Velocity distributions in nonlinear systems

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A growing array of numerical results obtained in our laboratory indicates that, in certain situations, the Maxwellian velocity distribution for a subensemble of low-mass test particles in equilibrium with a heat bath is not valid. This paper provides a theoretical framework in which the observed non-Maxwellian distributions can be understood. The basic arguments are as follows. When the mass of a test particle is small compared with the mass of the heat bath particles, and when this particle is subjected to a strong systematic force, the resulting dynamical motion of the test particle is subjected to a friction force that is nonlinear in the velocity of the test particle. The dynamics of the test-particle motion is then governed by a nonlinear Langevin equation, and the probability density of the stochastic variables must accordingly be obtained from a related nonlinear Fokker-Planck equation. The steady-state solutions of this differential equation are seen to correspond generally to non-Maxwellian velocity distributions.

I. INTRODUCTION

Determination of the velocity distribution function for certain particles in an inhomogeneous system is one of the most fundamental problems in statistical physics. These particles, representing only part of the system, are referred to in this paper as "particles of interest" or "test particles." The remainder of the system plays the role of a heat bath, these particles being termed the "bath particles" or "host particles."

Three features are worth emphasizing. When the test particles, assumed so dilute that they do not interact with one another, are small in mass and size relative to the host particles and, furthermore, when they are subjected to a systematic force of comparable or larger magnitude than the average stochastic force caused by the heat bath, the response of the heat bath particles to the rapidly changing states of the test particle is too slow for local equilibrium to be attained. Secondly, again because of time-scale considerations, the dynamics of the test particles is mainly determined by their interface with the local bath particles rather than through interactions with the averaged bulk environment. The behavior of the local bath interface, or "cage," is quite different from the bulk phase and is sensitively dependent on the motion of the test particle.[1] Thirdly, collisions of the test particles with the host particles are, in general, inelastic, and kinetic energy may not be a conservative quantity during these collisions. The resulting friction forces in a conventional hydrodynamics approach may be nonlinear in the velocity, suggestive of the problem of non-Newtonian flow,[2,3] leading to further mathematical complexities in the transport equations. Determination of the velocity distribution of such a subensemble is by no means a trivial matter.

In the case of Brownian motion,[4] heavy test particles are immersed in a fluid made up of light-weight bath particles. To describe Brownian motion, the Langevin equation[5] and the Fokker-Planck equation[6,7] have become powerful tools. Because of the slow motion of a Brownian particle, dynamic processes take place on such a long time scale that both the Brownian particle and the cage are fully mixed with the bulk environment. Every Brownian particle is a member of a quasicanonical ensemble that also comprises a large number of bath particles, and it is well known that at equilibrium the velocities of the Brownian particles are distributed through the Maxwell law.[8] This situation is a consequence of the existence of a double time scale: a short time related to the duration of the interaction and a much longer time related to the relaxation process.[9]

A different limiting case, the Lorentzian limit,[10,11] is less studied and is much less understood. In this case the mass of the test particle is considerably lower than that of the host particles. Dynamical processes of the test particle are rapid compared with the relaxation of the heat bath. In a case that has attracted even less attention, when the Lorentzian particle experiences a steep force field or possesses a steep intramolecular potential, every state of such a test particle has only a short lifetime. No matter how long an experiment lasts, perfect equilibrium in the interfacial region need not be reached, since the test particle changes its state rapidly and continuously, while, in response, the cage configuration readjusts much more slowly. In this sense Lorentzian test particles having different states are distinguishable and any nonlinear effects have to be taken into account explicitly. Though the energy exchange between the test particle and its heat bath tends to average out over a long time duration, there may exist preferences for certain states, and net effects may occur at the interface.[1,12–14] As Suzuki[15] has pointed out, fluctuations in nonlinear systems can produce order. In particular, the cage enclosing a test particle in an excited state behaves dynamically differently than if the particle were in its ground state.[1] This characteristic arises from the clear separation of the time scales used to measure the motions of different kinds of particles and is an opposite limit from the Brownian motion case. Because of this time-scale separation, the dynamics of the low-mass particle should be governed by nonlinear laws of physics.[9,10,16–18] The subensemble constructed by these Lorentzian test particles is generally noncanonical, since they contact only the cage for the time duration of interest. In this case the test particle moves as in a non-Newtonian fluid where the local viscosity depends upon the external force to which the test particle is subjected.[2,3]

