Nonlinear dissipation effect in Brownian relaxation

A. V. Plyukhin and A. M. Froese
Department of Physics and Engineering Physics, University of Saskatchewan, Saskatoon, Canada SK S7N 5E2
(Received 8 May 2007; published 14 September 2007)

In an ensemble of noninteracting Brownian particles, a finite systematic average velocity may temporarily develop, even if it is zero initially. The effect originates from a small nonlinear correction to the dissipative force, causing the equation for the first moment of velocity to couple to moments of higher order. The effect may be relevant when a complex system dissociates in a viscous medium under strongly nonequilibrium conditions.

DOI: 10.1103/PhysRevE.76.031121 PACS number(s): 05.40.Jc, 05.20.Dd, 05.60.Cd, 05.70.Ln

I. INTRODUCTION

Stochastic processes with nonlinear dissipation are ubiquitous and challenging to describe theoretically. Mathematical difficulties related to the nonlinearity of a corresponding stochastic differential equation are only part of the problem. A more subtle challenge is to establish fluctuation-dissipation relations which, in contrast to linear processes, cannot be phenomenologically justified [1]. Instead, a truly dynamical approach is usually needed when the dissipation force and statistical properties of the noise are deduced directly from underlying dynamics, rather than postulated *ad hoc*. Conventional assumptions of a phenomenological approach in the context of nonlinear response may be misleading. For instance, the assumption of Gaussian random force in the Langevin equation leads to the Fokker-Planck equation of second order, regardless of whether the dissipation force is linear or not. On the other hand, a kinetic approach leads to the second-order Fokker-Planck equation for a Brownian particle only in the lowest order of a perturbation technique, while in general the equation involves derivatives of order higher than 2 [1–4].

Nonlinear stochastic processes are usually associated with far-from-equilibrium dynamics. If a system is close to equilibrium, nonlinear dissipation usually appears as small corrections to the dominating linear friction and in many cases may be safely neglected. However, under certain circumstances, the contribution of linear terms may vanish identically or be strongly reduced. Then nonlinear dissipative effects come into the limelight and give rise to a variety of new physical effects.

An example, which has received particular attention in recent years, is the rectification of thermal fluctuations in the so-called adiabatic piston problem [5]. The problem concerns Brownian motion of a piston which separates a gas-filled cylinder into two compartments with different temperatures and gas densities. If the pressure on both sides of the piston is the same, the linear theory predicts zero average velocity of the piston, while the correct result is that the piston acquires a systematic average speed in the direction of the compartment with higher temperature. The effect may be readily explained using the Langevin equation with a small nonlinear correction, quadratic in the piston's velocity, to the dissipative force [6]. The effects of nonlinear friction on the Kramers relaxation rate were studied recently in [7], and in the context of rectification of thermal fluctuations in [8]. The aim of this paper is to draw attention to another problem—perhaps the simplest one—where nonlinear corrections to the dissipative force are essential and lead to a result qualitatively different from predictions of the linear response theory.

II. THE PROBLEM

Consider an ensemble of noninteracting Brownian particles diffusing in one dimension. The particles are identical but may have different initial velocities. Suppose the distribution of initial velocities $f_0(V)$ is similar to Fig. 1: it is asymmetric but in such a way that the average initial velocity of the ensemble is zero,

$$\langle V(0)\rangle = \int dV f_0(V) V = 0. \tag{1}$$

The question is whether $\langle V(t)\rangle$ for later time $t>0$ is positive, negative or zero?

