Brownian motion in fluctuating media

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Two-state Brownian motion is considered. One state is subjected to white noise while the other one is exposed to dichotomous noise. Such motion is described by a set of three connected Fokker-Planck equations. The switch probability density functions between the states are assumed to have a single exponential form. The equations for the partial moments of the particle velocity are solved recursively. The first moment vanishes as $t \to \infty$ while the second moment defines the effective diffusion coefficient. Estimates have been made of the Brownian motion near the critical point.

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I. INTRODUCTION

The motion of a particle suspended in a fluctuating medium is an interesting stochastic problem which has great practical importance. It is sufficient to mention near-critical systems and turbulent fluids as fluctuating media with many applications (supercritical extraction, fuel injection, cloud formation, etc.). Not only are the properties of the Brownian motion in such media changed compared with those in homogeneous media, but the source of the stochasticity is quite different.

The equation of motion of a Brownian particle in a homogeneous medium has the well-known Langevin form

$$\frac{du}{dt} = -\eta u + f(t) , \tag{1}$$

where u is a particle velocity, η is the friction constant divided by the mass of the particle, and $f(t)$ is the random force.

It is assumed in (1) that the influence of the surrounding medium on the Brownian particle consists of two parts: the systematic force $-\eta u$, which is defined by Stokes law with the characteristic time τ_1 equal to η^{-1} and the random force $f(t)$. It is also assumed that $f(t)$ changes very rapidly, so that its characteristic time τ_2 is smaller than τ_1 and than all other times which may appear in the problem. The common assumption is that $f(t)$ is white noise (i.e., $\tau_2=0$) with whose mean is zero and whose correlation function has the form

$$\langle f(t)f(t')\rangle = 2\Gamma\delta(t-t') . \tag{2}$$

Equation (2) assures the Markovian nature of the Brownian motion: at the instant of collision the Brownian particle "forgets" the previous collision. Viscosity hinders Brownian motion and near equilibrium the fluctuation-dissipation theorem applies, giving

$$\Gamma = \eta kT, \quad D = kT/\eta . \tag{3}$$

The latter expression is the well-known Einstein relation [1]. The character of Brownian motion can be quite different in an inhomogeneous medium. The latter may be visualized as a system which consists of clusters with uniform physical properties within each cluster. If the typical size of a cluster is similar to that of the Brownian particle, then all the particles are of similar size and they undergo random collisions with a mean free time $\tau \approx \tau_1 \approx \tau_2$. According to molecular-kinetic theory both D and η are proportional to τ, and $D \approx \eta$, in contrast to the Einstein relation (3). Finally, if the size of the Brownian particle becomes smaller than the size of a cluster, the situation changes again and in particular, the Brownian particle may have a prolonged interaction time with clusters of the bathing medium (i.e., $\tau_2 > \tau_1$). The question then arises of what will be the relation between D and η in this situation.

II. MODEL

To construct our model we assume that the clusters are not rigid but soft, i.e., they are able to capture the Brownian particle which, therefore, will sometimes be moving inside a cluster. If the velocity of the particle is not too great one can assume that the drag force acting upon the particle inside a cluster varies linearly with velocity with respect to that of the cluster, i.e.,

$$\frac{du}{dt} = \eta(w-u) , \tag{4}$$

where w is the velocity of the cluster. Equation (4) contains the natural assumption of equal viscosities for the motions inside and outside of the cluster.

We now consider the situation for which the clusters are not only soft but they also randomly appear and disappear. This occurs for clusters of the size of the correlation length near the critical points and of the size of large eddies in a turbulent fluid. The cluster velocity w in (4) is, therefore, a random variable. Hence, the velocity of the Brownian particle at the instant of cluster decay is also a random variable.

Although the source of stochasticity is different in Eqs. (1) and (4), the force acting upon the particle in Eq. (4) consists, as in Eq. (1), of a systematic part $-\eta u$ and a random part ηw. For the near-critical conditions in liquids and for homogeneous, isotropic, and stationary turbulences, the random variable w has a Gaussian spec-

trum with the zero mean and a "color" [rather than the white noise in Eq. (2)] correlation function

$$\langle w(t)w(t')\rangle = a^2 \exp\{-2\beta|t-t'|\} . \quad (5)$$

White noise (2) can be obtained from (5) by taking the limits

$$a \to \infty, \beta \to \infty, \quad a^2/\beta = \text{const} = 2D . \quad (6)$$

Hence, the following picture of the Brownian motion holds when one is close to a critical point of liquids or the turbulence is very developed so that the size of the Brownian particle is smaller than the correlation length or the smallest size of turbulence eddies. The Brownian particle is captured by a cluster, spends some time inside, moving according to (4), then is released when the cluster decays, moves among the single molecules according to (1), then captured again by another cluster, etc.