II. NONLINEAR FOKKER-PLANCK EQUATION

The nonlinear Langevin equation and the corresponding nonlinear Fokker-Planck equation have a long history.[8,16–27] Nonlinear effects have also recently been implicated in computer simulations of real dynamical systems, where a small test particle is subjected to large external forces.[18] These simulations have shown that the microscopic friction force experienced by the test particle depends linearly upon the test-particle velocity only when that velocity is low relative to the mean-square velocity of host particles. On the other hand, when the test-particle velocity approaches or exceeds the latter, a nonlinear dependence of the friction becomes significant. This causes a breakdown of the hydrodynamic concept.[28] Therefore, to describe adequately an ultrafast dynamical process, which involves small (both in mass and size) test particles experiencing forces from a steep potential from external sources, the use of a nonlinear Langevin equation is indicated.

For a pair of stochastic variables q and c, the genuinely nonlinear Langevin equation has the form[8,16–27]

$$\frac{dc}{dt}=E(q,c)+F(q,c,t)+G(q,c,t)\Gamma(t)\ , \tag{1}$$

$$c=\frac{dq}{dt}\ , \tag{2}$$

where $E(q,c)$ represents an external force acting on the test particle or a force from an internal potential barrier modified by interaction with the heat bath. Such forces, in general, may depend upon both q and c.[17,29] When E depends on c, it is no longer a conservative force and cannot be expressed as a position derivative of a genuine potential. The force $F(q,c,t)$ arises from the microscopic friction. For a nonlinear system this force may be a complicated function of q and c.[1,12,17,18]

The Langevin force $\Gamma(t)$ is usually assumed to be a Gaussian random variable with zero mean and δ correlation function. Of course, these are not necessary conditions. However, for simplicity of the mathematics, we still adopt these assumptions. This will not affect our final conclusions. As a matter of fact, San Miguel and Sancho[25] have derived a nonlinear Fokker-Planck equation from a nonlinear, non-Markovian Langevin equation, which is valid for small correlation times, and have shown that the approximate results for linear cases are reobtained. The noise strength may be absorbed into the function $G(q,c,t)$, so we have

$$\langle \Gamma(t)\rangle=0\ , \tag{3}$$

$$\langle \Gamma(t)\Gamma(\tau)\rangle=\delta(t-\tau)\ . \tag{4}$$

If G is a constant, Eq. (1) reduces to a Langevin equation with an additive noise force. Otherwise, one speaks of a Langevin equation with a multiplicative noise term.[30]

Generally speaking, because of the nonlinearities that are directly derived from many-body forces, a formal solution of the stochastic differential Eq. (1) cannot be obtained from purely mathematical manipulations. However, on the basis of Eq. (1) we are able to set up a Fokker-Planck-type equation so that the probability density of the stochastic variables x and v can be calculated. Detailed derivations of the nonlinear Fokker-Planck equation have been given by Risken[8] and by many other authors[25,31,32] as well. We will follow their methods below.

According to the classical theory of statistics,[33–36] the probability densities $P(x,v,t)$ at time t and $P(x,v,t+\tau)$ at time $t+\tau$, where τ is long compared with periods of fluctuations but short compared with the intervals in which any of the physical parameters change appreciably, are connected by

$$P(x,v,t+\tau)=\int W(x,v,t+\tau|x',v',t)P(x,v,t)dx'dv'\ , \tag{5}$$

where

$$W(x,v,t+\tau|x',v',t)$$

denotes the transition probability. This can be expressed as

$$W(x,v,t+\tau|x',v',t)=\left[1-\frac{\partial}{\partial x}M_x(x,v,t,\tau)-\frac{\partial}{\partial v}M_v(x,v,t,\tau)+\tfrac{1}{2}\frac{\partial^2}{\partial x^2}M_{xx}(x,v,t,\tau)\right.$$
$$\left.+\tfrac{1}{2}\frac{\partial}{\partial x\partial v}M_{xv}(x,v,t,\tau)+\tfrac{1}{2}\frac{\partial^2}{\partial v^2}M_{vv}(x,v,t,\tau)+\cdots\right]\delta(x-x')\delta(v-v')\ . \tag{6}$$

