# Diffusion processes with inertial effects and with boundary conditions – A solution to the Wang and Uhlenbeck problem

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The problem of Wang and Uhlenbeck on the imposition of boundary conditions for space in the Fokker–Planck–Kramers equation is solved for Brownian motion under uniform and gravitational potentials. These cases with the full consideration of inertial effects lead to a modified diffusion equation with time-dependent diffusion coefficients determined by the initial condition of the velocity distribution. Moreover, the former case is applied to the rate theory for the diffusion limited reaction in liquids and new results have been obtained especially for the short time behavior where inertial effects play an important role.

## 1. Introduction

Properties of diffusion processes within the framework of Fick's law are well-known and these are often found in standard textbooks treating the diffusion equation with boundary conditions [1,2]. The diffusion equation is valid for the long time limit where the motion of the Brownian particle is overwhelmingly governed by the random forces resulting from many collisions, whose dynamic behavior is essentially represented by the diffusion coefficient. However, when the time scale approaches toward that of a single collision, we must introduce another parameter characterizing the collision time. In this short time domain, we also have to take into account the change of the motion governed by laws of mechanics such as Newton's equation which describes motion in vacuum. In other words, the surrounding molecules behaves like a fluid in the large time scale, whereas in the short time, properties of individual molecules are shown up. Hence, in the long time limit, the change in momentum is not so important as that for the short time scale. Consequently, when we treat the diffusion processes of a particle in a low friction medium or we are interested in a dynamic processes in the short time region, we should take into account the distribution of the velocity as well as that of the position. The case where the former is accounted for is corresponding to Brownian motion with inertial effects. Although the usual procedure to treat inertial effects is to use the Fokker–Planck–Kramers equation (FPK), we have the difficulty in this procedure when we impose the boundary conditions in space, which was addressed explicitly Wang and Uhlenbeck long time ago [3]. And improvements are still made based on FPK [4,5] but these are worked out using approximate methods.

In this paper, we shall derive the modified diffusion equation which are not only identical to FPK but also subject in the boundary conditions in space. The present method is valid for the cases where Brownian motion takes place with (a) free, (b) gravitational and (c) harmonic potentials. These are the cases where the position of the Brownian particle is a Gaussian random variable in which diffusion processes with inertial effects in the natural boundary condition are fully known. It is shown that when inertial effects are considered, the diffusion coefficient depends explicitly upon time due to the projection of the distribution of the velocity onto the time coordinate without employing the projection operator method. As an application of the present work, we shall treat the diffusion limited chemical reactions where it is assumed that reaction takes place when a Brownian particle touches a sink in space. The time-dependent reaction rate $k$ without inertial effects based on the Smoluchowski equation is proportional to $t^{-1/2}$, which indicates that $k$ becomes enormously big when $t \to 0$, whereas $k$ from the present study avoids the divergence at $t \to 0$. It is also becomes clear that inertial effects make the dynamics slow. This treatment of the reaction rate is connected to the quenching of photoactivated molecules and arises explicitly from the dynamics of the Brownian particle, which has different aspects from the rate theory based on the assumption of the stationary state [6].

## 2. Theory and discussion

The Fokker–Planck–Kramers equation for the probability density $P(x, v, t)$ which describes the probability of finding a Brownian particle by $P(x, v, t)\, dx\, dv$ in the range of the position, $x$ and $x + dx$ as well as the velocity $v$ and $v + dv$ at time $t$ is given by the following expression:

$$\frac{\partial P(x,v,t)}{\partial t} + v\frac{\partial P}{\partial x} + \frac{f(x)}{m}\frac{\partial P}{\partial v} = \beta\frac{\partial (vP)}{\partial v} + \beta\frac{k_B T}{m}\frac{\partial^2 P}{\partial v^2}, \tag{1}$$