Contrary to its apparent simplicity, the question requires going beyond the standard theory of Brownian motion based on the linear Langevin equation and the corresponding second-order Fokker-Planck equation. Both approaches give the linear relaxation law $\partial_t\langle V(t)\rangle = -\gamma\langle V(t)\rangle$, and therefore predict that if the average velocity $\langle V(t)\rangle$ is zero initially, it remains so later on. The prediction is incorrect as one can see from the result of numerical experiment presented in Figs. 2 and 3. On the time scale of order $\tau = 1/\gamma$, a finite average

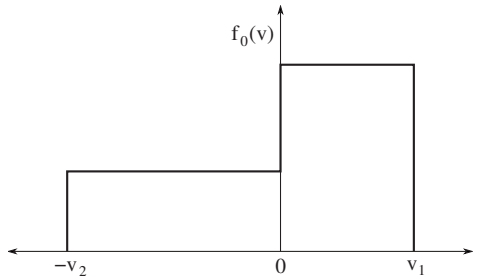

FIG. 1. Initial velocity distribution for an ensemble of Brownian particles, discussed in the paper. The widths and heights of the distribution's wings are chosen so that the average initial velocity $\langle V\rangle$ of the ensemble is zero, but the higher moments $\langle V^n\rangle$ are finite.

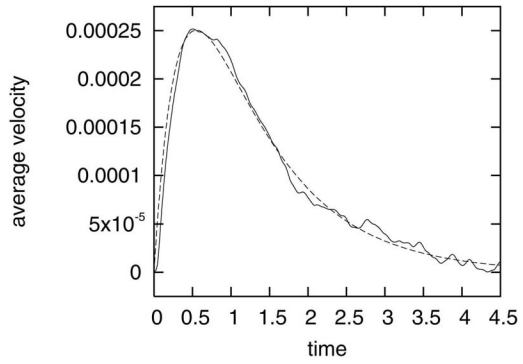

FIG. 2. Simulation (solid) and theoretical (dashed) curves for the time dependence of the average velocity $\langle V(t)\rangle$ of an ensemble with an initial distribution similar to Fig. 1. The molecule-particle mass ratio parameter is $\lambda=\sqrt{m/M}=0.1$. The widths of the distribution wings are $V_1=1/4$ and $V_2=1/2$. Velocity is in units $v_T=\sqrt{kT/m}$ and time is in units $\tau=(\lambda^2\gamma_0)^{-1}$.

velocity develops in the direction corresponding to the higher, narrower wing of the initial distribution, the right wing in Fig. 1. The particles moving to the right, have lower average initial speeds but are more numerous and give a larger contribution to $\langle V(t)\rangle$ than the particles moving to the left. The victory of the larger team of slower runners does not last very long: after reaching a peak at roughly one-half of τ, the function $\langle V(t)\rangle$ decays exponentially with the characteristic time of order τ. Yet, this transient time may be sufficiently long to cause measurable physical consequences.

The problem may be considered as a strongly idealized model of the dissociation of a complex system in a viscous medium. As will be shown, the effect may be significant only under nonequilibrium conditions when the initial energies of the particles are much higher than kT. This is a typical situation for many phenomena, including chemical reactions, the Coulomb fragmentation of multiply charged clusters and droplets, and processes involving fragmentation of complex molecular aggregates. If the system is initially at rest and all dissociated fragments have the same mass, Eq. (1) is just the condition of conservation of total momentum. For a system

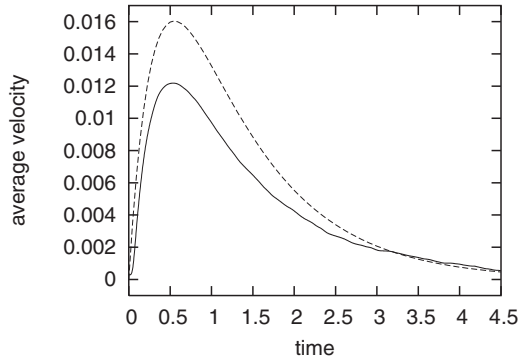

FIG. 3. Same as for Fig. 2, but for an initial velocity distribution with widths $V_1=1$ and $V_2=2$ (in units v_T) for the right and left wings, respectively. The corresponding ensemble is far from equilibrium, $V_1, V_2>\lambda$. The theoretical (dashed) curve, given by Eq. (16) overestimates the result of the simulation (solid curve).

in vacuum, the speed of the center of mass of fragments remains zero after dissociation. However, if dissociation happens in a viscous medium, the average velocity is temporarily finite, and the center of mass changes position even if the fragments are identical and have the same diffusion coefficients.