The moments

$$M_{\mu_1\mu_2\cdots\mu_n}(x',v',t,\tau)=\int(\mu_1-\mu_1')(\mu_2-\mu_2')\cdots(\mu_n-\mu_n')W(x,v,t+\tau|x',v',t)dx\,dv$$
$$=[v_1(t+\tau)-v_1(t)][v_2(t+\tau)-v_2(t)]\cdots[v_n(t+\tau)-v_n(t)]\Big|_{\{v_i(t)\}=\{\mu_i'\}}\ , \tag{7}$$

where μ_i $(i=1,2,\ldots,n)=x$ or v and $\nu_1(i=1,2,\ldots,n)=q$ or c. In the above, $q(t+\tau)$ and $c(t+\tau)$, being solutions of Eq. (1), have sharp values $q(t)=x$ and $c(t)=v$ at time t. The moments can be expanded into a Taylor series with respect to τ:

$$M_{\mu_1\mu_2\cdots\mu_n}(x,v,t,\tau)/n!=D_{\mu_1\mu_2\cdots\mu_n}(x,v,t)\tau+O(\tau^2) . \tag{8}$$

By taking into account only the linear terms in τ, we obtain the rate of change of the probability in terms of the Kramers-Moyal expansion,[37,38]

$$\frac{\partial P(x,v,t)}{\partial t}=\left[-\frac{\partial}{\partial x}D_x(x,v,t)-\frac{\partial}{\partial v}D_v(x,v,t)+\frac{\partial^2}{\partial x^2}D_{xx}(x,v,t)+\frac{\partial^2}{\partial x\partial v}D_{xv}(x,v,t)+\frac{\partial^2}{\partial v^2}D_{vv}(x,v,t)+\cdots\right]P(x,v,t) , \tag{9}$$

where the differential symbols act on $D_{\mu_1\mu_2\cdots\mu_n}(x,v,t)$ and $P(x,v,t)$. For the stochastic Eq. (1), the drift coefficients are

$$D_x(x,v,t)=v \tag{10}$$

and

$$D_v(x,v,t)=E(x,v)+F(x,v,t)+G(x,v,t)\frac{\partial}{\partial v}G(x,v,t) . \tag{11}$$

The diffusion coefficient is

$$D_{vv}(x,v,t)=G^2(x,v,t) . \tag{12}$$

All higher Kramers-Moyal coefficients $D_{\mu_1\mu_2\cdots\mu_n}$ with $n>3$ are zero.[8] In addition

$$D_{xv}(x,v,t)=D_{xx}(x,v,t)=0 . \tag{13}$$

We thus arrive at a nonlinear Fokker-Planck equation,

$$\frac{\partial P(x,v,t)}{\partial t}+v\frac{\partial P(x,v,t)}{\partial x}+\frac{\partial}{\partial v}\left[\left[E(x,v)+F(x,v,t)+G(x,v,t)\frac{\partial}{\partial v}G(x,v,t)\right]P(x,v,t)\right]-\frac{\partial^2}{\partial v^2}[G^2(x,v,t)P(x,v,t)]=0 , \tag{14}$$

which is similar to the one obtained by Risken[8] and other authors.[16–27] However, in those papers most of the attention was given to the position space, while the interest of the present paper is on the velocity space.

For non-Markovian processes, the conditional probability in Eq. (5) depends on the values of the stochastic variables at all earlier times. So do the moments and the Kramers-Moyal expansion coefficients. In such cases the differential equation is not of first order with respect to time t, and the distribution function cannot be uniquely determined from the given initial distribution and boundary conditions.[8] Information is then required, for example, about the initial rate of change of the distribution function. However, we can still apply Eq. (14) to such processes with the understanding that F is an effective microscopic friction. Of course, the Fokker-Planck equation is, strictly speaking, always an approximation, becoming exact only in the limit of infinitely large mass of the test particles.[39] In this limit, the nonlinearity also vanishes.

