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# A non-Fickian diffusion equation

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A non-Fickian diffusion equation, which differs from the usual (Fickian) diffusion equation by having an additional, second-order derivative term in time, is considered to describe the dynamics of a Brownian particle. Some useful perspectives on this generalized diffusion equation are presented, particularly with respect to the effect of a potential field. Two quantities of physical interest, namely the mean square displacement and the particle flux at an absorbing boundary, are considered in the process of a comparative study of the two diffusion equations. We also discuss the applicability of the non-Fickian diffusion equation to some systems of physical and practical interest.

## I. INTRODUCTION

The use of the diffusion equation to describe the overdamped motion of a Brownian particle (or of an analogous entity) is widespread in various branches of science and engineering. The dynamics of the Brownian particle is then described by the familiar diffusion equation

$$\frac{\partial n(x,t)}{\partial t}=D\frac{\partial^2 n(x,t)}{\partial x^2}, \tag{1}$$

where $n(x,t)$ can be regarded as the density or the concentration of the Brownian particles; $D$ is the diffusion coefficient. For simplicity, we have considered only one spatial dimension. For later purposes, let us recall the well-known fact that Eq. (1) can be derived at a macroscopic level by combining the Fick's law of diffusion

$$j(x,t)=-D\frac{\partial n(x,t)}{\partial x}, \tag{2}$$

and the continuity equation (number conservation)

$$\frac{\partial n(x,t)}{\partial t}+\frac{\partial j(x,t)}{\partial x}=0. \tag{3}$$

Equation (1) can also be derived, starting from a more microscopic level of description, e.g., from a discrete Markovian random walk model in the continuum and the long-time limits.[1] Equation (1) describes the Fickian diffusion, i.e., only the long-time dynamics of a Brownian particle which has lost memory of its short-time inertial motion.

The objective of this paper is to discuss a diffusion equation which is more general than Eq. (1) in that it can account for certain aspects of the short-time dynamics, at least in the absence of any potential field and also in the presence of a constant field. The diffusion describable by this equation will be referred to as a non-Fickian diffusion, for reasons to be explained in the next section. This diffusion equation is a little more involved than Eq. (1), but is simpler than, say, the phase-space Fokker–Planck equation[2] (often called the Kramers equation), from which it will be derived. The Kramers equation adequately describes both the short- and long-time dynamics of a Brownian particle in the presence or absence of a potential field. But this equation is difficult to solve, especially for finite boundaries, even in the absence of a potential field, whereas the diffusion equation which generalizes Eq. (1) is easier to handle in such cases. This generalized diffusion equation has, in fact, been known in the literature for quite some time.[3] However, it has not been much used in problems of physical interest. In this context, one would like to have some perspectives on the theoretical foundation, as well as the limitations, of this equation. We have attempted to deal with these issues in this paper. As applications to physical problems, we have considered two quantities of interest: (a) the mean square displacement of the Brownian particle, and (b) the time-dependent flux at an absorbing surface, of particles implanted in the bulk of a solid. The first quantity is of almost universal interest in connection with Brownian motion. The second quantity has a direct relevance to the dynamics of implanted positrons in solids[4] and also to the problem of aerosol coagulation on a surface.[5] We have shown that, in the long-time limit, the quantities (a) and (b) reduce to their counterparts obtained from the Fickian diffusion Eq. (1), thereby illustrating an essential feature of the generalized diffusion equation.

In the last section, we briefly discuss the general applicability of the non-Fickian diffusion equation to other physical systems of practical interest, e.g., superionic conductors, molten salts, and neutron diffusion in nuclear reactors.

## II. THE NON-FICKIAN DIFFUSION EQUATION

It will be useful to see how both the diffusion equations can be derived from an underlying equation, e.g., the Kramers equation that describes the dynamics of a Brownian particle at a "microscopic" level. Considering one spatial dimension, the Kramers equation for the phase-space distribution function $f(x,p,t)$ reads[2]

$$\frac{\partial f}{\partial t}+\frac{p}{m}\frac{\partial f}{\partial x}-\frac{\partial V}{\partial x}\frac{\partial f}{\partial p}=\gamma\frac{\partial}{\partial p}(pf)+mk_BT\gamma\frac{\partial^2 f}{\partial p^2}. \tag{4}$$

