Brownian motion in a fluctuating medium

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Abstract

A large class of processes describing Brownian motion in a medium with fluctuating viscosity is introduced. It is shown that a process out of this class satisfies detailed balance provided the medium is in equilibrium. Diffusive motion in the presence of fluctuating viscosity is investigated and bounds for the diffusion constant are presented. As a particular example, dichotomous viscosity fluctuations are considered and their influence on a Brownian particle is investigated. An explicit expression for the diffusion coefficient is obtained and analyzed in several limiting cases. © 1998 Published by Elsevier Science B.V.

Based on the seminal works of Smoluchowski, Einstein and Langevin (for the historical development of Brownian motion, see Ref. [1]) the diffusive behavior of an ensemble of Brownian particles suspended in a liquid is understood in terms of the motion of the individual particles. Their persistent irregular motion is caused by the impact of the surrounding liquid which exerts a force on the particle. This force can be subdivided into an average and a fluctuating part $F_{av}$ and $F_{r}(t)$, respectively. On average, the liquid takes away energy from the Brownian particle by decreasing its velocity relative to the liquid. For sufficiently small relative velocities, $v$, this contribution to the force is given by Stokes's formula,

$$F_{av} = -\gamma v,$$

where the friction constant $\gamma = c_{0}\eta R$ is determined by the viscosity $\eta$ of the liquid, a linear size $R$ of the particle and a constant $c_{0}$ given by the geometry of the particle [6]. For a sphere of radius $R$, $c_{0} = 6\pi$, and for a discus of radius $R$ moving perpendicular to its plane, $c_{0} = 16$. When the fluid is in thermal equilibrium, the random part of the force may be assumed to be Gaussian with zero mean value. Its correlation is related to the average force by a fluctuation dissipation theorem,

$$\langle F_{r}(t) F_{r}(s) \rangle = 2k_{B}T \delta(t - s),$$

where $k_{B}$ is the Boltzmann constant and $T$ the temperature of the liquid. Other systematic forces acting on the particle can easily be taken into account. The resulting Langevin equations and equivalent Fokker–Planck equations have been used for modelling many processes in physics, chemistry and other sciences [2,3]. As a particular example we mention a resistively shunted Josephson junction which is biased with a constant current [4]. At high temperatures the phase difference between the macroscopic wave functions across the junction changes in time in the same way as the position of a Brownian particle in a tilted periodic potential. The capacitance of the
junction corresponds to the mass of the Brownian particle and the impedance of the shunt resistor to the friction coefficient.

There are, however, various situations in which this simple Brownian motion picture does not yield an adequate description.

Imagine, for example, a liquid, that is very close to its critical point. The liquid then shows enormous density fluctuations. Since the viscosity is proportional to the density a strongly fluctuating viscosity results which causes fluctuations of the friction coefficient of the Brownian particle. As a second example we mention a Josephson junction with a fluctuating shunt resistor. Also there the coefficient controlling the energy dissipation fluctuates. Further one may consider Brownian particles with short range attractive interactions that may aggregate into clusters. These clusters may further grow but also decompose into smaller clusters and single Brownian particles. In this case, the mass and the geometry change randomly in time and influence the center of mass motion of a cluster in a way that cannot be properly described by a standard Langevin equation. Finally, we note that Robert Brown in his experiments with pollen grains in water in 1828 observed (see Ref. [11, p. 658] “their motion consisting not only of a change of place in the fluid, manifested by alterations in their relative positions, but also not infrequently by a change of form of the particle itself…”

We here will only consider the possibility of a fluctuating friction coefficient. For this class of models we suggest the following extended Langevin equations,

\[ \dot{x} = v, \]
\[ m \dot{v} = -\gamma(z) v - U'(x) + \sqrt{2\gamma(z) k_B T} f(t), \]

where a dot and a prime denote derivatives with respect to time \( t \) and position \( x \), respectively, and where \( f(t) \) is standardized Gaussian white noise, i.e.

\[ \langle f(t) \rangle = 0, \quad \langle f(t) f(s) \rangle = \delta(t-s). \]

We assume that \( z = z(t) \) is an environmental variable which influences the friction coefficient but does neither depend on the state \( (x,v) \) of the Brownian particle nor on the fluctuating force \( f(t) \). In particular this means that we neglect any backreaction of the state of the particle on the environment that would influence the viscosity. We note that the friction coefficient must be non-negative for all realizations of the environmental variable \( z(t) \). For the sake of simplicity we assume a stationary and Markovian time evolution of the environmental variable \( z(t) \). The latter is not very restrictive, since we can always consider a sufficiently large state space for \( z(t) \), i.e. \( z(t) \) may be vector with an appropriate number of components.