III. GENERALIZED FLUCTUATION-DISSIPATION RELATION

At steady state, $\partial P(x,v,t)/\partial t=0$, and Eq. (14) becomes

$$v\frac{\partial P(x,v)}{\partial x}+\frac{\partial}{\partial v}\left[\left[E(x,v)+F(x,v)+G(x,v)\frac{\partial}{\partial v}G(x,v)\right]P(x,v)\right]-\frac{\partial^2}{\partial v^2}[G^2(x,v)P(x,v)]=0 . \tag{15}$$

It can easily be demonstrated that Eq. (15) possesses a canonical (Maxwell-Boltzmann) solution if, and only if,

$$F(x,v)=\frac{1}{2}\frac{\partial G^2(x,v)}{\partial v}-\frac{v}{\langle v^2\rangle}G^2(x,v) \tag{16}$$

and further if $E(x)$ is assumed to be a conservative external force. Equation (16) can be viewed as a generalization of the fluctuation-dissipation relation in nonlinear noise problems, though its validity has never been proved and in fact is questionable beyond the Brownian motion limit. In general, $G^2(x,v)$ is not an even function of v; thus $F(x,v)\neq -F(x,-v)$. Since the test particle is just a generic particle, and the random force is produced by the host particles, there can be no loss of momentum or energy. Therefore, the following relations must hold:[39]

$$\langle F(x,v)\rangle+\frac{1}{2}\left\langle\frac{\partial G^2(x,v)}{\partial v}\right\rangle=0 \tag{17}$$

and

$$\langle G^2(x,v)\rangle+\langle vF(x,v)\rangle+\frac{1}{2}\left\langle v\frac{\partial G^2(x,v)}{\partial v}\right\rangle=0 , \tag{18}$$

where $\langle\ \rangle$ represent averages taken over the phase space. Assuming

$$\int_{-\infty}^{\infty}G^2(x,\pm\infty)P(x,\pm\infty)dx=0 ,$$

inserting $F(x,v)$ from Eq. (16), and integrating by parts, Eqs. (17) and (18) become

$$\langle vG^2(x,v)\rangle+\langle v^2\rangle\left\langle G^2(x,v)\frac{\partial P(x,v)}{\partial v}\right\rangle=0 \tag{19}$$

and

$$\langle v^2G^2(x,v)\rangle+\langle v^2\rangle\left\langle vG^2(x,v)\frac{\partial P(x,v)}{\partial v}\right\rangle=0 . \tag{20}$$

These conditions can be satisfied by assuming that $P(x,v)$ is canonical. Therefore, Eq. (16) is a reasonable assumption for the Brownian motion case where the velocity distribution is almost exactly Maxwellian.

Alkemade, van Kampen, and MacDonald[40] have discussed nonlinear Brownian motion utilizing a generalized Rayleigh model. In order to study the effect of the nonlinearity on the fluctuation for different orders of approximation, they systematically expanded the master equation in reciprocal powers of the piston mass. Under the assumption that the Gaussian distribution is always a steady-state solution of these equations, they were able to obtain an *a priori* relation between the stochastic properties of the fluctuations and the so-called "macroscopic" or "phenomenological" parameters that define the system. The relations thus derived are very similar to Eq. (16). However, their analysis is not necessarily applicable to condensed phase dynamics, where collisions with the piston are more or less sticky. If, at the same time, the molecular mass is not negligible in comparison with the piston mass, then the piston is neither Markovian in behavior nor weakly coupled to its environment. Furthermore, if the piston mass is smaller than the mass of the interacting molecules, the expansion of the master equation becomes divergent.

