Canonical dynamics: Equilibrium phase-space distributions

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Nosé has modified Newtonian dynamics so as to reproduce both the canonical and the isothermal-isobaric probability densities in the phase space of an N-body system. He did this by scaling time (with s) and distance (with $V^{1/D}$ in D dimensions) through Lagrangian equations of motion. The dynamical equations describe the evolution of these two scaling variables and their two conjugate momenta p_s and p_v. Here we develop a slightly different set of equations, free of time scaling. We find the dynamical steady-state probability density in an extended phase space with variables x, p_x, V, $\dot{\epsilon}$, and ζ, where the x are reduced distances and the two variables $\dot{\epsilon}$ and ζ act as thermodynamic friction coefficients. We find that these friction coefficients have Gaussian distributions. From the distributions the extent of small-system non-Newtonian behavior can be estimated. We illustrate the dynamical equations by considering their application to the simplest possible case, a one-dimensional classical harmonic oscillator.

I. INTRODUCTION

Classical "constant-temperature" calculations have been pursued for over a decade.[1,2] In this sense, "temperature" is a measure of the instantaneous kinetic energy in a system. Thus the corresponding dynamical equations include non-Newtonian accelerations designed to keep the kinetic energy $\sum p^2/2m$ constant. The non-Newtonian isothermal accelerations are useful in dissipative systems involving viscous flow, or heat flow, far from equilibrium. Such systems would heat rapidly in the absence of constraints. By now, many[3-6] distinct sets of differential equations of motion have been devised to keep the kinetic energy constant.

A somewhat different kind of constant-temperature calculation strives to reproduce the canonical phase-space distribution, so that the kinetic energy can fluctuate, with a distribution proportional to $\exp(-\sum p^2/2mkT)$. Obtaining the canonical distribution is desirable, at least in equilibrium work, in order to correlate the results of many-body simulations with Gibbs's and Jaynes's statistical mechanics. Andersen[7] has used occasional discontinuous "stochastic" collisions to induce the canonical distribution in many-body simulations.

Nosé achieved a major advance by showing that the canonical distribution can be generated with smooth, deterministic, and time-reversible trajectories. To do this he introduced a time-scale variable s, its conjugate momentum p_s, and a parameter Q. Nosé's augmented Hamiltonian[8]

$$H_{\text{Nosé}} = \Phi(q) + \sum p^2/2ms^2 + (X+1)kT \ln s + p_s^2/2Q \ , \tag{1}$$

contains a nonlinear collective potential in which the time-scale variable s oscillates. Thus the system, with X degrees of freedom, is coupled to a heat bath (described by the variables s and p_s). Nosé proved that the microcanonical distribution in the augmented set of variables is equivalent to a canonical distribution of the variables q,p', where the p' are the scaled momenta p/s. Thus the Hamiltonian (1) generates the canonical probability distribution *independent of the values chosen for* $H_{Nosé}$ *and* Q.

During the canonical-ensemble calculations just described, the volume V and temperature T are held fixed. Nosé demonstrated the usefulness of these ideas by carrying out several dense-fluid simulations using the Hamiltonian $H_{\text{Nosé}}$.

By allowing *length* to vary,[7] as well as time, Nosé generalized this work to include the isothermal-isobaric ensemble. These methods and ideas forge a remarkable link between the ensembles of statistical theory and atomistic dynamics. They suggest promising approaches for the investigation of nonequilibrium systems.

Here we exhibit steady-state (equilibrium) distributions for the new variables which play the role of thermodynamic friction coefficients. Our equations of motion are very much like Nosé's, but differ in that scaling of the time is not required. The new results for distributions make it possible to estimate finite-size effects on dynamical averages. In Sec. II we review Nosé's canonical equations of motion and introduce a version of them free of time scaling. In Sec. III we formulate the phase-space evolution of the many-body probability density $f_{NVT}(q,p,\zeta,Q)$ and exhibit a steady-state solution. We indicate the straightforward extension to include the isobaric case. With some additional effort, it seems likely that a stress-tensor version of this ensemble could be constructed along the lines pioneered by Rahman and Parrinello.[9] In the final section we illustrate the equations of motion with some representative trajectories for a single classical oscillator.