To account for this transient drift effect, one must take into account that the equation for the first moment of the velocity $\partial_t\langle V(t)\rangle=-\gamma\langle V(t)\rangle$ is closed only in lowest order in the small parameter $\lambda^2=m/M$, the mass ratio of a molecule (m) to a Brownian particle (M). At higher orders in λ, the first moment $\langle V(t)\rangle$ is coupled to the moments of higher orders $\langle V^n(t)\rangle$. If initially the first moment is zero, but the higher moments are finite, as for the initial distribution in Fig. 1, then $\langle V(t)\rangle\neq 0$ for $t>0$. To describe the problem quantitatively, one may adopt the approach based on either the Langevin equation for $V(t)$ or the Fokker-Planck equation for the distribution function $f(V,t)$. In what follows, we discuss both approaches and outline details of the numerical simulations presented in Figs. 2 and 3.

III. THEORY: LANGEVIN EQUATION

The microscopic derivation of the Langevin equation beyond the lowest order in $\lambda=\sqrt{m/M}$ was discussed in [10,11]. Here we outline the results and apply them to our problem. An appropriate perturbation technique is guided by anticipation that the velocity V of a Brownian particle is typically about λ times that of a molecule of the surrounding bath. This suggests working with the scaled velocity of the particle $v=\lambda^{-1}V$, which is expected to be of the same order as the thermal velocity of molecules v_T,

$$v=\lambda^{-1}V\sim v_T=\sqrt{\frac{kT}{m}}. \tag{2}$$

The microscopic equation of motion for the scaled velocity $v=V/\lambda$ (or for the scaled momentum $p=mv=\lambda MV$) involves the small parameter λ explicitly, and therefore is convenient for a perturbation analysis. The equation is coupled with bath degrees of freedom which may be "projected out" with an appropriate projection operator technique [9–11]. As a result, to lowest order in λ, one obtains the conventional linear Langevin equation

$$\dot{v}(t)=-\lambda^2\gamma_0 v(t)+\frac{\lambda}{m}F_0(t), \tag{3}$$

where the zero-centered fluctuating force $F_0(t)$ is related to the dissipation constant γ_0 through the fluctuation-dissipation relation

$$\gamma_0=\frac{1}{mkT}\int_0^\infty dt\langle F_0(0)F_0(t)\rangle. \tag{4}$$

The linear Langevin equation (3) leads to the following equations for the velocity moments [12]

$$\frac{d\langle v^n\rangle}{dt} = -\lambda^2 n\gamma_0\langle v^n\rangle + \lambda^2 n(n-1)\gamma_0 v_T^{-2}\langle v^{n-2}\rangle. \quad (5)$$

As discussed, these equations, obtained in lowest order in λ^2, are not sufficient for our purpose: the closed equation for the first moment $\partial_t\langle v\rangle = -\lambda^2\gamma_0\langle v\rangle$ clearly cannot account for the behavior presented in Fig. 2.

The next approximation for the Langevin equation involves a correction of order λ^4 and, for a homogeneous bath, has the form [10,11]

$$\dot{v}(t) = -\lambda^2\gamma_1 v(t) - \lambda^4\gamma_2 v^3(t) + \frac{\lambda}{m}F(t). \quad (6)$$

Besides the presence of the nonlinear dissipative term $-\lambda^4\gamma_2 v^3$, this equation differs from the linear one (3) by a higher order correction to the linear damping, and the fluctuating force

$$\gamma_1 = \gamma_0 + O(\lambda^2), \quad F(t) = F_0(t) + O(\lambda). \quad (7)$$

The explicit form of these corrections is not necessary for the purpose of this paper. The fluctuation-dissipation relation for the nonlinear dissipation coefficient γ_2 involves rather complicated correlation functions [11], and to the best of our knowledge, cannot be established phenomenologically. This is in contrast to the conventional fluctuation-dissipation relation (4) for the linear dissipation coefficient γ_0 which can be obtained using the prediction of equilibrium statistics $\langle v^2(t)\rangle \to kT/m$ in the long time limit.