When the above situations occur, there is no guarantee that the assumption of the canonical distribution and, consequently, the analysis is still valid. As a matter of fact, in non-Markovian processes, $F(x,v)$ should be understood to be an effective friction. It is frequency dependent and certainly relies on the relative time scales of the motions of the test and host particles. This time-scale difference is obviously not only related to the mass ratio of the two components but also to various orders of derivatives of the external force to which the test particle is subjected. If the applied potential is sufficiently steep, the test particle gains an instantaneous acceleration (or deacceleration) with a large systematic component and changes its state very rapidly. On the other hand, the neighboring host particles, whose motion is not directly affected by the external force, cannot foresee, and do not have time to respond to, such changes. In other words, information about the external force cannot be perfectly transmitted to the host particles. As a result, the dynamical process becomes microscopically irreversible, and the effective friction can no longer be wholly determined by fluctuations created by these heavy neighboring host particles. This causes a breakdown of the generalized fluctuation-dissipation relation given by Eq. (16), at least for some short-lived states. Therefore, the steep external potential plays a critical role in destroying the normal Maxwell-Boltzmann distribution of the small test particle. A discussion about the influence on the velocity distribution of a systematically imposed external field has been given in a previous molecular-dynamics study.[41] While the mean kinetic energy and the mean momentum of test particles are conservative quantities when averaged over the entire phase space, or for a long time duration, as indicated by Eqs. (19) and (20), they may not be conserved for every individual configuration. Moreover, in these ultrafast dynamical processes, the influence of the neighboring host particles on the test particle is also time scale dependent. Consequently, the modified external force is no longer conservative. In other words, the necessary conditions for Eq. (15) to have a canonical solution can in no way be satisfied. This strongly suggests that the distribution function of a nonlinear non-Markovian system is generally noncanonical.

IV. STEADY-STATE DISTRIBUTION FUNCTION IN VELOCITY SPACE

From the above discussion it becomes clear that the necessary and sufficient condition for a subensemble of test particles to achieve a canonical distribution depends on the validity of the generalized fluctuation-dissipation relation Eq. (16). This relation is usually assumed on the basis of a Maxwell-Boltzmann distribution. However, it may break down in ultrafast dynamical processes where the neighboring host particles do not communicate well with the rapidly changing test-particle states. The normal Maxwell-Boltzmann distribution is a consequence of the central limit theorem,[42] which assumes that the system be composed of a very large number N of mutually independent variables. If these variables are not independent, but each is correlated to at most only n other variables and $n \ll N$, then the theorem can still be used.[43] When a small test particle is subjected to a steep external potential that is not seen by the neighboring host particles, the motion of the test particle is not purely chaotic.[44] Some variables become correlated with one another. If the systematic force is strong compared with the random force, the motion of the test particle becomes partially predictable. A large proportion of the variables thus are mutually dependent. On the other hand, in the short time duration of the dynamical process of the test particle, the cage cannot be fully mixed with its heat bath. The test particle is in contact with only a few host particles. The condition required for the validity of the central limit theorem is broken down, and the ensemble can no longer be viewed as being canonical.

In the following, we discuss several special cases.

Case I. Constant friction parameter ζ, $F(x,v) = -\zeta v/M$, and $E = -1/M \partial U(x)/\partial x$. In this case the fluctuation-dissipation relation Eq. (16) is simplified to $G^2 = k_B T\zeta/M^2$. Under these assumptions, Eq. (15) describes ordinary Brownian motion. It is easy to show that the Maxwell-Boltzmann distribution

$$P_{\mathrm{MB}}(x,v) = P_0 \exp\left[-\frac{U(x)+(M/2)v^2}{k_B T}\right] \tag{21}$$

then satisfies this equation.

Case II. Space-dependent friction parameter:

$$F(x,v) = -\zeta(x)v/M ,$$

$$E = -\frac{1}{M}\partial U(x)/\partial x ,$$

and

$$G^2(x) = k_B T\zeta(x)/M^2 .$$

Equation (15) reduces to the linear Fokker-Planck equation with position-dependent friction. The steady-state solution of this equation is again canonical.

In order to obtain the velocity distribution as an explicit function, we rewrite the steady-state nonlinear Fokker-Planck equation in velocity space,

$$\frac{\partial}{\partial v}[\gamma(v)P(v)] = -\frac{1}{2}\frac{\partial^2}{\partial v^2}[C^2(v)P(v)] \; . \tag{22}$$

The general solution of Eq. (22) is

$$P(v) = \frac{P_0}{C^2(v)}\exp\left[-2\int\frac{\gamma(v)}{C^2(v)}dv\right] , \tag{23}$$

where P_0 is a normalization constant. For a linear system, $\gamma(v)=\zeta v$ and $C(v)=(2\zeta\langle v^2\rangle)^{1/2}$. Defining the reduced velocity $V\equiv v/\langle v^2\rangle^{1/2}$, we obtain the Maxwell distribution

$$P(v)\propto P_0 e^{-V^2/2} , \tag{24}$$

in agreement with case I.