$\gamma$ is the friction parameter and the other symbols have usual meanings. A potential field, $V(x)$, has been introduced in Eq. (4). We shall now take moments of $p$ over Eq. (4). It seems to us that this method brings out clearly the nature of the Fickian or the non-Fickian character of

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the ensuing diffusion equation. Taking the zeroth moment of momentum, $p$, over Eq. (4), we obtain the expected continuity equation[6]

$$\frac{\partial n(x,t)}{\partial t}+\frac{\partial j(x,t)}{\partial x}=0, \tag{5}$$

relating the number density

$$n(x,t)=\int_{-\infty}^{\infty} f(x,p,t)dp$$

to the current density

$$j(x,t)=\int_{-\infty}^{\infty} \frac{p}{m} f(x,p,t)dp.$$

The first moment leads to

$$m\frac{\partial j(x,t)}{\partial t}+2\frac{\partial}{\partial x}\int_{-\infty}^{\infty}\left(\frac{p^2}{2m}\right)f(x,p,t)dp$$
$$+\frac{\partial V(x)}{\partial x}n(x,t)=-m\gamma j(x,t). \tag{6}$$

In order to obtain a diffusion equation, i.e., an equation for $n(x,t)$, one needs to introduce some approximation in the second term of the left-hand side of Eq. (6). We now assume that $\gamma$ is large, which implies that the system can be regarded as close to the equilibrium Maxwellian distribution. In that case, we can decouple $f(x,p,t)$ as $f(x,p,t)\simeq n(x,t)\phi(p)$, where $\phi(p)$ is approximated by the Maxwellian distribution function. Equation (6) then yields

$$m\frac{\partial j}{\partial t}+k_BT\frac{\partial n}{\partial x}+\frac{\partial V}{\partial x}n=m\gamma j$$

or

$$j=-\left(D\frac{\partial n}{\partial x}+\frac{1}{m\gamma}\frac{\partial V}{\partial x}n\right)-\frac{1}{\gamma}\frac{\partial j}{\partial t}, \tag{7}$$

where $\int_{-\infty}^{\infty}(p^2/2m)\phi(p)dp$ has been replaced by $\frac{1}{2}k_BT$, the equipartition value. Eqs. (5) and (7) lead, after eliminating $j(x,t)$, to the non-Fickian diffusion equation for $n(x,t)$

$$\frac{1}{\gamma}\frac{\partial^2 n}{\partial t^2}+\frac{\partial n}{\partial t}=\frac{1}{m\gamma}\frac{\partial}{\partial x}\left(\frac{\partial V}{\partial x}n\right)+D\frac{\partial^2 n}{\partial x^2}, \tag{8}$$

with $D = k_BT/m\gamma$.

Let us note that, if we neglect the $(1/\gamma)(\partial^2 j/\partial t^2)$ term in Eq. (7), then for a zero or constant potential we obtain the usual diffusion equation. And, in the same spirit, if we neglect the $(1/\gamma)(\partial j/\partial t)$ term in Eq. (7), we recover the Fick's law when we identify $(k_BT/m\gamma)$ as $D$, the diffusion coefficient. With a nonconstant $V(x)$, this becomes the Fick's law for a potential field. However, if we do not neglect the $(1/\gamma)(\partial j/\partial t)$ term in Eq. (7), we obtain the generalized Fick's law of diffusion. Hence we may call Eq. (8), with the $(1/\gamma)(\partial^2 n/\partial t^2)$ term included, a non-Fickian diffusion equation.

A question of immediate concern is the role of this additional term in Eq. (8). Since this term contains a second-order derivative in time, we can expect that some short-time inertial behavior of the Brownian particle is retained in Eq. (8). In order to study this question, we consider a quantity of physical interest, namely, the mean square displacement $\langle x^2(t)\rangle$, defined as $\langle x^2(t)\rangle = \int_{-\infty}^{\infty} x^2 n(x,t)dx$. Using Eq. (8), and in the absence of a potential field, we find

$$\langle x^2(t)\rangle=(2D/\gamma)[-1+\gamma t+e^{-\gamma t}]. \tag{9}$$

In deriving Eq. (9), we have assumed an infinite domain $-\infty<x<\infty$ and

$$\langle x^2(t=0)\rangle=0;\quad \left(\frac{d}{dt}\langle x^2(t)\rangle\right)_{t=0}=0. \tag{10}$$