Since the fluctuating force is zero-centered to any order in λ, it follows from Eq. (6) that to order λ^4 the first moment is coupled to the third one,

$$\frac{d}{dt}\langle v\rangle = -\lambda^2\gamma_1\langle v\rangle - \lambda^4\gamma_2\langle v^3\rangle. \quad (8)$$

One must substitute here $\langle v^3(t)\rangle$ obtained in the lowest order in λ which according to (5) satisfies the equation

$$\frac{d}{dt}\langle v^3\rangle = -3\lambda^2\gamma_0\langle v^3\rangle + 6\lambda^2\gamma_0 v_T^{-2}\langle v\rangle. \quad (9)$$

Our interest is the solution of Eqs. (8) and (9) with the initial conditions

$$\langle v(0)\rangle = 0, \quad \langle v^3(0)\rangle \neq 0. \quad (10)$$

Clearly, in this case $\langle v(t)\rangle \sim \lambda^2$, so that the last term in the Eq. (9) can be neglected. Then, to order λ^2, the third moment decays exponentially $\langle v^3(t)\rangle = \langle v^3(0)\rangle e^{-3\lambda^2\gamma_0 t}$. Substituting this into Eq. (8) and recalling that $\gamma_1 = \gamma_0 + O(\lambda^2)$, one obtains

$$\langle v(t)\rangle = -\lambda^2\frac{\gamma_2}{2\gamma_0}\langle v^3(0)\rangle e^{-\lambda^2\gamma_0 t}(1 - e^{-2\lambda^2\gamma_0 t}). \quad (11)$$

Recall also that v is the scaled velocity, $v = V/\lambda$. For the true velocity V the result formally does not involve the small factor λ^2,

$$\langle V(t)\rangle = -\frac{\gamma_2}{2\gamma_0}\langle V^3(0)\rangle e^{-\lambda^2\gamma_0 t}(1 - e^{-2\lambda^2\gamma_0 t}). \quad (12)$$

However, one should keep in mind that the whole procedure applied above implies that $V \sim \lambda v_T$. This puts a constraint on the width Δ of the initial distribution $f_0(V)$,

$$\Delta < \lambda v_T. \quad (13)$$

Under this constraint $\langle V^3(0)\rangle$ is small and cannot exceed order $\lambda^3 v_T^3$.

For a far-from-equilibrium ensemble the above theory, strictly speaking, is not applicable. Yet, as one observes from Fig. 3, Eq. (12) predicts qualitatively correct behavior also for a "hot" initial distribution with $\Delta \sim v_T$. In these cases the first moment given by Eq. (12) is not small, $\langle V(t)\rangle \sim \lambda^0$.

According to the result (12), the first moment $\langle V(t)\rangle$ reaches the maximum at time $t_0 = (\ln 3/2)\tau \approx 0.55\tau$ where $\tau = \lambda^{-2}\gamma_0^{-1}$, which is seen in Fig. 2 to be in agreement with numerical simulation. To make more qualitative predictions, one needs an explicit expression for the ratio of the dissipative coefficients γ_2/γ_0, which is the prefactor in Eq. (12). Since a general result for this ratio is unknown, in the rest of the paper we discuss a specific model of Brownian motion—the Rayleigh model—for which our numerical experiment is carried out, and for which analytical results are available.

In the original Rayleigh model [2–4], a heavy Brownian particle moves in one dimension interacting with bath molecules through instantaneous elastic collisions, while molecules do not interact with one another at all. For this model the Fokker-Planck equation for the distribution function $f(V,t)$ can be readily obtained, as will be discussed in the next section. However, due to the singular character of the hard-wall potential, the derivation of a nonlinear Langevin equation for the original Rayleigh model is not quite straightforward. One may instead work with a generalized Rayleigh model where the particle interacts with molecules through a continuous repulsive potential. For a low density of bath molecules (when multiple collision are negligible) and for the time scale longer than the collision time τ_c, the original and generalized models are expected to give the same results. Using the generalized Rayleigh model, one obtains the following explicit expressions for the dissipative coefficients [11]:

$$\gamma_0 = \frac{8}{\sqrt{2\pi}}nSv_T, \quad \gamma_2 = \frac{4}{3\sqrt{2\pi}}nSv_T^{-1}. \quad (14)$$

