Generalization of Nosé's isothermal molecular dynamics

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

R. Stephen Berry*
Physical Chemistry Laboratory, Oxford University, Oxford OX1 3QZ, United Kingdom
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A generalization is given of the method introduced by Nosé for simulating isothermal behavior by molecular dynamics. An infinity of physically inequivalent choices for dynamics can be made to evaluate average properties of an equilibrated canonical ensemble. The availability of different choices may, we suggest, open the principal possibility of searching for a dynamics which will adequately mimic not only the equilibrium but also the time-dependent properties of a particular physical system.

I. BACKGROUND AND INTRODUCTION

The method of molecular dynamics[1] has become a tool fully integrated into the workshop of contemporary mechanics. Traditionally, being based on Hamiltonian mechanics, the method was appropriate for describing isoergic conditions and microcanonical ensembles. The highly desirable goal of putting this method into a form that yields properties of a canonical ensemble was achieved by Andersen[2] and recently by Nosé.[3] Of these only Nosé's scheme furnishes a continuous deterministic dynamics. It is based on extending the space of dynamical variables beyond that of the coordinates and momenta of the real particles to include one additional phantom coordinate and its conjugate momentum. The extra degree of freedom, if properly coupled to the physical system, acts as a heat bath for the real particles. Nosé devised a way to make such a coupling. His method has stimulated further formulations,[4] including the extension to time-dependent properties.[5,6]

The view uniformly shared in the literature is that the specific Nosé Hamiltonian with the logarithmic dependence on the phantom coordinate is the only one which can generate a continuous and deterministic dynamics capable of mimicking a canonical ensemble. This Hamiltonian implies a very specific coupling between the physical system and an effective bath and thus a very specific dynamics of time-correlation and relaxation processes in the physical system. The goal of this short communication is to show that, in fact, there are infinitely many other ways to couple the physical system to the phantom coordinate and momentum and still preserve the canonical ensemble character of the corresponding dynamics. In other words, we prove that there exist infinitely many *different* Hamiltonians of the extended system (consisting of the physical system and an effective bath) which possess all the properties of Nosé's Hamiltonian. Obviously, these Hamiltonians generate different dynamics and thus different time evolutions of the physical system. We concentrate here only on the conceptual aspect of the problem, drawing attention to the existence of many inequivalent dynamics corresponding to the same canonical ensemble, and giving an explicit prescription for generating all these dynamics. The detailed analysis of the different dynamics and the criteria for selecting a particular one will be the subject of a separate study. Here we note only that the freedom to *choose* a dynamics should, in principle, provide for the possibility of selecting a model which will not only adequately describe the equilibrium properties of a physical system but also will furnish information on time-dependent correlations and the rate of energy flow in different degrees of freedom.

Section II gives a brief review and introduces the notations of Nosé's method. In Sec. III the derivation of the generalization, which carries automatically an algorithm for making the construction, is presented. A brief discussion is given in the conclusion. Elsewhere,[7] we will discuss the basis and some subtle points of the Nosé method, the role of time scaling, some related conclusions concerning ergodicity and an indicative test of ergodicity which emerges from the generalized approach, and the extension of the method to simulate dynamically any statistical ensemble in which the number of particles is conserved.

II. THE METHOD OF NOSÉ

Following Nosé's notation, we use primed coordinates $\mathbf{q}' \equiv \{\mathbf{q}'_j\}$ and momenta $\mathbf{p}' \equiv \{\mathbf{p}'_j\}$ for the canonical variables of the physical system, and unprimed variables $\mathbf{q}$, $\mathbf{p}$, and $\mathbf{q}_j, \mathbf{p}_j$ for the coordinates and momenta of all the particles and of particle j, respectively, in what Nosé calls a "virtual system." If an additional degree of freedom, with coordinate s and momentum p_s, is appended, then the system is called an "extended system." There are therefore four systems to keep in mind, the physical (superscript p), the virtual (superscript v), the physical system extended (superscript pe), and the virtual system extended (superscript ve). The essence of Nosé's approach is to show that there is a way to choose the Hamiltonian of the extended system and, simultaneously, to relate the variables of the physical system to those of the virtual

system, such that the microcanonical partition function of the extended virtual system is proportional to the canonical partition function of the physical system; thus