The first condition sets an arbitrary constant equal to zero, while the second condition makes $\langle x^2(t)\rangle$ non-negative. Interestingly, Eq. (9) would be the same result as can be obtained from the Kramers equation in the absence of a potential field; in the latter case, $\langle x^2(t)\rangle$ will be calculated as

$$\langle x^2(t)\rangle=\int_{-\infty}^{\infty} dx\, x^2\int_{-\infty}^{\infty} f(x,p,t)dp.$$

This indicates that although the non-Fickian diffusion Eq. (9) does not possess as much information as the Kramers equation does, it, nevertheless, correctly yields at least one physical quantity which retains the full short-time (inertial) behavior. We shall now show that the same property for $\langle x^2(t)\rangle$ will prevail only for a constant potential field, i.e., for $(\partial V/\partial x)$ = constant. It should be recognized that a constant field is not without physical interest. In order to see how the potential field affects $\langle x^2(t)\rangle$, one needs, ideally, to solve both the Kramers Eq. (4) and Eq. (8) for the same potential field in question, and preferably for a class of potential fields, which is a difficult task. We have attempted a simpler analysis by taking recourse to the Langevin equation. The reason is that upon taking the appropriate moment over the Langevin equation with the white noise (see below) one can arrive at the same evolution equation for $\langle x^2(t)\rangle$, as with the non-Fickian diffusion equation, for the potential-free case and through some assumptions. We can then assess the validity of these assumptions for a general potential. Without any potential field, the Langevin equation reads

$$m\frac{d^2x}{dt^2}+m\gamma\frac{dx}{dt}=\xi(t), \tag{11}$$

with $\xi(t)$ having the white noise property

$$\langle\xi(t)\rangle=0;\quad \langle\xi(t)\xi(t')\rangle=c\delta(t-t'). \tag{12}$$

$c$ is a constant to be discussed shortly. The equation for $\langle x^2(t)\rangle$ is now arrived at through the following steps: Eq. (11) is multiplied by $x$, the terms on the left-hand side are rearranged, an ensemble average is taken, and it is assumed that $\langle x(t)\xi(t)\rangle=0$. A subsequent important step is to replace the resulting term $\langle(dx/dt)^2\rangle$ by the equipartition value $(k_BT/m)$. [Let us recall that this equipartition assumption also entered the derivation of Eq. (8).] These steps lead to

$$\frac{1}{\gamma}\frac{d^2}{dt^2}\langle x^2(t)\rangle+\frac{d}{dt}\langle x^2(t)\rangle=2D \tag{13}$$

from which the result (9) follows.

We next consider the Langevin equation for a potential field.

$$m\frac{d^2x}{dt^2}+m\gamma\frac{dx}{dt}=\psi(x)+\xi(t), \tag{14}$$

with $\psi(x) = -dV/dx$. For our analysis, it is convenient to rewrite Eq. (14) as a system of two first-order differential equations

$$\frac{dx}{dt}=u \tag{15a}$$

and

$$\frac{du}{dt}=-\gamma u+\frac{1}{m}\psi[x(t)]+\frac{1}{m}\xi(t). \tag{15b}$$

With $\psi=0$, i.e., for the field-free case, we have, from Eq. (15b),

$$u(t)=u_0e^{-\gamma t}+\frac{1}{m\gamma}\int_0^t\xi(t')e^{-\gamma(t-t')}dt', \tag{16}$$

where $u_0$ is the initial velocity. Through a similar procedure as with Eq. (11), we can write

$$\frac{1}{2}\frac{d}{dt}\langle u^2\rangle=-\gamma\langle u^2\rangle+\frac{1}{m}\langle u(t)\xi(t)\rangle. \tag{17}$$

That $\langle u(t)\xi(t)\rangle$ is nonzero follows from Eqs. (16) and (12). This nonzero value, which is a constant (independent of $t$) contributes to the equipartition of $\langle u^2\rangle$, as can be seen from Eq. (17). [The constant $c$ in Eq. (12) can be determined by requiring that $\langle u^2(t)\rangle$ obtained from Eq. (17) should tend to $k_BT/m$ as $t\rightarrow\infty$.]