where $m, f(x), \beta, k_B$ and $T$ are the mass, external force, friction coefficient, the Boltzmann constant and the absolute temperature, respectively. Wang and Uhlenbeck [3] noted long time ago that it was difficult to solve eq. (1) by imposing a boundary condition for $x$ even in the simplest case of free Brownian motion where $f(x) = 0$. The recent treatments [4,5] suggest that the problem has not been understood completely. We propose an approach to find the solution. To this end, as before [6], we introduce the function, $\Psi(x, u, t)$ by the expression:

$$\Psi(x,u,t) = \exp\left(\frac{k_B T}{2m}u^2\right) \int_{-\infty}^{\infty} P(x,v,t)e^{-iuv}\, dv \tag{2}$$

and transform eq. (1) onto

$$\frac{\partial \Psi(x,u,t)}{\partial t} + i\frac{\partial}{\partial x}\left(\frac{\partial \Psi}{\partial u} - \frac{k_B T}{m}u\Psi\right) + iu\frac{f(x)}{m}\Psi = -\beta u \frac{\partial \Psi}{\partial u}. \tag{3}$$

By expanding $\Psi(x,u,t)$ with respect to $u$,

$$\Psi(x,u,t) = \sum_{n=0}^{\infty} a_n(x,t)(iu)^n \tag{4}$$

we find that

$$\frac{\partial a_0(x,t)}{\partial t} = \frac{\partial a_1(x,t)}{\partial x}, \tag{5}$$

$$\frac{\partial a_1}{\partial t} + \beta a_1 - 2\frac{\partial a_2}{\partial x} - \frac{k_B T}{m}\frac{\partial a_0}{\partial x} + \frac{f(x)}{m}a_0 = 0, \tag{6}$$

$$\frac{\partial a_n}{\partial t} + \beta a_n - (n+1)\frac{\partial a_{n+1}}{\partial x} - \frac{k_B T}{m}\frac{\partial a_{n-1}}{\partial x} + \frac{f(x)}{m}a_{n-1} = 0 \quad (n = 2,3,4,\ldots), \tag{7}$$

where in view of eqs. (2) and (4), the distribution function $W(x,t)$ as a function of $x$ and $t$,

$$W(x,t) = a_0(x,t) = \int_{-\infty}^{\infty} P(x,v,t)\, dv, \tag{8}$$

and the flux $J(x,t)$ is given by

$$J(x,t) = -a_1(x,t) = \int_{-\infty}^{\infty} vP(x,v,t)dv. \tag{9}$$

The modified Smoluchowski equation (MS) obtained from eqs. (5)–(7) for $W(x,t)$ was given by an infinite continued fraction including the differential operator $d/dx$ when $v$ is distributed by the Maxwell function at $t = 0$. In general, MS which is equivalent to eq. (1) is complicated, because $d/dx$ and $f(x)$ do not commute. However, when (a) $f(x) = 0$ and (b) $f(x) =$ constant in which cases no coefficients in eq. (1) and (3) are explicit functions of $x$; in fact, $d/dx$ and $f(x)$ do commute so that MS will be found readily. This is a very important point to develop the present study where we confine ourselves to these two particular cases.

We shall obtain $W(x,t)$ in the cases of $f(x) = 0$ and $f(x) =$ constant. To this end, we note that since the operator, $d/dx$ commutes with $f(x)$, it may be treated as a constant in which case we can find $\Psi(x,u,t)$ easily directly from eq. (3) for the natural boundary of $x$. Or more directly, we can take the following approach. First, we note that the probability densities $W(x,t)$ for the both cases (a) and (b) are Gaussian for the natural boundary. Hence the characteristic function $\Phi(\xi,t)$ is given by

$$\Phi(\xi,t)=\langle \mathrm{e}^{-\mathrm{i}\xi x}\rangle=\int_{-\infty}^{\infty}W(x,t)\mathrm{e}^{-\mathrm{i}\xi x}dx=\exp[-\mathrm{i}\xi Z_1(t)-\tfrac{1}{2}\xi^2 Z_2(t)]\,, \tag{10}$$

where

$$Z_1(t)=\langle x(t)\rangle\,, \tag{11}$$

$$Z_2=\langle x^2(t)\rangle-\langle x(t)\rangle^2\,. \tag{12}$$

It is important to remember at this stage that the differential operator $\mathrm{d}/\mathrm{d}x$ in the $x$ space is just $\mathrm{i}\xi$ in the Fourier transformed domain of $\xi$ space in view of the identity,

$$\int_{-\infty}^{\infty}\frac{\mathrm{d}g(x)}{\mathrm{d}x}\mathrm{e}^{-\mathrm{i}\xi x}dx=\mathrm{i}\xi\int_{-\infty}^{\infty}g(x)\mathrm{e}^{-\mathrm{i}\xi x}\,\mathrm{d}x\,. \tag{13}$$