If, on the other hand, the system is nonlinear, but, following the integration in configurational space, the systematic friction and random force are related by

$$\gamma(v)/v = \alpha C^2(v)/\langle v^2\rangle , \tag{25}$$

then the velocity distribution has a noncanonical form,

$$P(v) = \frac{P_0}{C^2(v)}e^{-\alpha V^2} , \tag{26}$$

where α is chosen so that $\langle v^2\rangle = k_B T/M$. Therefore, the total kinetic energy is conserved. Equation (25) is a direct extension of the ordinary fluctuation-dissipation theorem. To conserve the total momentum, $C^2(v)$ must be an even function of v. Consequently, $\gamma(v)$ is an odd function of v.

In order to gain a concrete feeling about how the nonlinearity in the friction affects the distribution function, we further consider two specific forms of the friction. The first is

$$\gamma(V) = \zeta V(1+\chi|V|) , \tag{27}$$

where χ is a measure of the strength of the nonlinearity. Equation (27) corresponds to an increasing friction coefficient as the velocity of the test particle increases. Substituting Eq. (27) into Eq. (26) and taking the relation Eq. (25) into account, we obtain the distribution function in velocity space,

$$P(V) = \frac{A}{1+\chi|V|}e^{-\alpha V^2} , \tag{28}$$

where A is a normalization constant.

Figure 1 plots the velocity distributions from Eq. (28) for various χ. Distortion of the Maxwellian distribution function becomes more severe as the nonlinearity becomes an important factor. In the limiting case of $\chi=0$, Eq. (28) reduces to the Maxwellian form. All the broken curves displayed in Fig. 1 have higher peaks in the low-velocity limit and higher tails in the high-velocity range. These kinds of distributions have been previously observed in molecular-dynamics computer computations of low-mass particles or ions in heavy atom crystalline lattices.[14] The high tails of the distribution function reflect a higher abundance of "hot" particles compared with that given by the canonical distribution at the same temperature. In particular, if we denote as N the number of particles having kinetic energies greater than $100kT$, then

$$N(\chi=0.3186)/N(\chi=0)\approx 4\times 10^3 ,$$

$$N(\chi=0.5990)/N(\chi=0)\approx 3.5\times 10^5 ,$$

and

$$N(\chi=0.8591)/N(\chi=0)\approx 6.3\times 10^6 .$$

These contributions are certainly significant, particularly for highly activated barrier crossing or in quantum tunneling problems where the distribution tails play a dominant role.[45] To see the tail effects more clearly, Fig. 2 il-

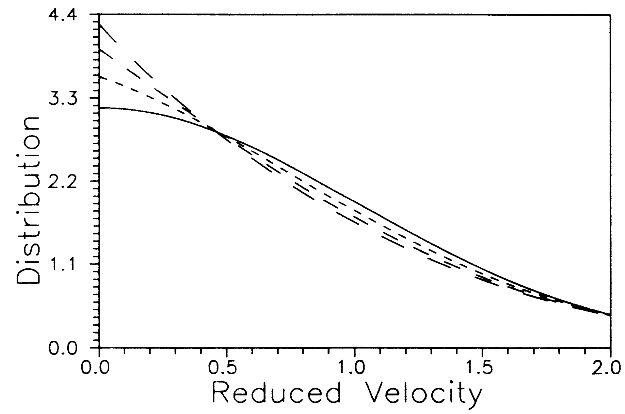

FIG. 1. Velocity distribution functions for nonlinear systems described by Eq. (28). The solid curve, corresponding to $\chi=0$, represents the Maxwell distribution (same for Figs. 2 and 3). The three dashed curves correspond to $\chi=0.3186$, 0.5990, and 0.8591 and, consequently, $\alpha=0.4060$, 0.3588, and 0.3281, in the order of increasing length of dash.

