Transient Rectification of Brownian Diffusion with Asymmetric Initial Distribution

A.V. Plyukhin and A.M. Froese
Department of Physics and Engineering Physics, University of Saskatchewan, Saskatoon, SK S7N 5E2, Canada
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In an ensemble of non-interacting 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 with conservation of momentum.

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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. 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 two.

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. 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. Some other effects related to the nonlinear dissipation are discussed in recent years.

In the adiabatic piston problem the fluctuation-induced drift originates from nonequilibrium and asymmetry. The current point of view is that these two ingredients are necessary in general for rectification of thermal fluctuations, i.e. for the physical realization of Maxwell’s demon. Asymmetry may be introduced by surroundings, as in the adiabatic piston problem, or by the geometry of the Brownian particle itself. In this paper, our concern is a transient rectification effect originating from asymmetric initial conditions.

II. THE PROBLEM

Consider an ensemble of non-interacting 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: asymmetric but in such a way that the average initial velocity of the ensemble is zero,

$$\langle V(0) \rangle = \int dV f_0(V) V = 0. \quad (1)$$

The question is whether $\langle V(t) \rangle$ for later time $t > 0$ is positive, negative or zero?
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 $v_{th} = \sqrt{kt/m}$ and time is in units $\tau = (\lambda^2 \gamma_0)^{-1}$.

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 $\langle \sigma(t) \rangle = 0$ for $t > 0$ (or for the scaled momentum $\sigma = \lambda M v$). Theoretical (dashed) curves, given by Eq. (10) overestimates the result of the simulation (solid curve).

To account for this transient rectification effect, one has to take into account that the equation for the first moment of the velocity $\sigma = -\gamma \langle V(t) \rangle$ 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 $\lambda$, 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 $\langle V(t) \rangle = 0$ 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 Fig. 2 and Fig. 3.

III. THEORY: LANGEVIN EQUATION

The microscopic derivation of the Langevin equation beyond the lowest order in $\lambda = \sqrt{m/M}$ was discussed recently in detail in [13]. 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 $\lambda$ 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 $v_{th}$,

$$v = \lambda^{-1} V \sim v_{th} = \sqrt{kt/m}. \quad (2)$$

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 $\lambda$ explicitly, and therefore is convenient for a perturbation analysis.
Our interest is the solution of Eqs. (8) and (9) with the initial conditions
\[ \langle v(0) \rangle = 0, \quad \langle v^3(0) \rangle \neq 0. \] (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 \( \lambda^2 \), the third moment decays exponentially \( \langle v^3(t) \rangle = \langle v^3(0) \rangle e^{-\lambda^2 \gamma_0 t}. \)

Substituting this into Eq. (3) and recalling that \( \gamma_1 = \gamma_0 + O(\lambda^2) \), one obtains
\[ \langle v(t) \rangle = -\lambda^2 \frac{\gamma_0}{2\gamma_0} \langle v^3(0) \rangle e^{-\lambda^2 \gamma_0 t}(1 - e^{-2\lambda^2 \gamma_0 t}). \] (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 \( \lambda^2 \),
\[ \langle V(t) \rangle = -\frac{\gamma_0}{2\gamma_0} \langle V^3(0) \rangle e^{-\lambda^2 \gamma_0 t}(1 - e^{-2\lambda^2 \gamma_0 t}). \] (12)

However, one should keep in mind that the whole procedure applied above implies that \( V \sim \lambda v_{th} \). This puts a constraint on the the width \( \Delta \) of the initial distribution \( f_0(V) \),
\[ \Delta < \lambda v_{th}. \] (13)

Under this constraint \( \langle V^3(0) \rangle \) is small and cannot exceed order \( \lambda^3 v_{th}^3 \).

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 \( \Delta \sim v_{th} \). 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 \( \gamma_2/\gamma_0 \), 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, 3, 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 to 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 \( \tau_c \), 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 \([13]\)

\[
\gamma_0 = \frac{8}{\sqrt{2\pi}} n S v_{th}, \quad \gamma_2 = \frac{4}{3\sqrt{2\pi}} n S v_{th}^{-1}. \tag{14}
\]

Here \( n \) is the concentration of molecules, \( S \) is the particle’s cross-section, and \( v_{th} = \sqrt{kT/m} \) is the thermal velocity of molecules in the bath. It is tempting to assume that the relation

\[
\frac{\gamma_2}{\gamma_0} = \frac{1}{6} v_{th}^{-2} = \frac{m}{6kT}, \tag{15}
\]

which follows from \([13]\), is in fact general but we leave this conjecture for further studies. Substituting \([15]\) into Eq. \([12]\), one finally obtains

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

Subsequently, the average displacement of the ensemble is

\[
\langle X \rangle = \int_0^\infty dt \langle V(t) \rangle = \frac{1}{18} \frac{1}{\gamma_0 \lambda^2 v_{th}} \langle V^3(0) \rangle. \tag{17}
\]