Here n is the concentration of molecules, S is the particle's cross section, and $v_T = \sqrt{kT/m}$ is the thermal velocity of molecules in the bath. It is tempting to assume that the relation

$$\frac{\gamma_2}{\gamma_0} = \frac{1}{6}v_T^{-2} = \frac{m}{6kT}, \quad (15)$$

which follows from (14), is in fact general but we leave this conjecture for further studies. Substituting (15) into Eq. (12), one finally obtains

$$\langle V(t)\rangle = -\frac{m}{12kT}\langle V^3(0)\rangle e^{-\lambda^2\gamma_0 t}(1-e^{-2\lambda^2\gamma_0 t}). \quad (16)$$

Subsequently, the average displacement of the ensemble is

$$\langle X\rangle = \int_0^\infty dt\langle V(t)\rangle = \frac{1}{18}\frac{1}{\gamma_0\lambda^2 v_T^2}\langle V^3(0)\rangle. \quad (17)$$

The result (16) for $\langle V(t)\rangle$, presented in Fig. 2 by dashed lines, is in good agreement with numerical simulation as long as the constraint (13) on the initial distribution is satisfied. Before discussing details of the simulation, let us derive the results using the language of the Fokker-Planck equation.

IV. THEORY: FOKKER-PLANCK EQUATION

For the original Rayleigh model, which involves only binary particle-molecule collisions, the Fokker-Planck equation can be readily obtained using the Kramers-Moyal expansion of the master equation [2–4]. To order λ^2, the equation has a familiar form

$$\frac{\partial f(v,t)}{\partial t} = \lambda^2\gamma_0 D_2 f(v,t), \quad (18)$$

where the second-order differential operator D_2 reads

$$D_2 = \frac{\partial}{\partial v}v + v_T^2\frac{\partial^2}{\partial v^2} \quad (19)$$

and γ_0 is given by (14). This equation corresponds to the linear Langevin equation (3) and produces Eq. (5) for the moments $\langle v^n(t)\rangle$ to order λ^2. The equation of order λ^4 has the form [2,4]

$$\frac{\partial f(v,t)}{\partial t} = \lambda^2\gamma_0 D_2 f(v,t) + \lambda^4\gamma_0 D_4 f(v,t), \quad (20)$$

where the fourth-order differential operator D_4 reads

$$D_4 = -\frac{\partial}{\partial v}v + \frac{1}{6}v_T^{-2}\frac{\partial}{\partial v}v^3 - 2v_T^2\frac{\partial^2}{\partial v^2} + \frac{3}{2}\frac{\partial^2}{\partial v^2}v^2 + \frac{8}{3}v_T^2\frac{\partial^3}{\partial v^3}v + \frac{4}{3}v_T^4\frac{\partial^4}{\partial v^4}.$$

For the first moment, Eq. (20) gives the following equation:

$$\frac{d}{dt}\langle v\rangle = -\lambda^2\gamma_0(1-\lambda^2)\langle v\rangle - \frac{1}{6}\lambda^4\gamma_0 v_T^{-2}\langle v^3\rangle. \quad (21)$$

Recalling the relations (7) and (15), one observes that the above equation is equivalent to Eq. (8) derived from the nonlinear Langevin equation. Therefore, the Fokker-Planck equation (20) gives the same results as the nonlinear Langevin equation (6). Note, however, that the Langevin equation (6) is derived directly from the Liouville equation [11] and is more general than the Fokker-Planck equation (20), which is obtained under the assumption of instantaneous binary collisions. In a general case, the λ^4-order Fokker-Planck equation has additional terms which disappear in the limit of instantaneous collisions [14,15].