$$Z_\mu^{ve}=C(E,T,Q,g)Z_c^p \ , \tag{1}$$

where the subscripts μ and c imply "microcanonical" and "canonical," respectively; $C(E,T,Q,g)$ is a calculable number, E is the energy of the microcanonical ensemble, T is the temperature of the canonical ensemble, and Q and g are parameters used to define the Hamiltonian of the extended system. Specifically, Nosé defines the relation between the virtual and physical systems as follows:

$$\mathbf{q}_i=\mathbf{q}_i' , \quad \mathbf{p}_i=s\mathbf{p}_i' \ . \tag{2}$$

The mass of the ith particle of the virtual system is[6]

$$m_i=s^2m_i' \ , \tag{3}$$

where m_i' is its physical mass. The Hamiltonian of the virtual extended system of Nosé is

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

where k is the Boltzmann constant, ϕ is the potential of the physical system and it is the same for the virtual system, the parameter Q plays the role of the mass of the additional degree of freedom s, and g is a parameter depending, in Nosé's formulation, on the number of particles N and the choice of time scaling. If conventional, "unscaled" time t is used, then Eq. (1) holds for $g=3N+1$; if "scaled" time t', defined by $dt'=dt/s$, is used, then for Eq. (1) to be satisfied, we must set $g=3N$. We shall not reproduce here the Hamilton equations of the virtual extended system, the corresponding non-Hamiltonian equations of the physical extended system into which they translate, the proof of Eq. (1), or the conclusion, obvious from Eq. (1), that for any function $A(\mathbf{q}',\mathbf{p}')=A(\mathbf{q},\mathbf{p}/s)$, the canonical and microcanonical averages over the respective physical and extended virtual phase spaces satisfy

$$\langle A(\mathbf{q}',\mathbf{p}')\rangle_c^p=\langle A(\mathbf{q},\mathbf{p}/s)\rangle_\mu^{ve} \ . \tag{5}$$

These can be found in Ref. 2 or, in a different form, in Ref. 4. If the Hamilton equations obtained from Hamiltonian (4) generate an ergodic dynamics in the phase space of the virtual extended system then the dynamical time average of any physical quantity $A(\mathbf{q}'(t),\mathbf{p}'(t))=A(\mathbf{q}(t),\mathbf{p}(t)/s(t))$ will be equal to $\langle A(\mathbf{q},\mathbf{p}/s)\rangle_\mu^{ve}$ and thus, due to Eq. (5), to the canonical ensemble average of this quantity.

III. THE GENERALIZATION OF NOSÉ'S SCHEME

We now introduce a set of Hamiltonians like Nosé's, but generalized, and show that they lead to Eqs. (1) and (5). Let $f_{i\lambda}(s)$, $h_{i\lambda}(s)$ $(i=1,\ldots,N;\ \lambda=x,y,z)$, $u(s)$, and $v(s)$ be real nonvanishing differentiable functions of s. (The nonvanishing property can be relaxed, so long as the integrals which appear are well defined.) Let us introduce the following relations between the primed and unprimed momenta and coordinates, respectively:

$$p_{i\lambda}'=p_{i\lambda}/h_{i\lambda}(s) \ , \tag{6a}$$

$$p_s'=p_s/u(s) \ , \tag{6b}$$

$$q_{i\lambda}'=q_{i\lambda}f_{i\lambda}(s) \ . \tag{6c}$$

The generalized Hamiltonian of an extended system is defined as

$$H(\mathbf{q}',\mathbf{p}',s,p_s')=\sum_i \frac{(\mathbf{p}_i')^2}{2m_i'}+\phi(\{\mathbf{q}_i'\})+\frac{(p_s')^2}{2Q}+kTv(s) \ . \tag{7}$$

In terms of the unprimed variables this Hamiltonian takes the form

$$H(\mathbf{q},\mathbf{p},s,p_s)=\sum_{i,\lambda} p_{i\lambda}^2/[2m_i'h_{i\lambda}^2(s)]+\phi(\{f_{i\lambda}(s)q_{i\lambda}\})+p_s^2/[2u^2(s)Q]+kTv(s) \ . \tag{8}$$