Consequently, the total process of the Brownian particle and the environmental fluctuation is Markovian and governed by a master equation of the following type,

\[ \frac{\partial}{\partial t} p(x,v,z; t) = (L_{\gamma(z)} + \hat{A}) p(x,v,z; t), \]

where \( p(x,v,z; t) \) is the joint probability for finding the particle at time \( t \) at \( (x,v) \) and the environmental variable at \( z \), and where \( L_{\gamma(z)} \) is the Fokker–Planck operator of the Brownian particle for a fixed value of the environmental variable \( z \),

\[ L_{\gamma(z)} = -\frac{\partial}{\partial x} v + \frac{\partial}{\partial v} \left( \frac{\gamma(z)}{m} v + \frac{1}{m} U'(x) \right) + \frac{\gamma(z) k_B T}{m^2} \frac{\partial^2}{\partial v^2}. \]

The master operator \( \hat{A} \) describes the dynamics of the environmental variable.

If the environment that causes both the fluctuating forces acting on the Brownian particle and the fluctuations of the friction coefficient is in thermal equilibrium, the process of the environmental variable necessarily must obey detailed balance,

\[ \hat{A} \rho_{\gamma}^z = \hat{\rho}_{\gamma}^z \hat{A}^+, \]

where \( \hat{A}^+ \) denotes the time-reversed backward operator of the \( z \)-process. For the sake of simplicity we have assumed that there are no external fields that transform odd under time reversal with the consequence that the equilibrium probability density of the process \( z(t) \) transforms even under time reversal. In order that detailed balance holds for the total Markov process consisting of the Brownian particle and the environmental variable, the friction coefficient \( \gamma(z) \) must transform even under time reversal,
\[ \gamma(\tilde{z}) = \gamma(z), \quad (8) \]

where \( \tilde{z} = (\varepsilon_1 z_1, \varepsilon_2 z_2, \ldots, \varepsilon_n z_n) \) denotes the time-reversed image of the environmental state \( z \). Here \( \varepsilon_i = \pm 1 \) are the parities of the components \( z_i \) of the environmental state \( z \) under time reversal. One verifies by inspection that the master operator of the total process indeed satisfies the symmetry relation necessary for detailed balance.

\[ (L_{\gamma(z)} + \Lambda) \hat{\rho}^{eq} = \hat{\rho}^{eq}(\tilde{L}_{\gamma(z)}^+ + \tilde{\Lambda}^+), \quad (9) \]

where \( \hat{\rho}^{eq} \) is the multiplicative operator with the joint equilibrium probability density \( \rho^{eq}(x, v, z) \) and \( \tilde{L}_{\gamma(z)}^+ \) denotes the time-reversed backward operator of the Brownian particle with fixed environmental variable \( \tilde{z} \).

\[ \tilde{L}_{\gamma(z)}^+ = -v \frac{\partial}{\partial x} - \left( \frac{\gamma(\tilde{z})}{m} - \frac{1}{m} U'(x) \right) \frac{\partial}{\partial v} + \frac{\gamma(\tilde{z}) k_B T}{m^2} \frac{\partial^2}{\partial v^2}. \quad (10) \]

The equilibrium density of the total process is given by the product of the Maxwell–Boltzmann distribution of the Brownian particle and the equilibrium density of the environmental variable \( z \).

\[ \rho^{eq}(x, v, z) = Z^{-1} e^{-[\frac{1}{2} m v^2 + U(x)]/(k_B T)} \rho_x^{eq}(z). \quad (11) \]

This expression for \( \rho^{eq}(x, v, z) \) is obviously invariant under time reversal. Together with Eq. (9) this proves our claim that the process as defined by Eqs. (3), (7) and (8) fulfills detailed balance.

In the remainder of this Letter we discuss Brownian motion in the absence of a potential, i.e. for \( U(x) = 0 \). We will concentrate on the behavior of the particle’s mean-square displacement \( \langle x^2(t) \rangle \) in the limit of long times \( t \). In this context the behavior of the long-time limit of the position-velocity correlation function \( \lim_{t \to \infty} \langle x(t) v(t) \rangle \) is important. If it is finite, the particle’s motion is diffusive,

\[ \langle x^2(t) \rangle = 2 D t, \quad (12) \]

where

\[ D = \lim_{t \to \infty} \langle x(t) v(t) \rangle. \quad (13) \]

If the limit vanishes, the particle moves subdiffusively and if it diverges then it moves superdiffusively.