II. CANONICAL DISTRIBUTION FROM NON-NEWTONIAN DYNAMICS (REF. 10)

The equations of motion from Nosé's Hamiltonian (1) are

$$\dot{q} = p/ms^2, \ \dot{p} = F(q), \ \dot{s} = p_s/Q, \qquad \dot{p}_s = \sum p^2/ms^3 - (X+1)kT/s \ . \tag{2}$$

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These coupled first-order equations take a simpler form if the time scale is reduced by s, so that $dt_{\text{old}} \equiv s\, dt_{\text{new}}$. All of the rates given in (2) can then be expressed as derivatives with respect to t_{new} (for which we will still use the superior dot notation)

$$\dot{q} = p/ms,\ \dot{p} = sF,\ \dot{s} = sp_s/Q,$$
$$\dot{p}_s = \sum p^2/ms^2 - (X+1)kT\ . \tag{3}$$

The somewhat inconvenient variable s can then be eliminated from the equations (3) by rewriting the coordinate-evolution equations in terms of q, $\dot{q}$, and $\ddot{q}$:

$$\ddot{q} = \dot{p}/ms - (p/ms)\dot{s}/s = F/m - \dot{q}p_s/Q \equiv F(q)/m - \zeta\dot{q}\ . \tag{4}$$

The thermodynamic friction coefficient $\zeta \equiv p_s/Q$ which appears in the second-order equations (4) evolves in time according to a first-order equation

$$\dot{\zeta} = \left[\sum m\dot{q}^2 - (X+1)kT\right]\Big/Q\ . \tag{5}$$

Nosé showed that the phase-space distribution resulting from the equations (2) is canonical in the variables $q, p/s$. In the next section we show that the distribution resulting from equations (4) and (5) can be made canonical too, and in such a way as to avoid time scaling. To do this we redefine $p \equiv m\dot{q}$ and replace Nosé's $X+1$ by X obtaining[10]

$$\dot{q} = p/m,\ \dot{p} = F(q) - \zeta p,\ \dot{\zeta} = \left[\sum p^2/m - XkT\right]\Big/Q\ . \tag{6}$$

Berendsen[6] has just suggested a close relative of (6) in which ζ rather than $\dot{\zeta}$ is proportional to $\Delta E_{\text{kin}} \equiv \sum p^2/2m - XkT/2$. Notice that Berendsen's equations are not reversible in time. The equations (6) are much less severely damped than Berendsen's. An extreme opposite limiting case, in which ΔE_{kin} is identically zero and time reversibility is retained, has been achieved by setting the friction coefficient equal to $(\sum Fp/m)/(\sum p^2/m)$ or, equivalently, by "velocity scaling."[1-4]

III. PHASE-SPACE EVOLUTION OF $f_{NVT}(q,p,\zeta)$

Because the variables q, p, and ζ used in (6) are *independent*, we can easily calculate the components of the flow of probability density $f(q,p,\zeta)$ in $(2X+1)$-dimensional space. The equations governing the motion in this space are *not* Hamiltonian. Therefore the derivatives $\partial\dot{q}/\partial q$ and $\partial\dot{p}/\partial p$ do not generally sum to zero. Thus the analog of Liouville's equation, expressing the conservative flow of probability with time, including flow in the ζ direction, is

$$\partial f/\partial t + \dot{q}\,\partial f/\partial q + \dot{p}\,\partial f/\partial p + \dot{\zeta}\,\partial f/\partial\zeta + f[\partial\dot{q}/\partial q + \partial\dot{p}/\partial p + \partial\dot{\zeta}/\partial\zeta] = 0\ . \tag{7}$$

Consider a density function f_{NVT} proportional to the following exponential:

$$f_{NVT} \propto \exp\left[-\left\{\Phi(q) + \sum p^2/2m + Q\zeta^2/2\right\}\Big/kT\right]\ . \tag{8}$$

The nonvanishing terms in (7) obtained from this density function are as follows:

$$\begin{aligned}
&\dot{q}\,\partial f/\partial q = (f/kT)\sum Fp/m,\\
&\dot{p}\partial f/\partial p = (f/kT)\sum(-F+\zeta p)p/m,\\
&\dot{\zeta}\,\partial f/\partial\zeta = (f/kT)\left[\left[-\sum p^2/m + XkT\right]\Big/Q\right]\zeta Q,\\
&f\,\partial\dot{p}/\partial p = (f/kT)(-XkT\zeta)\ .
\end{aligned} \tag{9}$$

Inspection shows that these terms sum to zero, provided that the coefficient of kT in the dynamical equation (6) for the friction coefficient is chosen equal to the number of independent degrees of freedom in the set q,p. In the usual molecular dynamics simulation, with periodic boundaries, the center of mass and its velocity are fixed so that this number of degrees of freedom is $D(N-1)$ for a D-dimensional N-body system. Thus the canonical distribution (8) is a steady equilibrium solution of the flow equation (7) and satisfies the equations of motion (6).

In commenting on an earlier draft of this manuscript, Brad Holian pointed out that the phase-space distribution (8) can be used to *derive* the equation of motion for the friction coefficient ζ. To see this, note that the canonical distribution (8) satisfies (7) if, *and only if,* ζ follows the relaxation equation (6) of Nosé. *Thus Nosé's canonical equations of motion are unique.* Other relaxation equations, such as Berendsen's, cannot lead to the canonical distribution (8).