Our problem then becomes a special case of the general theory of the two-state random walk [2] in which a particle can be in one of two states for a random period of time, with each of the states having different dynamics and a different switch density for a jump to the second state. These two states can be quite different. Let us consider a few examples.

1. In continuous-time random walk theory [3], which has been applied to the transport properties of disordered solids, a random walker is either at rest or in free motion.

2. Collisions of finite duration and the free motion between collisions have been considered for the study of molecular rotation [4].

3. The model in which two states correspond to motion in the positive or negative directions has been used for the analysis of chromotographic processes [5].

4. Thermal escape from a linear potential well with a barrier height which switches at random between two values [6]. The same phenomenon of resonant activation has been studied for the simpler model of random jumps between two free states with finite lifetimes [7].

5. Concept of the mean first-passage time which has many applications in physics, chemistry, and biology has been extended to the two-states dynamics for different boundary conditions [8].

Our case is slightly more complicated than those considered above since the random noise in (4) is not white noise, which would bring us to a three-state rather than to a two-state system.

The simplest realization of color noise (5) is so-called dichotomous noise, which alternatively takes on the values $\pm\eta a$ with an equal exponential switch probability density function for the two states

$$\psi(t) = \beta \exp(-\beta t) , \quad (7)$$

where β^{-1} is the average time between switches. Therefore, the dynamic equation (4) is now replaced by the following two equations:

$$\frac{du}{dt} = -\eta u + \eta a , \quad (8)$$

$$\frac{du}{dt} = -\eta u - \eta a , \quad (9)$$

where, according to Eq. (5), a defines the strength of the noise.

The motion inside a cluster is described by Eqs. (8) and (9) with a random switching between these two states, so that the average time between switches is equal to β^{-1}. In addition, the Brownian particle switches from the motion inside a cluster to the motion outside a cluster among single molecules described by Eq. (1). We assume that this random switching is characterized by the exponential switch probability similar to (7),

$$\psi_i(t) = \alpha_i \exp(-\alpha_i t), \quad i = 1,2 . \quad (10)$$

The characteristic time α_i^{-1} has a simple physical meaning. Since $\int_0^\infty t\psi_i(t)dt = \alpha_i^{-1}$, α_1^{-1} defines the average time in state 1 outside a cluster whose dynamics is described by Eq. (1) and α_2^{-1} defines the average time in state 2 inside a cluster whose dynamics are given by Eqs. (8) and (9).

We shall work with the Fokker-Planck equations corresponding to the Langevin equations (1), (8), and (9) [1]. Since the $v_i(t)$, $i = 1,2,3$, entering these equations are random variables which depend both on the state and on the time, their properties can be described by three probability densities $p_i(v,t)$, where the probability that $v \le v_i(t) < v + dv$ is equal to $p_i(v,t)dv$. In general, the $p_i(v,t)$ must be calculated as the solution of an integral equation. Choosing the switch probability densities ψ, ψ_1, and ψ_2 to have the form shown in Eqs. (7) and (10) simplifies our analysis to the Markovian form and reduces the integral equations to differential equations. If we suppose that the system is in state $i = 1$, then (10) implies that the probability that it makes a transition to state $i = 2$ (or $i = 3$) is equal to $\alpha_2 dt$. Analogously, the system in state $i = 2$ ($i = 3$) has the probability $\alpha_1 dt$ to make a transition to state $i = 1$ and the probability βdt for the jump to state $i = 3$ ($i = 2$). The three equations for the $p_i(v,t)$ are derived by enumerating the ways in which these functions change as functions of time, taking into account the possibilities of spontaneous transitions whose kinetics are embodied in Eqs. (1), (8), and (9). The appropriate procedure is similar to that used to derive a diffusion equation from the Langevin equation, and for the case of two states, was considered in detail in Ref. [9]. We find that the coupled equations for the $p_i(v,t)$ are

$$\frac{\partial p_1}{\partial t} = \eta \frac{\partial}{\partial v}(vp_1) + D\eta^2 \frac{\partial^2 p_1}{\partial v^2} + \alpha_1(p_2 + p_3) - 2\alpha_2 p_1 , \quad (11)$$

$$\frac{\partial p_2}{\partial t} = \eta \frac{d}{dv}(vp_2) - a\eta \frac{\partial p_2}{\partial v} + \alpha_2 p_1 - \alpha_1 p_2 + \beta(p_3 - p_2) , \quad (12)$$

$$\frac{\partial p_3}{\partial t} = \eta \frac{\partial}{\partial v}(vp_3) + a\eta \frac{\partial p_3}{\partial v} + \alpha_2 p_1 - \alpha_1 p_3 + \beta(p_2 - p_3) . \quad (13)$$

Notice that the $p_i(v,t)$ are the marginal probabilities of the partial velocity

$$p_i=\int_{-\infty}^{\infty}P_i(x,v,t)dx \tag{14}$$

as distinguished from the full distribution functions P_i which depend on the coordinates of the Brownian particle as well.