The microcanonical distribution for the extended system, considered as depending on the unprimed variables $\mathbf{q}$, $\mathbf{p}$, s, and p_s, is

$$\rho_\mu(\mathbf{q},\mathbf{p},s,p_s)=\delta(H(\mathbf{q},\mathbf{p},s,p_s)-E) \ , \tag{9}$$

and the corresponding microcanonical partition function is defined by

$$Z_\mu=\int\cdots\int d\mathbf{q}\,d\mathbf{p}\,ds\,dp_s\rho_\mu(\mathbf{q},\mathbf{p},s,p_s) \ . \tag{10}$$

Now we switch to the primed variables, continuing to consider $\mathbf{q}'$ and $\mathbf{p}'$ as physical variables. For convenience, we define the Jacobian scaling function

$$J(s)\equiv u(s)\prod_{i,\lambda}\frac{h_{i\lambda}(s)}{f_{i\lambda}(s)} \ . \tag{11}$$

The microcanonical partition function is, in terms of the primed variables,

$$Z_\mu=\int\cdots\int d\mathbf{q}'d\mathbf{p}'ds\,dp_s'J(s)\delta(H(\mathbf{q}',\mathbf{p}',s,p_s')-E) \ . \tag{12}$$

Next we assume that the equation

$$H(\mathbf{q}',\mathbf{p}',s,p_s')-E=0 \ , \tag{13}$$

considered as an equation for s, has a single solution s_0 for each $\mathbf{q}'$, $\mathbf{p}'$ and p_s'. This solution can be written in terms of v^{-1}, the function inverse to $v(s)$, as

$$s_0=v^{-1}\left[\left[E-\sum_i\frac{(\mathbf{p}_i')^2}{2m_i'}-\phi(\{\mathbf{q}_i'\})-\frac{(p_s')^2}{2Q}\right]\Big/kT\right] . \tag{14}$$

We also assume that $v'(s)\equiv dv(s)/ds$ is not zero at $s=s_0$.

Now we invoke the property of the δ function that if s_0 is the only root of a differentiable function $f(s)$ then

$$\delta(f(s))=\delta(s-s_0)/f'(s)\ , \tag{15}$$

where $f'(s)\equiv df(s)/ds$. Using this property and following Nosé's pathway we rewrite the microcanonical partition function (12) as

$$Z_\mu=\int\cdots\int d\mathbf{q}'d\mathbf{p}'ds\,dp_s'(kT)^{-1}G(s)\delta\left[s-v^{-1}\left[\left[E-\sum_i\frac{(\mathbf{p}_i')^2}{2m_i'}-\phi(\{\mathbf{q}_i'\})-\frac{(p_s')^2}{2Q}\right]\Big/kT\right]\right]\ , \tag{16}$$

where

$$G(s)\equiv J(s)/v'(s)\ . \tag{17}$$

The transformation from $\delta(H-E)$ to $\delta(s-s_0)$ allows integration over s so that the integrand becomes $G(s_0)/kT$, where s_0 is defined by Eq. (14). Until now the choice of the scaling functions $f_{i\lambda}(s)$, $h_{i\lambda}(s)$, $u(s)$, and of the function $v(s)$ in the Hamiltonian (8) was restricted only by the requirements of differentiability and that they do not vanish. If one selects these functions in such a way that the function $G(s)$ constructed from them [cf. Eqs. (11) and (17)] satisfies the condition

$$G(s_0)=F(E,Q,T;p_s')\exp\left[-\left[\sum_i[(\mathbf{p}_i')^2/2m_i']+\phi(\{\mathbf{q}_i'\})\right]\Big/kT\right]\ , \tag{18}$$

where $F(E,Q,T;p_s')$ is an integrable function of p_s', then Eq. (16) eventually transforms into

$$Z_\mu=C(E,Q,T)Z_c\ , \tag{19}$$

where

$$Z_c=\int\int d\mathbf{q}'d\mathbf{p}'\exp\left[-\left[\sum_i\frac{(\mathbf{p}_i')^2}{2m_i'}+\phi(\{\mathbf{q}_i'\})\right]\Big/kT\right] \tag{20}$$

is the canonical partition function of the physical system and $C(E,Q,T)$ is a constant. Of course, Eq. (19) immediately implies Eq. (5).