To extend these ideas to the isothermal-isobaric case is straightforward. Reduced coordinates $x \equiv q/V^{1/D}$ are introduced, as is also a fixed "external pressure" P_{ext} and relaxation time τ. The equations of motion

$$\dot{x} = p/mV^{1/D},\ \dot{p} = F - (\dot{\epsilon}+\zeta)p,\ \dot{\zeta}Q = \sum p^2/m - XkT\ ,$$
$$\dot{\epsilon} = \dot{V}/DV,\ \ddot{\epsilon} = (P - P_{\text{ext}})V/\tau^2 kT\ , \tag{10}$$

have the steady equilibrium solution $f_{NPT} \propto V^{N-1}\exp(-\Psi/kT)$, where

$$\Psi \equiv \Phi(xV^{1/D}) + \sum p^2/2m + Q\zeta^2/2 + D\dot{\epsilon}^2\tau^2 kT/2 + P_{\text{ext}}V\ . \tag{11}$$

IV. CANONICAL HARMONIC OSCILLATOR

To illustrate the changes in viewpoint discovered by Nosé we consider a one-dimensional harmonic oscillator with the mass, force constant, and initial values of q and p all taken to be unity. We consider equations for which the values of q^2 and p^2 have averaged values of unity. The microcanonical equations of motion

$$\dot{q} = p,\ \dot{p} = -q \tag{12}$$

generate closed elliptical trajectories in the two-dimensional qp phase space. See Fig. 1(a). For this same oscillator Nosé's canonical equations [with X in (2) taken to be zero and s initially unity] take the form

$$\dot{q} = p/s^2,\ \dot{p} = -q,\ \dot{s} = p_s/Q,\ \dot{p}_s = p^2/s^3 - 1/s\ . \tag{13}$$

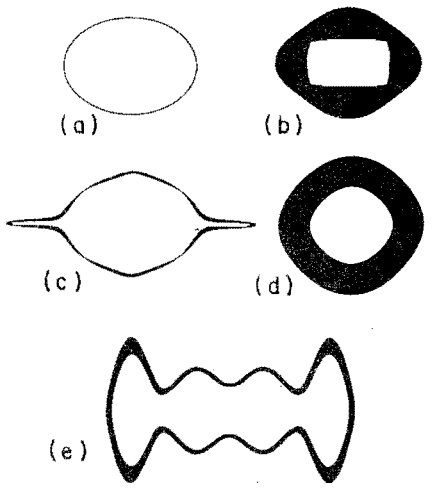

FIG. 1. (a) Elliptical orbit for an oscillator described by Eqs. (12). The abscissa is q, the ordinate is p. The major-to-minor axis ratio of unity has been increased in plotting to fit the Tektronix hard-copy screen area symmetrically. This same increase applies to each figure. All data were obtained on the Digital Equipment Corporation VAX 11/780 computer at the Physics Department (Lausanne) using a fourth-order Runge-Kutta integration in double precision with time steps in the range 0.01 down to 0.001. (b) Long-time qp trajectory for Eqs. (13) or (14) with initial values $q=1$, $p=1$, $s=1$, $p_s=0$, and $Q=1$. (c) Same as (b) with $Q=0.1$. (d) Long-time qp trajectory for Eqs. (15) with initial values $q=1$, $p=1$, $\zeta=0$, and $Q=1$. (e) Same as (d) with $Q=0.1$.

For large Q these equations simply reproduce the microcanonical behavior shown in Fig. 1(a). In Figs. 1(b) and 1(c) we show trajectories for $Q=1.0$ and 0.1 using the same initial conditions. For the larger Q, the trajectories in qp space gradually fill in a region between two limiting curves. For the smaller Q the trajectories develop more nearly singular turning points and the size of the filled region diminishes. When a new time is introduced, with $dt_{\text{old}} \equiv s dt_{\text{new}}$ and

$$\dot{q}=p/s,\ \dot{p}=-qs,\ \dot{s}=sp_s/Q,\ \dot{p}_s=(p/s)^2-1\ , \tag{14}$$

exactly the same trajectories are produced, but at different rates. This is a good check of the numerical integration.

Finally, if we abandon time scaling and redefine $p \equiv \dot{q}$ we have

$$\dot{q}=p,\ \dot{p}=-q-\zeta p,\ \dot{\zeta}=(p^2-1)/Q\ . \tag{15}$$

Solutions for these equations appear in Figs. 1(d) and 1(e). The small-Q limit of (15) can be inferred from these figures. The oscillator moves between widely-separated turning points at velocity ± 1.

These examples illustrate that a single oscillator is not sufficiently chaotic to reproduce the canonical distribution from a single initial condition. The trajectories are, however, stable and cover a relatively large part of the oscillator phase space for reasonable values of the parameter Q. For unreasonable values of Q (either very small or very large) it is not at all clear that even large systems will behave in a canonical (as opposed to microcanonical) way. A study of the number dependence and Q dependence of the phase-space density for a series of small systems might help to clarify this point.

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