III. FIRST TWO MOMENTS

The quantities of primary interest are the moments of the particle velocity. Define the partial moments $\mu_{n,i}(t)$ by

$$\mu_{n,i}\equiv\int_{-\infty}^{\infty}v^n p_i(v,t)dv\ . \tag{15}$$

By multiplying Eqs. (11)–(13) by v^n and integrating by parts one finds the following equations for $\mu_{n,i}$:

$$\frac{\partial\mu_{n,1}}{\partial t}=-n\eta\mu_{n,1}+n(n-1)D\eta^2\mu_{n-2,1}+\alpha_1(\mu_{n,3}+\mu_{n,2})-2\alpha_2\mu_{n,1}\ , \tag{16}$$

$$\frac{\partial\mu_{n,2}}{\partial t}=-n\eta\mu_{n,2}+na\eta\mu_{n-1,2}+\alpha_2\mu_{n,1}-\alpha_1\mu_{n,2}+\beta(\mu_{n,3}-\mu_{n,2})\ , \tag{17}$$

$$\frac{\partial\mu_{n,3}}{\partial t}=-n\eta\mu_{n,3}-na\eta\mu_{n-1,3}+\alpha_2\mu_{n,1}-\alpha_1\mu_{n,3}+\beta(\mu_{n,2}-\mu_{n,3})\ . \tag{18}$$

While it is easy to solve these equations recursively as a function of time, the interesting features are contained in the asymptotic values which are obtained by setting the derivatives equal to zero. Equations (16)–(18) for $n=0$ yield

$$\mu_{0,1}=\frac{\alpha_1}{\alpha_1+2\alpha_2},\quad \mu_{0,2}=\mu_{0,3}=\frac{\alpha_2}{\alpha_1+2\alpha_2}\ . \tag{19}$$

Equations (19) have a clear physical meaning. Since the $p_i(v,t)$ are defined as probability densities, the partial moments of zeroth order satisfy the condition $\mu_{0,1}+\mu_{0,2}+\mu_{0.3}=1$.

Equations (16)–(18) for $n=1$ result in the following forms for the first partial moments:

$$\mu_{1,1}=0\ ,\qquad \mu_{1,2}=-\mu_{1,3}=\frac{a\eta\alpha_2}{(\eta+\alpha_1+2\beta)(\alpha_1+2\alpha_2)}\ , \tag{20}$$

so that the asymptotic value of the first moment satisfies

$$\mu_1=\mu_{1,1}+\mu_{1,2}+\mu_{1,3}=0\ . \tag{21}$$

Finally, the second partial moments follow readily from Eqs. (16)–(18) with $n=2$:

$$\mu_{2,1}=\frac{\eta\alpha_1(\alpha_1+2\eta)D}{(\alpha_1+2\alpha_2)(\alpha_1+2\alpha_2+2\eta)}+\frac{2\alpha_1\alpha_2\eta a^2}{(\alpha_1+2\alpha_2)(\alpha_1+2\beta+\eta)(\alpha_1+2\alpha_2+2\eta)}\ , \tag{22}$$

$$\mu_{2,2}=\mu_{2,3}=\frac{\alpha_1\alpha_2\eta D}{(\alpha_1+2\alpha_2+2\eta)(\alpha_1+2\alpha_2)}+\frac{2\eta\alpha_2(\eta+\alpha_2)a^2}{(\alpha_1+2\alpha_2)(\alpha_1+2\beta+\eta)(\alpha_1+2\alpha_2+2\eta)}\ . \tag{23}$$

From Eqs. (22) and (23) one finds for the asymptotic value of the second moment $\mu_2=\mu_{2,1}+\mu_{2,2}+\mu_{2,3}$

$$\mu_2=\frac{\eta\alpha_1 D}{\alpha_1+2\alpha_2}+\frac{2\eta\alpha_2 a^2}{(\alpha_1+2\alpha_2)(\alpha_1+2\beta+\eta)}\ . \tag{24}$$

Another way to write (24) is by defining an effective diffusion coefficient D_{eff} by $\mu_2=D_{\text{eff}}\eta$, yielding

$$D_{\text{eff}}=\frac{\alpha_1 D}{\alpha_1+2\alpha_2}+\frac{2\alpha_2 a^2}{(\alpha_1+2\alpha_2)(\alpha_1+2\beta+\eta)}\ . \tag{25}$$

The first term in (24) and (25) describes the contribution of the state subjected to white noise while the second term is determined by the state exposed to dichotomous noise. It is instructive to examine some limiting cases of (25) to see how they correspond with previously known results.

