Generalization of Nosé's isothermal molecular dynamics: Necessary and sufficient conditions of dynamical simulations of statistical ensembles

Julius Jellinek
Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

R. Stephen Berry
Department of Chemistry and the James Franck Institute, The University of Chicago, Chicago, Illinois 60637
(Received 8 March 1989)

We examine the necessary and sufficient conditions that a dynamics is suited for mimicking a specified statistical ensemble. Some delicate points related to the Nosé scheme and its generalizations are clarified.

The preceding Comment[1] by Hoover discusses a "non-Hamiltonian approach" to simulate the canonical ensemble by molecular dynamics. The general problem can be formulated as the question "what are the necessary and sufficient conditions for a dynamics to simulate a canonical or any other nonconservative ensemble?"

Nosé's prescription[2,3] for using dynamics to generate properties of a canonical ensemble, as well as its subsequent generalizations[4,5] for canonical and other nonconservative ensembles, consist of two separate conceptual steps. First, a relation is established between an extended (and possibly augmented[4]) phase space of "virtual" variables[2–5] and the corresponding phase space of the physical variables of interest. This is achieved by (a) choosing the scaling functions which relate the physical variables to their corresponding virtual counterparts and (b) by selecting a Hamiltonian[2,3] or Hamiltonians[4,5] in the phase space of the virtual variables, such that the microcanonical partition function defined in this space is proportional to the desired partition function defined in the phase space of the physical variables. The consequence of this *ensemble-ensemble* relation between the two spaces is that for any function of the physical variables only, the microcanonical average calculated in the phase space of the virtual variables is equal to the desired ensemble average calculated in the physical phase space. The derivation can be based also on weighted microcanonical distribution functions in the phase space of virtual variables.[4]

The second step establishes an *ensemble-dynamics* relation in the phase space of the virtual variables. This is done by generating a (scaled-time) dynamics in this phase space from the Hamiltonian selected in the first step and assuming this dynamics is ergodic with respect to the (weighted) microcanonical ensemble defined in the same space. (Of course it would be desirable to be able to demonstrate ergodicity.) Then that microcanonical average of *any* phase function in this space can be calculated as its time-average along the trajectory generated by the corresponding dynamics. In view of the *ensemble-ensemble* relation established in the first step, for functions depending on only the physical variables, the calculated time-averages are equal to their desired ensemble averages, canonical or other, in the physical phase space. Thus the equivalence of the dynamical time-averages and the desired ensemble averages for physical quantities is contingent on the ergodicity of the dynamics with respect to the (weighted) microcanonical ensemble in the extended (and possibly augmented) phase space of the virtual variables. This condition remains true notwithstanding the fact that the actual dynamical calculations can be carried out in terms of the physical variables.

The special role of the phase space of virtual variables[4] is that only in this space can the dynamics be Hamiltonian and thus only in this space can they obey the Liouville theorem. The latter is used in the proof of the von Neumann–Birkhoff theorem[6,7] which provides the only presently known framework for formulating the ergodic property of a dynamics with respect to an ensemble. Consequently the ergodicity relation is established in a conceptually complete fashion only between Hamiltonian dynamics and microcanonical ensembles. As shown in Ref. 4, this relation has a specific invariance under the transformation of time scaling. This invariance establishes the ergodicity between a scaled-time *non-Hamiltonian* dynamics and a corresponding *weighted* microcanonical ensemble.

In accordance with the von Neumann–Birkhoff theorem the metric indecomposability of the energy surface (or part of it) under the mapping defined by the dynamics is the necessary and sufficient condition for ergodicity. It is not sufficient for the dynamics to be Hamiltonian, i.e., to satisfy the Liouville equation or theorem, or even for the Hamiltonian generating this dynamics to obey the ensemble-ensemble correlation formulated above, in order for ergodicity to be guaranteed.[4]

Hoover suggests[1,8,9] that the canonical ensemble can be mimicked by a specific set of non-Hamiltonian dynamics which in the one-dimensional case can be n-parametrized as follows:

$$\dot{q}=p/m, \quad \dot{p}=-d\phi(q)/dq-\zeta_n p^n/[(mkT)^{n-1}]^{1/2}\,, \\ \dot{\zeta}_n=(p^{n+1}-np^{n-1}mkT)/\tau^2[(mkT)^{n+1}]^{1/2}\,, \tag{1}$$

where $n=1,3,5,\ldots$, the overdot denotes a time derivative and the rest of the notation is the same as in Ref. 1.

The argument invoked[8,9] is that these dynamics satisfy the equation for the flow of the probability density f_n in the phase space

$$\partial f_n/\partial t+\dot{q}\partial f_n/\partial q+\dot{p}\partial f_n/\partial p+\dot{\zeta}_n\partial f_n/\partial\zeta_n + f_n(\partial\dot{q}/\partial q+\partial\dot{p}/\partial p+\partial\dot{\zeta}_n/\partial\zeta_n)=0\ , \qquad (2)$$

with

$$f_n=C\exp\{-[p^2/2m+\phi(q)+Q\zeta_n^2/2]/kT\},\ \ Q=kT\tau^2\ , \qquad (3)$$

where C is a constant. Equation (2) can be viewed as a remnant of the Liouville equation for non-Hamiltonian flows.

