we will demonstrate that this actually happens for a system as simple as a one-dimensional harmonic oscillator.

III. CANONICAL HARMONIC OSCILLATOR

In the preceding section we derived three different sets of equations of motion. Each of these equations should produce chaotic trajectories. Thus we are free to choose the most convenient set. Since Eqs. (5)–(8) include s to the fourth power, and s may assume values in the interval (0,1) the numerical integration algorithm may become unstable. Therefore we used Eqs. (16)–(19) in our investigations of the harmonic oscillator. The equations of motion of the harmonic oscillator in the phase space of the physical variables are given by

$$\frac{dq'}{dt'} = \frac{p'}{s} , \tag{35}$$

$$\frac{dp'}{dt'} = -\frac{q'}{s} - \frac{2s^2 p_s' p'}{Q} , \tag{36}$$

$$\frac{ds}{dt'} = \frac{s^3 p_s'}{Q} , \tag{37}$$

$$\frac{dp_s'}{dt'} = \frac{2}{s^2}(p'^2 - kT) - \frac{2(p_s')^2 s^2}{Q} , \tag{38}$$

where we used $m = 1$ and the spring constant $K = 1$, i.e., we introduced reduced variables by choosing $K^{-1/2}$ as the unit of length and $(m/K)^{1/2}$ as the unit of time. As already mentioned in the preceding section, due to our scaling [Eq. (3)] all equations are coupled in contrast to the Nosé-Hoover equations. From Eqs. (22) and (24) we find that the mean of the kinetic energy is equal to the desired value. However, the virial theorem is only fulfilled if the system is ergodic and chaotic.

The set of equations (35)–(38) represents a system of two degrees of freedom. Since there is one integral of motion, the energy H', the trajectories of the system are confined on a three-dimensional hypersurface in phase space. If there is another integral of motion, the system is confined on a two-dimensional torus on the energy surface and the system is integrable. The trajectories of such a system are commonly presented in the form of Poincaré surfaces of section (see [14] and references therein). For an integrable system the intersections of a trajectory with the surface of section lie on curves. If the motion is periodic a finite number of points is obtained. If the motion is quasiperiodic, infinitely many points form a continuous curve. Trajectories of these types are called regular. When there is no additional integral of motion the intersection points irregularly cover part of the surface of section. The motion is then denoted as stochastic or chaotic.

For our system we choose the surface of section as follows: the coordinate s has to be one and the momentum p_s' should be greater than or equal to zero. The remaining degrees of freedom in phase space are q', p'. This choice of the surface of section has the advantage that the intersection area with trajectories is bounded in the surface. Since H' [Eq. (20)] is conserved, it gives the equation from which the momentum p_s' can be calculated for points in the surface of section. If $s = 1$, we obtain

$$p_s' = \pm\{Q[2H' - (p')^2 - (q')^2]\}^{1/2} . \tag{39}$$

Because of the positive term under the square root, a boundary curve in the p'-q' plane is obtained. Consequently, we see whether the whole allowed phase space is covered by a chaotic trajectory or not. Another choice of the Poincaré surface of section, like the condition $p_s = 0$ used in [7,8], does not restrict the intersection area. Thus it is not clear from such a surface of section whether all trajectories are chaotic or not. The disadvantage of our selected surface of section is that we have to choose different s values for different H'/kT ratios. Nevertheless, our choice allows us to distinguish between different types of trajectories, if $H'/kT \approx 1$. This can be seen from the following consideration. The maximum value of s: $s = \exp(H'/2kT)$, i.e., $s < 2$ for $H'/kT \approx 1$, is obtained for $q' = p' = p_s' = 0$. Thus s assumes values in the interval (0,2), and consequently we should find intersections of trajectories with the surface of section defined by $s = 1$. We finally emphasize that a distinction between regular and chaotic regions in phase space by Poincaré surfaces of section of systems with two degrees of freedom is only possible if trajectories are compared for the same value of the conserved quantity H'. Only in this situation is a well-defined representation of the dynamics in the surface of section obtained. The numerical solution of the equations of motion was obtained by a fourth-order predictor corrector scheme.

In Fig. 1 we present the p'-q' surface of section for the solution of Eqs. (35)–(38) for different initial conditions. The mass for this plot is $Q = 10$. The mean of the kinetic energy was set $kT/2 = 0.25$, and the conserved energy was $H' = 0.5$ for all initial conditions. As the figure shows, we find regular and chaotic behavior depending on the initial condition. Trajectories close to the center of the surface of section $[(q', p') = (0,0)]$ are chaotic, whereas trajectories closer to the boundary of the intersection area are regular. The boundary of the intersection area is given by the outermost solid line. Moreover, it seems that the chaotic regions are confined between regular tori. Thus the motion is never sufficiently chaotic for a fully statistical description [7,8]. However, the deviation of the virial from the statistical value is small. We

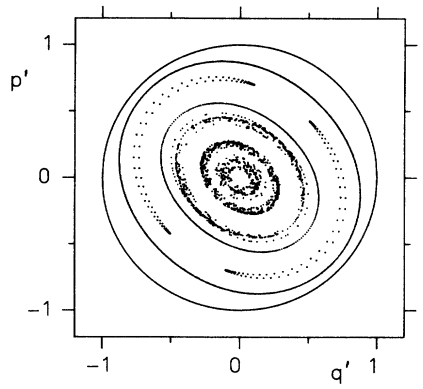

FIG. 1. Poincaré surface of section for $Q=10$ and different initial conditions.

found a maximum deviation of 1%. It seems that although the motion is regular the trajectories cover a large enough part of the phase space to provide nearly ergodic averages for the virial.