It is obvious that there are infinitely many different sets of the functions $f_{i\lambda}(s)$, $h_{i\lambda}(s)$, $u(s)$, and $v(s)$, such that each set satisfies the condition (18). Thus there are infinitely many different Hamiltonians (8) for which equalities (19) and (5) hold. Nosé's Hamiltonian with $h_{i\lambda}(s)=s$, $f_{i\lambda}(s)=1$, $u(s)=1$, and $v(s)=g\ln s$ is only one example. The different Hamiltonians generate different dynamics. Those of the dynamics which are ergodic in the phase space of the extended virtual system will produce the same time averages of physical quantities $A(\mathbf{q}',\mathbf{p}')$ equal to their canonical ensemble averages. The dynamics, however, are inequivalent indeed: they generate different time evolutions of the physical system.

IV. DISCUSSION

The main conclusion to be drawn from the derivation presented above is that one can use many different continuous and deterministic dynamics for mimicking the canonical ensemble behavior of a physical system. We note that even the present derivation is by no means the most general. One may introduce a scaling into the distribution function: $\rho(\mathbf{q},\mathbf{p},s,p_s)w(s)=\delta(H(\mathbf{q},\mathbf{p},s,p_s)-E)$, where $w(s)$ is a continuous nonvanishing function. In the context of the ergodic problem this scaling is equivalent to the scaling of the time. The latter can be used to "tune" a dynamics generated by *any* continuous Hamiltonian for an extended system and as a result to obtain time-averaged properties of a physical system corresponding to the canonical (or other) ensemble averages. These more general aspects require a more elaborate discussion and they will be presented elsewhere.[7] Our purpose here has been to point out that there is a freedom of choice in the selection of the extended system and its Hamiltonian, a freedom which has not yet been exploited.

The freedom to choose what we call the "scaling functions," i.e., the functions $h_{i\lambda}(s)$, $f_{i\lambda}(s)$, $u(s)$, and the function $v(s)$, is essentially limited only by the requirement (18). It is convenient but not necessary to have the p_s' dependence factor out into F as it does in Eq. (18). A weaker condition is to require that the integral of $G(s_0(\mathbf{q}',\mathbf{p}',p_s))$ over p_s is proportional to a canonical distribution function over the phase space of the physical system.

We suggest that it may be possible to choose a particular set of scaling functions so that the resulting dynamics will adequately mimic not only the averaged ensemble behavior of a physical system, but also the specificity of its coupling to an external thermostat and the details of its time evolution. An appropriate choice of the Hamiltonian of the extended system should allow, for example, for reproducing the transport properties of particular physical systems as well as their time-correlation functions. The recognition of the possibility to *choose* a dynamics is particularly important for theoretical studies driving at simulating physical systems under well-defined experimental conditions.

The idea that adding a single extra degree of freedom and its conjugate momentum to the phase space of the physical system can be enough to make this system obey the canonical distribution was already a substantial advance not only for modeling but also for providing insight into the relation between dynamics and statistical ensembles. As follows from the preceding, the extra degree of freedom probably can do more; if appropriately coupled to the physical system it might be a powerful de-

vice for improving the realism of our dynamical models and for extending our capability to adequately simulate not only static averaged but also transport and time-dependent properties of different physical systems. As was mentioned, specific realizations of different types of dynamics and the criteria for their selection will be the subject of separate studies.

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*Permanent address: Department of Chemistry and the James Franck Institute, The University of Chicago, Chicago, IL 60637.

[1]B. J. Alder and T. E. Wainwright, J. Chem. Phys. **31**, 459 (1959); **33**, 1439 (1960); for a review, see J. Kusick and B. Berne, in *Statistical Mechanics Part B,* edited by B. Berne (Plenum, New York, 1977), Vol. 6, Chap. 2.

[2]H. C. Andersen, J. Chem. Phys. **72**, 2384 (1980).

[3]S. Nosé, J. Chem. Phys. **81**, 511 (1984); Mol. Phys. **52**, 255 (1984).

[4]W. G. Hoover, Phys. Rev. A **31**, 1695 (1985).

[5]D. J. Evans and B. L. Holian, J. Chem. Phys. **83**, 4069 (1985).

[6]J. R. Ray and A. Rahman, J. Chem. Phys. **82**, 4243 (1985).

[7]J. Jellinek, J. Phys. Chem. **92**, 3163 (1988).