As shown,[4] for $n=1$ Eqs. (1) define a dynamics identical to the physical-variable dynamics of Nosé [cf. Eqs. (4) in Ref. 4] which has its origin in the Hamiltonian dynamics in the space of the virtual variables. Thus in the case $n=1$ all the conceptually necessary steps, including the step of microcanonical ensemble-Hamiltonian dynamics correlation (in which the conditions for ergodicity are formulated), are carried out to establish the equality of the dynamical time-averages and the canonical ensemble averages for physical quantities. This is, however, not the case for $n>1$. The situation with a conceptually complete justification of Eqs. (1) for $n>1$ is more complex and, strictly speaking, such a justification is nonexistent at present. One way to attempt to provide for it is to try to find for each $n>1$ a corresponding "parent" Hamiltonian dynamics in the space of the virtual variables. Another option is to examine the possibility of formulating an analog of the von Neumann–Birkhoff theorem which would be valid for non-Hamiltonian systems. It is clear that the fact that a dynamics satisfies Eq. (2), with a phase space density of the type of Eq. (3), does not guarantee that this dynamics indeed generates a Boltzmann distribution in the *physical phase space.* Equation (2) is a necessary but not a sufficient condition. A transparent example is

$$f=C\exp\{-[p^2/2m+\phi(q)+\psi(\zeta)]/kT\}\ , \qquad (4)$$

$$\dot{q}=p/m,\ \ \dot{p}=-d\phi(q)/dq,\ \ \dot{\zeta}=\exp[\psi(\zeta)/kT]\ , \qquad (5)$$

where $\psi(\zeta)$ is any differentiable function of ζ. We use this extreme case, in which the (q,p) space is decoupled from the ζ space, as an illustration to stress our point.

The different dynamics which satisfy Eq. (2) with a probability density of the type of Eq. (3) possess, however, the property that they generate the canonical distribution *along their corresponding trajectories.* The particular dynamics, Eqs. (5), generate the Boltzmann distribution

$$\exp\{-[p^2/2m+\phi(q)]/kT\} \qquad (6)$$

along a trajectory confined to an energy shell

$$p^2/2m+\phi(q)=\text{const} \qquad (7)$$

in the (q,p) space, where this distribution degenerates into a constant. By solving Eq. (2) with respect to f for a given set of dynamical equations, one finds the probability density generated by the corresponding dynamics *along its trajectory.* Using this approach, one can convince oneself[10] that the different n-labeled dynamics defined by Eqs. (1) indeed generate the Boltzmann distribution (3) *along their corresponding trajectories.* The answer to the question of whether these dynamics are capable of mimicking the canonical ensemble in a particular volume of the (q,p,ζ) space depends then on whether their corresponding trajectories pass through almost all points of this volume, or equivalently, whether this volume is metrically indecomposable under mappings defined by the dynamics. Two conclusions may be drawn from this analysis. First, similar to the case of Hamiltonian dynamics, metric indecomposability is a necessary condition for a non-Hamiltonian dynamics to be ergodic with respect to a nonconservative ensemble. Second, in distinction with the case of Hamiltonian dynamics, metric indecomposability is not a sufficient condition for a non-Hamiltonian dynamics to be ergodic with respect to a nonconservative ensemble. The dynamics must also satisfy Eq. (2) in which the probability density f is that of the desired nonconservative ensemble. However, satisfying the two requirements [Eq. (2) and metric indecomposability] simultaneously seems to be sufficient for a non-Hamiltonian dynamics to simulate a nonconservative ensemble.

An important practical advantage of the Hamiltonian approach to dynamical simulation of nonconservative systems is that it allows one to easily construct infinitely many different dynamics. Not all of these dynamics will indeed be capable of mimicking the desired nonconservative ensemble. To interrogate the dynamics a practical indicative test of ergodicity has recently been suggested.[4] This test may also be used on dynamics generated by Eqs. (1). Comparing two or more of these dynamics or, even better, comparing them with a dynamics of Hamiltonian origin known to generate the canonical ensemble averages for the same physical system may tell us whether the dynamics, Eqs. (1), do or do not produce the canonical averages.

The Comment[1] prompts us also to remark on a few points made in it and repeated also in the literature which, in our view, require clarification. It has been claimed that Hamiltonian dynamics or their derivatives cannot provide for different time scales or rates of evolution for different degrees of freedom. Quite the contrary, we believe that our generalization of Nosé's scheme[4,5] provides explicitly for such a capability through the judicious selection of the scaling functions $h(s)$, $f(s)$, and $u(s)$ defining the Hamiltonian of the extended, and possibly augmented, system in the space of the virtual variables.