Next assume $\psi\neq 0$, but a constant [independent of $x(t)$]. We can still assert that $\langle u\psi\rangle$ is zero; consequently, no additional term will appear in Eq. (17) and the equipartition of $\langle u^2\rangle$ will obtain. But, for $\psi\neq$constant, $\langle u(t)\psi[x[(t)]\rangle$ is unlikely to vanish, leading to an additional term in Eq. (17), and hence hindering the equipartition of $\langle u^2\rangle$. To see its further consequence, consider $x(t)$ now given by

$$\begin{aligned}x(t)=&\frac{u_0}{\gamma}(1-e^{-\gamma t})\\&+\frac{1}{m}\int_0^t dt'\left(\int_0^{t'}e^{-\gamma(t-t'')}\psi[x(t'')]dt''\right)\\&+\frac{1}{m}\int_0^t dt'\left(\int_0^{t'}e^{-\gamma(t-t'')}\xi(t'')dt''\right),\end{aligned} \tag{18}$$

where, for simplicity, we have put $x(t=0)=0$. For $\psi=0$ or constant, we can put $\langle x\xi\rangle=0$, a necessary step used earlier in this section to obtain the differential Eq. (13) for $\langle x^2(t)\rangle$. For general $\psi(x)$, it is not possible to make an *a priori* statement about $\langle x\xi\rangle$.

Summing up these observations, we can say that the mean square displacement $\langle x^2(t)\rangle$ of a Brownian particle obtained from the non-Fickian diffusion Eq. (8), agrees with that obtained from the Kramers equation (4), in the presence of a constant field. For a more general potential, such an agreement is not expected. We are not aware of any previous study in the literature of the utility and the limitations of the non-Fickian diffusion Eq. (8), based on the type of analysis presented in this section.

## III. OTHER QUANTITIES OF PHYSICAL INTEREST

We have noted in the earlier section that an explicit knowledge of $n(x,t)$ is not necessary in order to obtain $\langle x^2(t)\rangle$. It will be of interest to consider a physical quantity whose evaluation requires an explicit knowledge of $n(x,t)$. In this section, we deal with such a quantity, and consider a problem which, at a formal level, has relevance to the dynamics of implanted positrons (or other particles) in solids, and also to aerosol physics. An idealized model is considered: a semi-infinite medium is bounded at $x=0$ by a perfectly absorbing surface. A highly localized profile of particles is implanted initially (at $t=0$) at some distance $x_0$ in the interior of the medium. The implanted particles will diffuse and some will get absorbed as they reach the boundary at $x=0$. We shall calculate the time-dependent flux $J(t)$ at the boundary using the non-Fickian diffusion Eq. (8) with $V=0$, and show that for $\gamma t\gg 1$, i.e., in the long-time approximation, the result for $J(t)$ reduces to that obtained from the Fickian diffusion Eq. (1). We need to solve Eq. (8) with $V=0$, i.e.,

$$\frac{\partial^2 n}{\partial t^2}+\gamma\frac{\partial n}{\partial t}=D\gamma\frac{\partial^2 n}{\partial x^2},\quad (0\leqslant x<\infty) \tag{19}$$

with the conditions

$$\begin{aligned}&n(x=0,t>0)=0;\quad n(x\rightarrow\infty,t>0)\rightarrow 0;\\&n(x,t=0)=\delta(x-x_0),\end{aligned} \tag{19a}$$

and

$$\left(\frac{\partial n(x,t)}{\partial t}\right)_{t=0}=0. \tag{20}$$

The last condition ensures the non-negativity of $n(x,t)$. The solution of Eq. (19) is conveniently affected by applying Fourier sine transform to $n(x,t)$ with respect to the space variable $x$. For brevity, we shall cite the main results. The flux $J(t)$ is defined as

$$J(t)=D\left(\frac{\partial n(x,t)}{\partial x}\right)_{x=0}. \tag{21}$$

After some algebra, we find

$$J(t)=\frac{2D}{\pi}e^{-\gamma t/2}\left(G_1+\frac{\gamma}{2}G_2\right), \tag{22}$$

where

$$G_2=\frac{\pi x_0}{4D\sqrt{(D\gamma t^2-x_0^2)}}I_1\left(\sqrt{\frac{\gamma}{D}}\sqrt{(D\gamma t^2-x_0^2)}\right),\quad 0<x_0<\sqrt{D\gamma}t \tag{23}$$

and $G_1 = \partial G_2/\partial t$, $I_1$ being the modified Bessel function. In the approximation $\gamma t \gg 1$ and for $(D\gamma t^2 - x_0^2) \gg 0$, the Bessel functions in $G_1$ and $G_2$ can be replaced by their asymptotic forms, and we obtain

$$J(t) \simeq \frac{x_0}{\sqrt{4\pi D}(t\sqrt{t})} e^{-x_0^2/4Dt}. \tag{24}$$

Equation (24) is the exact result for $J(t)$ obtained by using Eq. (1). It will be of interest to apply Eq. (8) to the problem of implanted positrons in solids, using a more realistic implantation profile, and a bulk decay rate for positrons, etc. We intend to study this problem in a separate paper.