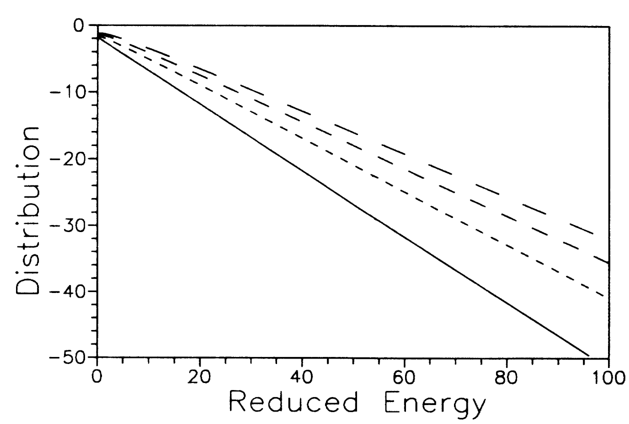

FIG. 2. Same as for Fig. 1, but the distribution functions are plotted on a logarithmic scale vs reduced energy V^2.

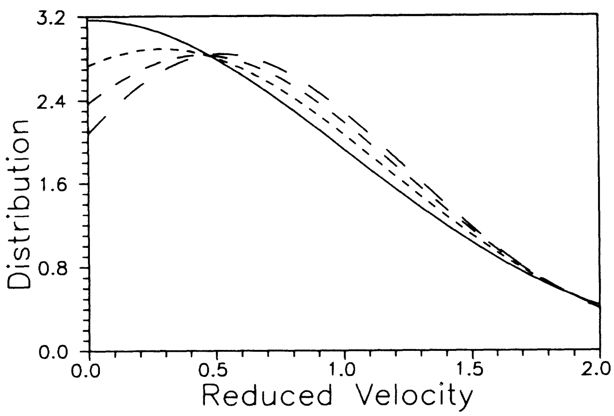

FIG. 3. Velocity distribution functions for nonlinear systems described by Eq. (30). The three dashed curves correspond to $\chi=0.3897$, 0.8233, and 1.2789 and, consequently, $\alpha=0.6073$, 0.6779, and 0.7270, in the order of increasing length of the dash.

lustrates the distributions on a logarithmic scale.

The second type of friction to be discussed has the form

$$\gamma(V)=\frac{\xi V}{1+\chi|V|}, \tag{29}$$

which has also been found in a recent molecular-dynamics (MD) calculation.[18] In this case the friction coefficient decreases with V. Substitution of Eq. (29) into Eq. (26), together with Eq. (25), yields

$$P(V)=\frac{2\alpha(1+\chi|V|)}{\sqrt{\alpha\pi}+\chi}e^{-\alpha V^2}. \tag{30}$$

Figure 3 shows that the deviation from the Maxwell distribution increases with χ. In both of the above cases the nonlinear velocity dependence of the friction in Eqs. (27) and (29) prevents the Maxwellian distribution from occurring.

Equations (15) and (22) were derived on the basis of Ĭto's definition of stochastic integration.[19] According to this definition,

$$\int_0^\tau \phi(w(\tau'),\tau')dw(t') = \lim_{\Delta\to 0}\sum_{i=0}^{N-1}\phi[w(\tau_i),\tau_i][w(\tau_{i+1})-w(\tau_i)], \tag{31}$$

where

$$w(\tau)=\int_t^{t+\tau}\Gamma(t')dt' \tag{32}$$

and

$$\Delta=\max(\tau_{i+1}-\tau_i),\quad 0=\tau_0<\tau_1<\cdots<\tau_n=\tau. \tag{33}$$

When Stratonovich's definition,[22]

$$\int_0^\tau \phi(w(\tau'),\tau')dw(\tau') = \lim_{\Delta\to 0}\sum_{i=0}^{N-1}\phi\left[\frac{w(\tau_i)+w(\tau_{i+1})}{2},\frac{\tau_i+\tau_{i+1}}{2}\right]\times[w(\tau_{i+1})-w(\tau_i)], \tag{34}$$

is applied, Eq. (22) has the form

$$\frac{\partial}{\partial v}[\gamma(v)P(v)]=-\tfrac{1}{2}\frac{\partial}{\partial v}C(v)\frac{\partial}{\partial v}[C(v)P(v)]. \tag{35}$$

Even though Eq. (35) has a form different from Eq. (22), it would have been equally possible to carry through the discussion in Sec. IV using the Stratonovich definition of stochastic integration.