V. SIMULATION

In our molecular dynamics simulation, we use the generalized Rayleigh model in which the Brownian particle moves in one dimension interacting with molecules through a finite-range repulsive parabolic potential, while molecules do not interact with one another. In this model, discussed in detail in [11], the particle-molecule collision time τ_c is finite and does not depend on the velocity of the molecule. A characteristic parameter of the model is $N=nSv_T\tau_c$, which is an average number of molecules simultaneously interacting with the particle. In simulation, the linear molecular density nS was chosen to make N of order 1. In this case, multiple particle-molecule collisions are rare, and one can expect that the result should be close to that for the original Rayleigh model with instantaneous binary collisions.

To mimic unbounded diffusion of a particle, we have used two sources of molecules located far from the particle that generate a bath with a Maxwellian velocity distribution and a constant density. The first condition is easily accommodated by selecting incoming molecule velocities from the distribution,

$$\phi(v) = \frac{nSv}{v_T\sqrt{2\pi}}\exp\left(\frac{-v^2}{2v_T^2}\right), \quad (22)$$

while controlling the rate of molecule generation with a Poisson process is one possibility that is consistent with the second condition. With such a velocity distribution, the total flux at each source is $\Phi=\int_0^\infty\phi(v)dv=nSv_T/\sqrt{2\pi}$. The Poisson distribution for the period between molecule injections is then $P(\tau)=\exp(-\Phi t)$, which will maintain an average linear density of nS around the particle.

An ensemble of particles is emulated by performing multiple runs, resetting the system between each run with the new particle initial conditions selected from the appropriate distribution functions, and averaging the results of all runs together. For a symmetric velocity distribution function $f_0(v)$, the simulation reproduced familiar results of linear Brownian motion including the exponential decay of the velocity correlation function on a time scale $t>\tau_c$ and deviation from exponential form for $t<\tau_c$, which is in agreement with the theory developed in [11].

Consider now an asymmetric initial distribution such as that shown in Fig. 1. Let $x=V/v_T$ be the dimensionless velocity of the particle. Also let x_1,x_2 be the widths and c_1,c_2 be the heights of the right and left wings of the distribution $f_0(x)$, respectively. The conditions of normalization $\int dx f_0(x)=1$ and of zero first moment $\int dx f_0(x)x=0$ give

$$c_1x_1 + c_2x_2 = 1, \quad c_1x_1^2 - c_2x_2^2 = 0 \quad (23)$$

and, therefore,

$$c_1 = \frac{x_2}{x_1}\frac{1}{x_1+x_2}, \quad c_2 = \frac{x_1}{x_2}\frac{1}{x_1+x_2}. \quad (24)$$

The theoretical prediction is given by Eq. (16),

$$\langle x(t)\rangle = -\tfrac{1}{12}\langle x^3(0)\rangle e^{-t/\tau}(1-e^{-2t/\tau}), \tag{25}$$

where $\tau=(\lambda^2\gamma_0)^{-1}$, and the initial third moment, according to (24), equals

$$\langle x^3(0)\rangle = \frac{x_1x_2}{4}(x_1-x_2). \tag{26}$$

Recall that the theory outlined in the preceding sections applies under the close-to-equilibrium constraint (13), which requires that x_1 and x_2 must be of order λ or less. Note that for small λ, this condition is not easy to satisfy in simulation. Since $\langle x(t)\rangle \sim \langle x^3(0)\rangle \leqslant \lambda^3$, one needs a very large number of runs (larger than λ^{-6}) to average out fluctuations and find the function $\langle x(t)\rangle$ with reasonable precision. On the other hand, a strongly nonequilibrium ensemble with the initial distribution widths $x_1, x_2 \sim 1$ is easier to simulate since in this case $\langle x(t)\rangle \sim 1$, which requires a relatively small number of runs.