## IV. DISCUSSION

In this paper we have discussed a non-Fickian diffusion equation, outlined its derivation from an underlying kinetic equation in phase-space (the Kramers equation) and provided some perspectives on this diffusion equation. In this process, we have considered two quantities of physical interest. One of these, namely $\langle x^2(t) \rangle$, does not require a direct knowledge of $n(x,t)$, while the other one, the particle flux $J(t)$, does. The idea is to see some complementary aspects of the diffusion equation. For simplicity of presentation, we have considered only one space dimension.

We have shown in Sec. II that the non-Fickian diffusion would not be reliably applicable in the case of a potential field if the latter is not a constant. It does point to an inherent limitation of this diffusion equation. However, for a constant field, which is not without physical interest, this diffusion equation deserves further study.

We may note that the Kramers equation is difficult to solve for semi-infinite or finite geometries, whereas the generalized diffusion equation is analytically tractable in such cases. Further comparative studies of Eq. (8) and the Kramers equation (and also the Boltzmann equation in the number-conserving relaxation time approximation[7]) for zero or a constant field should be of interest.

We shall conclude with some general remarks on the applicability of the non-Fickian diffusion equation to systems of practical interest. In this context, we may first recall that Eq. (8) is expected to yield information beyond that given by Eq. (1) in cases where $\gamma t \sim 1$. The latter indicates that in cases where $\gamma$ is low, i.e., the mobility is high, and for short times, Eq. (8) will be more appropriate and useful. Due to recent developments in picosecond and femtosecond technologies, experimental observations of Brownian motion in these time domains are now feasible and are expected to explore the time domain shorter than that covered by the ordinary diffusion Eq. (1).

In the context of diffusion in solids, we note that the behavior of $\langle x^2(t) \rangle$, as given by Eq. (9), implies a constant thermal velocity for the Brownian particle in the short-time domain when $\gamma t \ll 1$. This would be more realistic for Brownian motion in a fluid than for hopping motion in solids. The non-Fickian diffusion would, therefore, be more meaningfully applicable to those solids where a fluidlike motion for the Brownian particle can be discernible. The motion of one of the ionic species in superionic conductors,[8] e.g., AgI, which are characterized by a high ionic conductivity, is reminiscent of Brownian motion in a fluidlike system. In fact, the Kramers equation has been used to describe the dynamics of one of the ionic species in superionic conductors, for example, that of Ag in AgI, with a view to covering both the short-time domain where some vestiges of inertial effect are present, and the long-time diffusive regime.[8] Some molten salts have high ionic conductivity and a non-Fickian diffusion can be applicable to these systems as well.

We next consider neutron diffusion in nuclear reactors. It is interesting to find that Weinberg and Wigner[9] consider a non-Fickian diffusion equation of the form of Eq. (8) and remark that the effect due to the $(1/\gamma)(\partial^2 n/\partial t^2)$ term cannot always be neglected, particularly in the outer boundary of reactors. For a quantitative estimate of the time domain for which Eq. (8) may provide a better description of the Brownian dynamics, we note that for Ag in AgI, the Ag ion has a high mobility with $D \simeq 10^{-5}$ $cm^2/s$. At $T \simeq 300$ K, we then have $\gamma_{Ag} = k_B T/(mD)_{Ag} \simeq 10^{13}$. Therefore, $\gamma t \simeq 1$ in the time domain from picoseconds to femtoseconds. For aerosol dispersal, such a short-time domain may not be necessary. Lastly, referring to positron diffusion in solids, it is reported[10] that positrons implanted in solids can reach the surface even when they are not yet thermalized. In order to study the dynamics of such positrons, the Kramers Eq. (4) will be necessary. It may be recalled that the Fokker–Planck equation [Eq. (4) without the $(\partial V/\partial x)(\partial f/\partial p)$ term] has been used[11] to discuss the thermalization of positrons in solids. It will be of some interest to apply Eq. (8) to the case of epithermal positrons in solids.

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