In the absence of a potential the Langevin equation (3) can formally be integrated for an arbitrary environmental processes \( z(t) \). One obtains for the velocity

\[ v(t) = e^{-\Gamma(t)} v_0 + \int_0^t ds e^{-[(\Gamma(t) - \Gamma(s))] \sqrt{\frac{2 \Gamma(s) k_B T}{m}} f(s), \quad (14) \]

where \( v_0 \) is the initial velocity and

\[ \Gamma(t) = \frac{1}{m} \int_0^t ds \gamma(z(s)). \quad (15) \]

Upon a further integration the position at time \( t \) follows. For the velocity-position correlation function one then obtains after some algebra

\[ \langle x(t) v(t) \rangle = \left( v_0^2 - \frac{k_B T}{m} \right) \int_0^t ds \langle e^{-\Gamma(s)} \rangle \]

\[ + \frac{k_B T}{m} \int_0^t ds \langle e^{-\Gamma(s)} \rangle. \quad (16) \]

The averages on the right-hand side have to be performed over all realizations of the environmental process \( z(t) \). Since for each realization of \( z(t) \) the function \( \Gamma(t) \) monotonically increases with \( t \), the first term on the right-hand side can be neglected for large \( t \). Using Eq. (13) the diffusion coefficient becomes

\[ D = \frac{k_B T}{m} \int_0^\infty ds \langle e^{-\Gamma(s)} \rangle. \quad (17) \]

This is one of the main results of this Letter.

By means of Jensen’s inequality \( \langle \exp[\xi] \rangle \geq \exp(\langle \xi \rangle) \), which holds for arbitrary random numbers \( \xi \), a lower bound for the diffusion coefficient results,

\[ D \geq D_0, \quad (18) \]

where

\[ D_0 = \frac{k_B T}{\langle \gamma \rangle}. \quad (19) \]

Here \( \langle \gamma \rangle = \langle \gamma(z(t)) \rangle \) denotes the average friction constant. Hence, the diffusion coefficient in a fluid
with fluctuating viscosity is in general larger than in a fluid with the constant, average viscosity. For subdiffusive motion $D$ must vanish and accordingly, the average friction constant must diverge. Note that this is only a sufficient condition for the occurrence of subdiffusive motion.

An upper bound of the diffusion coefficient may be obtained in the following way. The function $\Gamma(s)$ in (17) may be considered as $s/m$ times the time average of the fluctuating friction $\gamma(z(s'))$ in the time interval $[0, s]$, cf. Eq. (15). Using again Jensen's inequality, we find $\exp[-\Gamma(s)] \leq (1/s) \int_0^s ds' \exp[-c\gamma(z(s'))/m]$. Putting this into the right-hand side of Eq. (17) we may interchange the $s'$-integral and the average over the viscosity fluctuations. Due to the stationarity of the viscosity the resulting average is independent of $s'$ and the remaining $s'$-integral is trivial to do. We find

$$D \leq \frac{k_B T}{m} \int_0^\infty ds \langle e^{-s\gamma(z(s))/m} \rangle. \quad (20)$$

The average is taken over the ensemble of all possible realizations of the random friction coefficient $\gamma = \gamma(z(t))$. Hence, the right-hand side of Eq. (20) may be interpreted as the average diffusion coefficient $D_{q\delta}$ in an ensemble with quenched disorder: Each ensemble member has a constant but random friction with the same distribution as in the dynamic case. Consequently, the diffusion constant in a system with dynamic disorder is generally smaller than for quenched disorder with the same distribution,

$$D \leq D_{q\delta}. \quad (21)$$

Interchanging the average and the time integration we find for $D_{q\delta}$,

$$D_{q\delta} = k_B T \langle \gamma^{-1} \rangle. \quad (22)$$

For superdiffusive motion, $D$ diverges and consequently $\langle \gamma^{-1} \rangle$ must also diverge.