Figure 2 shows intersections of the trajectory with the surface of section for the initial condition $(q',p')=(1,0)$, $(s,p_s')=(1,0)$, and $Q=0.6$. From the plot it is obvious that the trajectory is chaotic and covers the whole energy surface. Consequently, time averages should be equal to isothermal ensemble averages. This is reflected in the virial. The deviation from the desired value (-0.5) for this trajectory is 0.01%. The kinetic energy agrees with the desired value within 0.008%, and the variation of the total energy is 2×10^{-7}%. Of course, the precision of the result depends on the number of time steps and the time step itself. For the current result, we performed 5×10^{7} time steps with the step size 1×10^{-4}.

Additionally, we calculated the intersections of trajectories with the surface of section defined by $p_s'=0$ for the initial conditions used in [8], but with $H'=0.5$. As expected from Fig. 2, all trajectories were chaotic. Since the intersections of the trajectory with the surface of section, shown in Fig. 2, cover the whole accessible phase space, all trajectories are chaotic for $H'=0.5$, $kT=0.5$, and $Q=0.6$.

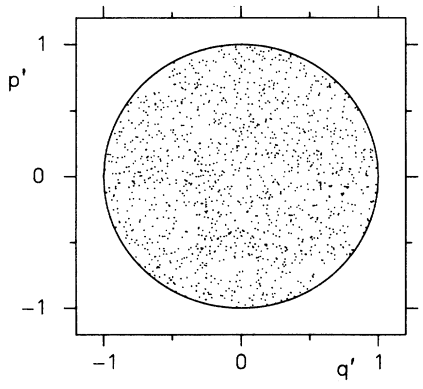

FIG. 2. Poincaré surface of section for $Q=0.6$ and the initial condition $(q',p')=(1.0,0.0)$.

We also used slightly higher and several smaller Q values for the same parameters H' and kT. All the calculated trajectories were chaotic and the virial was equal to the ensemble average within the precision of the calculations. Furthermore, we investigated the effect of the initial conditions on the dynamics of the system for different H'/kT ratios. If we fix the kinetic energy (say $kT=0.5$) and change arbitrarily the initial condition for q', we will find different energies H'. A large value of H'/kT causes a slow exploration of the energy surface. The surfaces of section show jumps of a trajectory between different two-dimensional tori, i.e., we see a behavior usually observed in intermittent chaotic motions [14]. Therefore we recommend choosing the initial condition such that the total energy of the system is approximately equal to kT. For any choice of the initial condition with $H'=kT$ we found Q values which yield global chaotic trajectories. Moreover, when the energy is larger than 0.5 the motion is already chaotic for larger Q $(Q>0.6)$ values. On the other hand, for smaller energies we had to use smaller Q values.

In addition, we calculated the fluctuations of the energy $H_0=p'^2/2+q'^2/2$ and found agreement with the expected value for a canonical ensemble. We also solved Eqs. (27)–(30) for the harmonic oscillator. As expected, these equations also yield chaotic behavior. However, we had to perform extensive calculations to obtain precise averages for the kinetic energy and the virial.

From our calculations we conclude that canonical time averages can be obtained even for the harmonic oscillator by extending Nosé's idea. A different scaling is sufficient to produce global chaotic trajectories. A further extension of the phase space, as discussed by Hamilton [8], Kusnezov, Bulgac, and Bauer [9], and Bulgac and Kusnezov [10] is not necessary. As outlined in the preceding section, the virial theorem is fulfilled if the system is ergodic. Since the original Nosé equations provide exactly the same conclusions, Hamilton's extension is inadequate in global chaotic systems. There remains just another constant which has to be specified. In the case of the harmonic oscillator the additional extension provides a stronger perturbation of the oscillator than in the Nosé-Hoover equations, allowing for a global stochastic motion.

IV. CONCLUSIONS

In the present study we modified Nosé's idea of coupling a system via scaling to a heat bath. Instead of the scaling function $u=s$ we used $u=s^2$. This coupling leads to more perturbed equations of motion. Furthermore, a decoupling of a part of the equations as in Hoover's formulation is not possible. The system is always more strongly coupled to the heat bath. We also answered the question of which time averages are automatically fulfilled and found that in the virtual variable formulation the virial theorem is satisfied and that the average of the kinetic energy is not necessarily equal to the desired value. On the other hand, in the physical

variable formulation the virial theorem is not necessarily fulfilled but the mean of the kinetic energy is equal to the given value, if the time scaling of Eq. (15) is used. However, if the dynamics is sufficiently chaotic the equipartition of energy holds and in the virtual variable formulation the mean kinetic energy is equal to the desired value. Furthermore, the virial theorem is satisfied in the physical variable formulation. From these considerations we conclude that the enforcement of the virial, as introduced by Hamilton [8], is not the best way of generating a chaotic dynamics. For an already chaotic system the additional coupling is an unnecessary complication. We showed numerically that our scaling provides equations of motion which are sufficiently chaotic for a fully statistical description even for a one-dimensional harmonic oscillator, as long as the mass parameter Q is appropriately chosen. This is not possible with the Nosé-Hoover equations [7]. Thus or modification of Nosé's idea allows us to investigate the effect of a deterministic and hence time-reversible coupling to a heat bath of one degree of freedom on a simple system such as the one-dimensional harmonic oscillator. An extension of the phase space by two or more degrees of freedom, as proposed in [9], is not necessary.

As mentioned previously, our modification is not the only possible extension of Nosé's idea. More general modifications, which also should yield chaotic trajectories, are discussed in [11]. As a further example for an extension, we analytically investigated a scaling of the coordinates: $\mathbf{q}_i' = s\mathbf{q}_i$. Even with Nosé's scaling of the momenta this additional scaling should generate global chaotic trajectories.

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