The simulation has been performed for $\lambda=0.1$, $N=nSv_T\tau_c=1$, time step $\Delta t=0.1\tau_c$, and various parameters of the initial two-wing distribution $f_0(x)$ in Fig. 1. Time in Figs. 2 and 3 is given in units of velocity correlation time $\tau=(\lambda^2\gamma_0)^{-1}$ which, according to (14), is related to the collision time τ_c by $\tau_c/\tau=(8/\sqrt{2\pi})\lambda^2 N$.

Figure 2 corresponds to the initial velocity distribution $f_0(x)$ with left and right maximum velocities $x_1=1/4$ and $x_2=1/2$, respectively. This is a close-to-equilibrium ensemble, $x_1, x_2 \sim \lambda$. For this case, Eqs. (24) and (26) give $c_1=8/3$, $c_2=2/3$, and $\langle x^3(0)\rangle=-1/128$. As discussed above, this case requires a large number of runs to minimize relative fluctuations. The presented plot (solid line) is the average over about 5×10^7 runs. Despite still visible fluctuations, the data and theoretical prediction (16) are clearly in good agreement.

Figure 3 corresponds to the distribution with maximum velocities $x_1=1$ and $x_2=2$. In this case, $c_1=2/3$, $c_2=1/6$, and $\langle x^3(0)\rangle=-0.5$. The corresponding ensemble includes "hot" Brownian particles with initial velocities $x>\lambda$ $(V>\lambda v_T)$, so that the major assumption of the theory is not satisfied. It is not surprising then that in this case the theoretical prediction (25) distinctly overestimates the simulation curve. Qualitative theory for a strongly nonequilibrium ensemble remains a challenge.

VI. CONCLUDING REMARKS

In this paper we considered a simple diffusion phenomenon which originates from nonlinear dissipation and requires description beyond the level of the linear response theory. Namely, for an initial distribution with zero mean velocity but nonzero third moment $\langle V^3(0)\rangle$, an ensemble of Brownian particles temporarily acquires a finite mean velocity of order $\langle V^3(0)\rangle/v_T^2$, where v_T is the thermal speed of the bath molecules. Close to equilibrium the effect is very small: for $\langle V^3(0)\rangle \sim \lambda^3 v_T^3$, the net displacement of the ensemble $\langle X\rangle$, according to Eq. (17), is linear in λ and is negligible for all reasonable parameters. On the other hand, under nonequilibrium conditions, when initial energies of the particles are much higher than kT, the effect is not necessarily small. For instance, if $\langle V(0)^3\rangle \sim \lambda^0$, the displacement decreases with the mass ratio, $\langle X\rangle \sim \lambda^{-2}$, and may be comparable with the other characteristic lengths of the problem. Nonequilibrium conditions are relevant, for instance, in the context of the Kramers problem of the escape from a deep potential well when a particle must acquire energy considerably higher than kT to pass over the barrier. It was shown recently in [7], that in this case nonlinear dissipation effects may be of considerable importance. However, we have found, quite expectedly, that for strongly nonequilibrium initial conditions the theory is consistent with numerical simulations only qualitatively.

The nature of the effect discussed in this paper is quite obvious. Referring to the distribution in Fig. 1, one notices that although the average speed of left-moving particles (with $v<0$) is initially the same as that of right-moving particles (with $v>0$), the value of the third velocity moment is higher for the former. Thus, the left-moving particles slow down faster due to the presence of the nonlinear friction term $-\gamma_2 v^3$, and the net drift is positive. However, let us note that despite its simplicity, the problem requires a rather delicate treatment. The results follow immediately from the nonlinear Langevin equation (6), but this equation requires microscopic derivation and cannot be obtained, to the best of our knowledge, via the phenomenological theory of nonlinear Brownian motion [13]. One nontrivial feature of the Langevin equation (6) is that the fluctuating force is non-Gaussian. As a consequence, the corresponding Fokker-Planck equation (20) contains velocity derivatives of order higher than 2. Although Eq. (20) in general does not preserve positivity of the solution, it is found to give a consistent description of the problem. In particular, its stationary solution is Maxwellian, as one can immediately verify. Note that this comforting property holds also in higher orders in λ, at least for the case of instantaneous binary collisions [3,4] (although in general the situation seems less clear [15]).