We note that the second moment of the velocity is given by $\langle v^2(t) \rangle = k_B T/m$ as already follows from Eq. (11). However, $\langle v^2(t) \rangle = k_B T/m$ is in general different from $(\gamma_0/m)D$, a form that holds for ordinary Brownian motion. It is therefore not possible to determine the diffusion coefficient $D$ of Brownian particles in a fluctuating medium from a measurement of the second velocity moment. However, one may show that the response of the average velocity to a constant external force $F$ is determined by the diffusion coefficient,

$$\langle v \rangle = \frac{D}{k_B T} F. \quad (23)$$

Hence, the mobility $\mu$ of the Brownian particle in a fluctuating medium satisfies the Einstein relation,

$$\mu = \frac{D}{k_B T}. \quad (24)$$

This is a mere consequence of the fluctuation-dissipation relation of the Langevin equation (3) and holds independently of the nature of the environmental fluctuations.

Finally we will discuss a particularly simple example of generalized Brownian motion, namely the free diffusion of a particle in a medium with only two possible values of viscosity. The waiting times of the viscosity states are exponentially distributed [5],

$$\gamma(z) = \gamma_0 + z(t), \quad \langle z(t)z(s) \rangle = ab e^{-|t-s|/\tau} \quad (25)$$

where the stationary Markovian dichotomous process $z(t)$ takes either the value $-a$ or $b$, $0 \leq a \leq \gamma_0$, $b \geq 0$. The transition rates from the low to the high viscosity state is denoted by $\alpha$ and the reverse rate by $\nu$. They are just the inverses of the mean waiting times $\tau_a$ and $\tau_b$ of the respective initial states $a$ and $b$,

$$\alpha = 1/\tau_a, \quad \nu = 1/\tau_b. \quad (26)$$

Assuming $\alpha \nu = b \mu$ (or $\alpha \tau_a = b \tau_b$) we find $\langle z(t) \rangle = 0$. Hence, $\gamma_0$ is the average viscosity. The process $z(t)$ is exponentially correlated,

$$\langle z(t)z(s) \rangle = ab e^{-|t-s|/\tau} \quad (27)$$

with the correlation time $\tau$ given by

$$\frac{1}{\tau} = \frac{1}{\tau_a} + \frac{1}{\tau_b} = \mu + \nu. \quad (28)$$

In the present case the extended Langevin equations become

$$m\ddot{x}(t) + (\gamma_0 - a)\dot{x}(t) = \sqrt{2(\gamma_0 - a)k_B Tf(t),}$$

$$m\ddot{x}(t) + (\gamma_0 + b)\dot{x}(t) = \sqrt{2(\gamma_0 + b)k_B Tf(t).} \quad (29)$$
with Gaussian standardized white noise \( f(t) \), see Eq. (4). The switching between these equations is governed by the dichotomous process \( z(t) \). It is random and occurs with Poissonian statistics.

The master equation (5) for the time evolution of the probabilities \( p_+(x, v, t) = p(x, v, z(t) = b; t) \) and \( p_-(x, v, t) = p(x, v, z(t) = -a; t) \) has the form [7]

\[
\frac{\partial}{\partial t} p_+(x, v, t) = L_{\gamma_0 + b} p_+(x, v, t) - \nu p_+(x, v, t)
\]

\[
\frac{\partial}{\partial t} p_-(x, v, t) = L_{\gamma_0 - a} p_-(x, v, t) + \nu p_+(x, v, t)
\]

where \( L_{\gamma_0 + b} \) and \( L_{\gamma_0 - a} \) are the Fokker–Planck operators in the states with higher and lower friction, \( \gamma(z) = \gamma_0 + b, \gamma_0 - a \), respectively.

For the marginal probability density of the Brownian particle

\[
P(x, v, t) = p_+(x, v, t) + p_-(x, v, t)
\]

and the auxiliary function

\[
W(x, v, t) = b p_+(x, v, t) - a p_-(x, v, t)
\]

one obtains the following equations from the master equation (30),

\[
\frac{\partial}{\partial t} P(x, v, t) = L_{\gamma_0} P(x, v, t) + \frac{k_B T}{m^2} \frac{\partial^2 W(x, v, t)}{\partial v^2},
\]

\[
\frac{\partial}{\partial t} W(x, v, t) = L_{\gamma_0 + \theta} W - \frac{1}{m} W(x, v, t)
\]

\[
+ \frac{Q}{m^2} \left( v + \frac{k_B T}{m} \frac{\partial}{\partial v} \right) P(x, v, t),
\]

where \( \theta = b-a \) and \( Q = \langle z^2(t) \rangle = ab \) characterize the asymmetry and variance of the viscosity fluctuations, respectively.