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 \([2, 3, 4, 8]\). To order \( \lambda^2 \), the equation has a familiar form

\[
\frac{\partial f(v, t)}{\partial t} = \lambda^2 \gamma_0 D_2 f(v, t), \tag{18}
\]

where the second order differential operator \( D_2 \) reads

\[
D_2 = \frac{\partial}{\partial v} v + v_{th}^2 \frac{\partial^2}{\partial v^2} \tag{19}
\]

and \( \gamma_0 \) 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 \( \lambda^2 \). The equation of order \( \lambda^3 \) has the form \([2, 3]\)

\[
\frac{\partial f(v, t)}{\partial t} = \lambda^2 \gamma_0 D_2 f(v, t) + \lambda^3 \gamma_0 D_4 f(v, t). \tag{20}
\]

where the forth-order differential operator \( D_4 \) reads

\[
D_4 = -\frac{\partial}{\partial v} v + \frac{1}{6} v_{th}^2 \frac{\partial}{\partial v} v^3 - 2 v_{th}^2 \frac{\partial^2}{\partial v^2} v + \frac{3}{2} \frac{\partial^2}{\partial v^2} v^2 + 8 v_{th}^2 \frac{\partial^3}{\partial v^3} v + \frac{4}{3} v_{th}^4 \frac{\partial^4}{\partial v^4}. \tag{21}
\]

For the first moment, Eq. \([20]\) gives the following equation

\[
\frac{d}{dt} \langle v \rangle = -\lambda^2 \gamma_0 (1 - \lambda^2) \langle v \rangle - \frac{1}{6} \lambda^4 \gamma_0 v_{th}^2 \langle v^3 \rangle. \tag{22}
\]

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 \([7]\). Note, however, that the Langevin equation \([10]\) is derived directly from the Liouville equation \([13]\) and is more general than the Fokker-Planck equation \([20]\), which is obtained under the assumption of binary particle-molecule collisions.

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 \([13]\), the particle-molecule collision time \( \tau_c \) is finite and does not depend on the velocity of the molecule. A characteristic parameter of the model is \( N = nS v_{th} \tau_c \), which is an average number of molecules simultaneously interacting with the particle. In simulation, the linear molecular density \( nS \) is 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 Boltzmann distribution

\[
\phi(v) = \frac{nS}{v_{th} \sqrt{2\pi}} \exp \left( -\frac{v^2}{2v_{th}^2} \right), \tag{23}
\]

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 \( \Phi = \int_0^\infty \phi(v) dv = nS v_{th} \sqrt{2\pi} \). The Poisson distribution for the period between molecule injections is then \( P(\tau_m) = \exp(-\Phi t) \), 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 [13].

Consider now an asymmetric initial distribution such as that shown in Fig. 1. Let \( x = V/v_{th} \) 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 \( f_0(v) \), respectively. The conditions of normalization \( \int dx f_0(x) = 1 \) and of zero first moment \( \int dx f_0(x) x = 0 \) give
\[
\begin{align*}
c_1 x_1 + c_2 x_2 &= 1, \quad c_1 x_1^2 - c_2 x_2^2 = 0 \tag{24}
\end{align*}
\]
and therefore,
\[
\begin{align*}
c_1 &= \frac{x_2}{x_1 x_1 + x_2}, \quad c_2 = \frac{x_1}{x_2 x_1 + x_2} \tag{25}
\end{align*}
\]
The theoretical prediction is given by Eq. [12],
\[
\langle x(t) \rangle = -\frac{1}{12} \langle x^3(0) \rangle e^{-t/\tau}(1 - e^{-2t/\tau}) \tag{26}
\]
where \( \tau = (\lambda^2 \gamma_0)^{-1} \), and the initial third moment, according to [25], equals
\[
\langle x^3(0) \rangle = \frac{x_1 x_2}{4}(x_1 - x_2) \tag{27}
\]
Recall that the theory outlined in previous sections applies under the close-to equilibrium constraint [13], which requires that \( x_1 \) and \( x_2 \) must be of order \( \lambda \) or less. Note that for small \( \lambda \), this condition is not easy to satisfy in simulation. Since \( \langle x(t) \rangle \sim \langle x^3(0) \rangle \leq \lambda^3 \), one needs a very large number of runs (larger than \( \lambda^{-6} \)) to average out fluctuations and find the function \( \langle x(t) \rangle \) with reasonable precision. On the other hand, a strongly non-equilibrium 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 \( \lambda = 0.1, N = a S v_{th} \tau_c = 1 \), step size \( \Delta t = 0.1 \tau_c \), 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 [13], is related to the collision time \( \tau_c \) by \( \tau_c / \tau = (8/\sqrt{2\pi}) \lambda^2 N \).

Fig. 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. (25) and (27) 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 \( 5 \times 10^7 \) runs. Despite still visible fluctuations, the data and theoretical prediction [14] are clearly in good agreement.

Fig. 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 \( x > \lambda (V > \lambda v_{th}) \), so that the major assumption of the theory is not satisfied. It is not surprising then that in this case the theoretical prediction [20] distinctly overestimates the simulation curve. Qualitative theory for a strongly non-equilibrium ensemble remains a challenge.

Acknowledgments

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