The key parameter in the problem is the nonlinear dissipation coefficient γ_2. It can be expressed in terms of rather complex correlation functions of the fluctuating force. We are able to calculate it explicitly only for the Rayleigh model where hydrodynamic effects are completely ignored. Note however, that the expression for the average velocity (12) involves γ_2 in the combination γ_2/γ_0. One might speculate that in the general case the ratio γ_2/γ_0 does not differ too much from the relation (15) obtained for the Rayleigh model. With this assumption, one can apply the results for the case of diffusion in a medium with finite viscosity, estimating the velocity relaxation time $\tau=1/\lambda^2\gamma_0$ from the Stokes-Einstein relation $D=(kT/M)\tau=\lambda^2 v_T^2\tau$. If $\langle V^3(0)\rangle \sim v_T^3$, then Eq. (17) gives the ensemble's displacement as $\langle X\rangle \sim 0.1\tau v_T \sim 0.1\lambda^{-2}D/v_T$. For the diffusion coefficient $D\sim 10^{-5}$ cm^2/s (a small molecule in water), $v_T\sim 10^4$ cm/s, and the mass ratio $\lambda^2=10^{-4}$, one estimates $\langle X\rangle \sim 10$ nm, which is the characteristic length scale for many processes including chemical reactions and transport in membrane channels.

ACKNOWLEDGMENT

This work was supported by NSERC.

[1] N. G. van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1992).
[2] N. G. van Kampen, Can. J. Phys. **39**, 551 (1961).
[3] C. T. J. Alkemade, N. G. van Kampen, and D. K. C. MacDonald, Proc. R. Soc. London, Ser. A **271**, 449 (1963).
[4] A. V. Plyukhin, Physica A **351**, 198 (2005).
[5] Ch. Gruber and J. Piasecki, Physica A **268**, 412 (1999); E. Kestemont, C. Van den Broeck, and M. M. Mansour, Europhys. Lett. **49**, 143 (2000); T. Munakata and H. Ogawa, Phys. Rev. E **64**, 036119 (2001).
[6] A. V. Plyukhin and J. Schofield, Phys. Rev. E **69**, 021112 (2004).
[7] M. F. Gelin and D. S. Kosov, J. Chem. Phys. **126**, 244501 (2007).
[8] P. Meurs, C. Van den Broeck, and A. Garcia, Phys. Rev. E **70**, 051109 (2004); C. Van den Broeck, R. Kawai, and P. Meurs, Phys. Rev. Lett. **93**, 090601 (2004); C. Van den Broeck, P. Meurs, and R. Kawai, New J. Phys. **7**, 10 (2005).
[9] P. Mazur and I. Oppenheim, Physica (Utrecht) **50**, 241 (1970); J. M. Deutch and I. Oppenheim, Faraday Discuss. Chem. Soc. **83**, 1 (1987).
[10] H. Mori, H. Fujisaka, and H. Shigematsu, Prog. Theor. Phys. **51**, 109 (1974); J. T. Hynes, R. Kapral, and M. Weinberg, Physica A **81**, 485 (1975).
[11] A. V. Plyukhin and J. Schofield, Phys. Rev. E **68**, 041107 (2003).
[12] W. T. Coffey, Yu. P. Kalmykov, and J. T. Waldron, *The Langevin Equation* (World Scientific, Singapore, 2004).
[13] Yu. L. Klimontovich, Phys. Usp. **37**, 737 (1994); B. Lindner, New J. Phys. **9**, 136 (2007); W. Ebeling, J. Dunkel, U. Erdmann, and S. Trigger, J. Phys.: Conf. Ser. **11**, 89 (2005); J. B. Avalos and I. Pagonabarraga, Phys. Rev. E **52**, 5881 (1995); N. Banai and L. Brenig, Physica A **119**, 512 (1983).
[14] N. van Kampen and I. Oppenheim, Physica A **138**, 231 (1986).
[15] A. V. Plyukhin, Europhys. Lett. **75**, 15 (2006).