Mean values of observables of the Brownian particle, i.e. of functions \( F(x, v) \), are given by

\[
\langle F(t) \rangle_w = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dv F(x, v) P(x, v, t).
\]

Respective expressions may be defined with respect to \( W(x, v, t) \).

\[
\langle F(t) \rangle_w = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dv F(x, v) W(x, v, t).
\]

Note that the mean values of the constant function \( F(x, v) = 1 \) are \( \langle 1 \rangle = 1 \) and \( \langle 1 \rangle_w = \langle z(t) \rangle = 0 \).

In order to determine the mean-square displacement \( \langle x^2(t) \rangle \) we use the master equation in the form of Eq. (33) from which we find the following set of five coupled equations for the second moments of \( x \) and \( v \),

\[
\frac{d}{dt} \langle x^2(t) \rangle = 2 \langle x(t) v(t) \rangle,
\]

\[
\frac{d}{dt} \langle x(t) v(t) \rangle = \langle v^2(t) \rangle - \frac{\gamma_0}{m} \langle x(t) v(t) \rangle
\]

\[
- \frac{1}{m} \langle x(t) v(t) \rangle_w,
\]

\[
\frac{d}{dt} \langle x(t) v(t) \rangle_w = \langle v^2(t) \rangle_w
\]

\[
- \left( \frac{\gamma_0 + \theta}{m} + \frac{1}{\tau} \right) \langle x(t) v(t) \rangle_w
\]

\[
- \frac{Q}{m} \langle x(t) v(t) \rangle,
\]

\[
\frac{d}{dt} \langle v^2(t) \rangle = -\frac{2\gamma_0}{m} \langle v^2(t) \rangle - \frac{2}{m} \langle v^2(t) \rangle_w
\]

\[
+ \frac{2\gamma_0 k_B T}{m^2},
\]

\[
\frac{d}{dt} \langle v^2(t) \rangle_w = -\left( \frac{2\gamma_0 + \theta}{m} + \frac{1}{\tau} \right) \langle v^2(t) \rangle_w
\]

\[
- \frac{2Q}{m} \langle v^2(t) \rangle + \frac{2Q k_B T}{m^2}.
\]

One may first solve the last two equations which form a closed subset and then Eqs. (37) and (38). The resulting moments relax exponentially to constant asymptotic values. Hence, the asymptotic behavior of the mean-square displacement \( \langle x^2(t) \rangle \) indeed is diffusive, cf. Eqs. (12) and (13). The infinite time limit of the position velocity correlation may directly be found as the solution of the algebraic equations resulting from Eqs. (37)–(40) with left-hand sides put to zero. The resulting expression for the diffusion coefficient has the form

\[
D = D_0 \left( 1 + \frac{ab}{(\gamma_0 - a)(\gamma_0 + b) + m\gamma_0/\tau} \right).
\]
where \( D_0 = k_B T / \gamma_0 \) is Einstein's diffusion coefficient of ordinary Brownian motion with the average friction coefficient \( \gamma_0 \). Obviously, \( D \geq D_0 \), cf. Eq. (18).

The most striking difference between \( D_0 \) and \( D \) is the mass dependence of \( D \), which is a decreasing function of \( m \) while the diffusion coefficient \( D_0 \) for ordinary Brownian motion is mass independent. The mass dependence of \( D \) is most pronounced when \( \gamma_0 \) is close to \( a \), i.e. when there is a state with very weak friction. The diffusion coefficient \( D \) then approximately becomes

\[
D = D_0 \left( 1 + \frac{b \tau}{m} \right). \tag{42}
\]

The diffusion coefficient \( D \) tends to the classical form \( D_0 \) in several limiting cases: (a) For fast viscosity fluctuations, i.e. for \( \tau \to 0 \); due to its inertia the Brownian particle then hardly is affected by the resulting fluctuations of the friction coefficient. (b) For weak viscosity fluctuations, i.e. for \( ab \to 0 \). This limit may be approached in different ways: either both amplitudes vanish together, or only one of the amplitudes, say \( a \), goes to zero, while the other one is fixed; in order that the average value of the friction fluctuations vanishes, \( \langle z(t) \rangle = 0 \), the waiting time \( \tau_a \) must diverge.

In the limit of slow viscosity fluctuations, when \( \tau \to \infty \), \( D \) takes the form

\[
D = D_0 \left( 1 + \frac{ab}{(\gamma_0 - a)(\gamma_0 + b)} \right). \tag{43}
\]

The same form is valid for the overdamped dynamics (formally \( m = 0 \) in (29)). This expression also coincides with the quenched disorder diffusion coefficient \( D_{qd} \) as it results from Eq. (22). For finite values of \( \tau \) the inequality (21) strictly holds.

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