Calling the "bath" coordinate s of Nosé a "time-scaling" variable implies physical significance for this variable that it, in fact, does not possess. Although in the original formulation of Nosé,[2,3] s could appear as a time-scaling or mass-scaling[11] variable, from a more fundamental physical point of view it is neither. As is shown in Ref. 4, the only role of s is as a source or a sink of energy for the physical system; its coupling to the physical system regulates all the flows of energy. The transformation of time scaling is a totally independent transformation.[4]

Finally, a word about the correlation between the unscaled-time Hamiltonian and scaled-time non-Hamiltonian dynamics. A dynamics in the present context is a trajectory and a time defining the rate of evolution. While the operation of scaling of the time does not alter the embedding of a trajectory in the phase space and alters only the rate at which the trajectory is traversed—making this rate nonuniform—the unscaled-time averages and the scaled-time averages calculated along the same trajectory are, in general, different. Thus, two dynamics which differ only in the rate of their time change cannot, in general, both produce time-averages equal to the same canonical (or any other) ensemble averages. To force two dynamics evolving in unscaled and scaled time, respectively, to produce the *same* time averages one must choose *different Hamiltonians* for them. But then the trajectories generated by the two dynamics will be different. Thus, two or more dynamics evolving in different times of which *each one* is expected to be capable of mimicking the *same* specified ensemble for the physical system (these are the only dynamics of interest), indeed generate *different* trajectories.

Neglect of this fact can cause confusion and misunderstanding. Of the two dynamics defined by Eqs. (13) and Eqs. (14) in Ref. 9, which are generated from the same Hamiltonian but use different times, only the latter is "legitimate" for simulating the canonical ensemble. To legitimize Eqs. (13), i.e., to make them suitable for simulating the canonical ensemble as Eqs. (14) do, one has to correct the last of Eqs. (13) by replacing the term $1/s$ by $2/s$. This value is obtained when one uses the correct value $X=1$ for the number of degrees of freedom, and not $X=0$ as used in Ref. 9 (we employ the notations of Ref. 9). The two dynamics correspond then to different Hamiltonians, one with the potential-energy term for the Nosé variable $2kT\ln s$ and the other with $kT\ln s$, and they generate different trajectories. Note also that in Ref. 9 use of the same axes in Fig. 1 for plotting the coordinate-momentum manifolds mapped out by Eqs. (14) and Eqs. (15) may leave the impression that the dynamics generated by these equations are different. Although the same symbols are used in the two sets of Eqs. (14) and (15) for the coordinate and momentum, respectively, these equations, unlike Eqs. (13) and (14), represent the same dynamics but expressed in terms of two different phase spaces.[4] In Fig. 1 of Ref. 9 graphs (b) and (d) are images of the same dynamics in two different coordinate-momentum spaces as are graphs (c) and (e).

In Ref. 12 the ambiguity regarding the different phase spaces is removed. Still, a statement about "... three equivalent forms of Nosé's equations of motion" is made. Our remarks concerning Eqs. (13)–(15) of Ref. 9 can be repeated here. The two sets of equations (3) and (5) of Ref. 12, are indeed equivalent in that they express the same scaled-time dynamics in terms of two different phase spaces. However Eqs. (2) (Ref. 12) are not those of Nosé and they cannot simulate the canonical ensemble. The correct set of the unscaled-time Nosé equations is obtained from the Hamiltonian (1) (Ref. 12) in which the $NDkT$ coefficient is replaced by $(ND+1)kT$. This set of equations generates a trajectory *different* from the generated by Eqs. (3).[12] The same type of misunderstanding emerges in Ref. 13, where it is claimed that "trajectories under NH (Nosé–Hoover) and Nosé dynamics follow the same paths..." which, in fact, is not the case.[4] Further details on the effect of the time-scaling transformation, on rewriting the dynamics in terms of different phase spaces, as well as on other delicate aspects of the Nosé scheme and its generalizations can be found in Ref. 4.

One of us (J.J.) is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. W-31-109-Eng-38. One of us (R.S.B.) acknowledges support by a grant from the U.S. National Science Foundation.

[1]W. G. Hoover, preceding paper, Phys. Rev, A **40**, 2814 (1989).
[2]S. Nosé, J. Chem. Phys. **81**, 511 (1984).
[3]S. Nosé, Mol. Phys. **52**, 244 (1984).
[4]J. Jellinek, J. Phys. Chem. **92**, 3163 (1988).
[5]J. Jellinek and R. S. Berry, Phys. Rev. A **38**, 3069 (1988).
[6]A. I. Khinchin, *Mathematical Foundations of Statistical Mechanics* (Dover, New York, 1969).
[7]A. Münster, *Statistical Thermodynamics* (Academic, New York, 1969).
[8]W. G. Hoover, *Molecular Dynamics,* Vol. 258 of *Lecture Notes in Physics* (Springer-Verlag, Berlin, 1986).
[9]W. G. Hoover, Phys. Rev. A **31**, 1695 (1984).
[10]S. Nosé, Mol. Phys. **57**, 187 (1986).
[11]J. R. Ray and A. Rahman, J. Chem. Phys. **82**, 4243 (1985).
[12]H. A. Posch, W. G. Hoover, and F. J. Vesely, Phys. Rev. A **33**, 4253 (1986).
[13]D. J. Evans and B. L. Holian, J. Chem. Phys. **83**, 4069 (1985).