1. The limit $\alpha_1\to\infty$ corresponds to a situation in which the particle stays mainly in the Brownian state (1), and if it leaves this state, it returns almost immediately. Then, as it follows from (25),

$$D_{\text{eff}}=D\ . \tag{26}$$

2. For the similar limit $\alpha_2\to\infty$, only states (8) and (9) are important and

$$D_{\text{eff}}=\frac{\eta a^2}{\alpha_1+2\beta+\eta}\ . \tag{27}$$

3. If the transitions between state (1) and states (8) and (9) are symmetric, i.e., $\alpha_1=\alpha_2=\alpha$, then (25) reduces to

$$D_{\text{eff}}=\frac{D}{3}+\frac{2a^2}{3(\eta+\alpha+2\beta)}\ . \tag{28}$$

4. The limits $a\to\infty$ and $\beta\to\infty$ with $a^2/\beta=2D$ correspond, according to (6), to the transition from dichotomous to white noise. Then, (28) reduces to (26), which is the expected result since both states become identical.

5. The limit $\alpha\to 0$ means that there is no interaction between the states. Then they make additive contributions to the second moment μ_2 and to D_{eff}. The known results [10] for D and $a_2/(\eta+2\beta)$ [with the numerical factors 1/3 and 2/3 connected with initial conditions (19)] follow from (28).

IV. CONCLUSIONS

Extensive studies of Brownian motion near instability points have been made in the 1970s. The theoretical analyses were concerned with the critical points of pure substances [11–17] and binary mixtures [18,19] as well as with the convective instability [20]. Some semiquantitative experiments have been performed near the critical

points of pure substances [21] and binary mixtures [22]. However, only one set of hydrodynamic equations (with different types of corrections—compressibility, spatial, and temporal dispersion, non-Boussinesq approximation, etc.) was a basis of all theoretical analysis while we considered here the two-state systems.

Indeed, we consider the motion of a Brownian particle which is able to be in one of two states with random switching between them. The first is the usual Brownian state exposed to white Gaussian noise while the second state is subjected to color noise which is chosen to be dichotomous noise. The latter is described by two (sub)states with random switching between them. The simplest (Markovian) case was considered in which the both switching probability density functions have a simple exponential form.

It is found that the asymptotic ($t \to \infty$) first moment of the particle velocity vanishes, and the second moment is given by the simple equation (24). The effective diffusion coefficient of the Brownian particle (25)–(28) is a combination of the diffusion coefficient D and the viscosity η of the medium as well as of the characteristic switching times α_1^{-1}, α_2^{-1}, and β^{-1}.

Our results can be applied to the quantitative analysis of the Brownian motion near the critical point. The general behavior depends on the relation between the size of the Brownian particle and the correlation length which defines the typical size of a cluster. The latter increases when the critical point is approached. If the size of the Brownian particle is so small that in the immediate vicinity of the critical point it becomes smaller than the correlation length, the effects considered above may become important. Then, clusters will occupy a progressively larger part of the volume of a system as the critical point is approached, and the effective diffusion coefficient will change from (26) to (27). One can estimate the dependence of D_{eff} given by (27) on the vicinity to the critical point. If the velocity distribution of clusters is Maxwellian, then $a^2 \sim kT/m \sim R^{-3}$, where m and R are the mass and the size of a cluster, respectively. The characteristic times α^{-1} and β^{-1} will be proportional to R divided by some adiabatic velocity c. The correlation length R is proportional to $[(T-T_c)/T_c]^{-\nu}$ with $\nu \approx 0.67$ while c and η have only a weak singularity near the critical point. Therefore, if the situation described above will be achieved in a real experiment, the diffusion coefficient of the Brownian particle will show a drastic decrease very close to the critical point, $D_{\text{eff}} \sim [(T-T_c)/T_c]^{1.3}$

Brownian motion in the vicinity of the critical point was studied experimentally by Martizen and collaborators almost 30 years ago [21]. They found that the diffusion coefficient decreased fourfold over the interval 0.5–0.2 K near the critical point, which agrees qualitatively with our estimates, namely $[D(T-T_c=0.5\ \text{K})]/[D(T-T_c=0.2\ \text{K})]=[0.5/0.2]^{1.34} \approx 3.5$. However, the more quantitative experiments are needed. Another interesting possibility would be an application of the idea presented in this work to systems of colloidal particles especially those which covered by weakly absorbed monolayers.

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