From the above discussion we can draw the conclusion that the steady-state distribution of a nonlinear system in velocity space is generally non-Maxwellian. This conclusion is consistent with a variety of recent computer MD results,[1,12–14,41,46] which show systematic deviations from Maxwellian distributions for subensembles of low-mass particles when subjected to large forces in a heat bath composed of heavy host particles.

V. DISCUSSION AND CONCLUSIONS

A question regarding the results obtained above may be raised. It is true that the steady-state solution of Eq. (15) or Eq. (22) is generally noncanonical, but it may still be argued that dynamical processes for a nonlinear system may not be governed by the stochastic Eq. (1). One may also ask whether the probability density is a solution of the nonlinear Fokker-Planck Eq. (14) with the given initial probability and boundary conditions. In fact, Ferrario and his co-workers[47,48] have shown that equilibrium non-Gaussian properties may cause a deviation of the decay of excited states from a linear response behavior, which seems to indicate that a velocity-dependent friction coefficient may break down the ordinary Fokker-Planck picture. In other words, the relaxation does not follow the normal fluctuation-dissipation relation. Assumptions were certainly necessary in deriving the nonlinear Fokker-Planck equation in Sec. II. Such approximations, however, are necessary since any dynamical process involving nonlinear and non-Markovian effects is too complicated to be solved exactly using *ab initio* analytic methods. The many-body classical dynamics, which lies behind these complicating effects, is the reason that one must generally rely on computer methods to study these distributions.

The ordinary Fokker-Planck equation is frequently used to derive the Maxwell-Boltzmann distribution function. Deviations from the Maxwell-Boltzmann distribution in nonlinear systems cannot depend on the validity of the ordinary Fokker-Planck picture. On the contrary, the deviations are a necessary consequence of the breakdown of this picture. Our above discussion is based on a nonlinear Fokker-Planck equation, which reduces to the ordinary Fokker-Planck equation, with an attendant canonical distribution, in the Brownian motion limit. In particular, the fluctuation-dissipation relation becomes inappropriate when the friction coefficient is velocity dependent. This is exactly equivalent to the discovery of Ferrario *et al.*[47,48] and others.[49,50]

In spite of these many-body complications, an intuitive picture of these processes may be constructed.[18] Because of the nonlinear feature, the friction parameter is a function of the velocity of the test particle, and it becomes intuitively obvious, whatever analysis is performed, that the distribution function cannot generally be canonical. As an example, the theory of gas dynamics tells us that when an object moves supersonically, its velocity being greater than the mean thermal velocity of the gas particles, the friction force experienced by this object increases dramatically. Local turbulence and shock waves are formed[51] in a random manner. This nonlinear effect is caused by the slow response of the gas environment. This effect is expected to persist in microscopic regimes, particularly in the condensed phase. A test particle, whose mass is small relative to the host particles and is subjected to a strong external force, behaves like a supersonic object. The situation caused by such nonlinearities may be even more complicated because of the non-Markovian effects, which introduce a frequency dependence on the friction. Though the whole system remains in a state of thermal equilibrium, local nonequilibrium or, more precisely, local partial order may exist because of continuous perturbations in the interfacial region separating the test particle from its heat bath. This effect may be especially important when the low-mass test particle is crossing or climbing a sharp potential barrier and is thus subjected to a strong force field.

Fluctuations in nonlinear systems can propagate unstable barrier dynamics to other regions and transfer information from short- to long-time dynamics.[52] In these situations the fluctuation-dissipation relation is generally not applicable, reminiscent of the case where a liquid is subjected to a rapidly oscillating external field[45,46] or to a rapidly moving surface.[53] While Eq. (16) is the necessary and sufficient condition that a linear system possesses a canonical distribution, it is not a law of nature. Its existence has never been proven by any theory or experiment. As a matter of fact, our previous MD calculations have already raised strong suspicions about its validity for the special cases discussed in this and previous papers.

Moreover, couplings among different modes of the system often introduce additional contributions to the effective potential, which then perturb the Fokker-Planck equation.[54] Obviously, not all of these complications involved in a nonlinear dynamical process are contained in Eqs. (15) or (22). However, there is no reason to believe that these extra complications would sweep away the noncanonical behavior, since this behavior is a necessary consequence of the nonlinearity, which has already been embodied in Eq. (14).

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