With this in mind, we do not need to get involved with $\mathrm{d}/\mathrm{d}x$ explicitly. Since we are confined to cases (a) and (b), we can regard $\mathrm{d}/\mathrm{d}x$ as $\mathrm{i}\xi$ in $\Phi(\xi,t)$. We emphasize here not to tempt to apply this method to the harmonic potential where although the process is Gaussian, $\mathrm{d}/\mathrm{d}x$ does not commute with $f(x)$. We find by differentiating eq. (10) with respect to $t$ and taking the inverse Fourier transform that

$$\frac{\partial W(x,t)}{\partial t}=\tfrac{1}{2}z_2(t)\frac{\partial^2 W(x,t)}{\partial x^2}-z_1(t)\frac{\partial W(x,t)}{\partial x}\,, \tag{14}$$

$$z_1(t)=\frac{\mathrm{d}Z_1}{\mathrm{d}t}\,, \tag{15}$$

$$z_2(t)=\frac{\mathrm{d}Z_2}{\mathrm{d}t}\,. \tag{16}$$

Note that eq. (14) is MS which is now subject to the introduction of boundary conditions for $x$ and the first term on the right hand side in eq. (14) due to fluctuations in $x$ represents the diffusion process with a time dependent coefficient and the second term can be regarded as a force arising from the non-zero value for $\langle x(t)\rangle$, which is also time-dependent. Since the latter term makes it difficult to impose the boundary condition on eq. (14), we confine ourselves to the simple case of $z_1(t)=0$, where our modified diffusion equation (5) becomes

$$\frac{\partial W(x,t)}{\partial t}=\tfrac{1}{2}z_2(t)\frac{\partial^2 W(x,t)}{\partial x^2}\,. \tag{17}$$

On setting

$$\tau(t) = \tfrac{1}{2}\int_0^t z_2(t')\,\mathrm{d}t' = \tfrac{1}{2}[Z_2(t) - Z_2(0)]\,, \tag{18}$$

we see that

$$\frac{\partial}{\partial t} = \tfrac{1}{2}z_2(t)\frac{\partial}{\partial \tau}\,, \tag{19}$$

from which it follows that eq. (17) can be reduced to the ordinary diffusion equation

$$\frac{\partial W(x,\tau)}{\partial \tau} = \frac{\partial^2 W(x,\tau)}{\partial x^2}\,. \tag{20}$$

The mathematical properties of eq. (20) with the boundary condition in $x$ are well-known [1,2]. We can readily extend the case in eq. (20) to the three dimensional spherically symmetric Brownian motion. If we denote the radial distance by $r$, the second partial derivative on the right hand side of eq. (20) should be replaced by the Laplacian, which leads to

$$\frac{\partial W(r,\tau)}{\partial \tau} = \frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial W(r,\tau)}{\partial r}\right]. \tag{21}$$

As is well-known, if we put

$$W(r,\tau) = \frac{Q(r,\tau)}{r}\,, \tag{22}$$

we see that

$$\frac{\partial Q(r,\tau)}{\partial \tau} = \frac{\partial^2 Q(r,\tau)}{\partial r^2}\,, \tag{23}$$

which shows directly that eq. (23) is identical to eq. (20). The one- and three-dimensional fluxes, $J(x,t)$ and $J_r(r,t)$ are given by

$$J(x,t) = -\tfrac{1}{2}z_2(t)\,\frac{\partial P(x,t)}{\partial x} \tag{24}$$

and

$$J_r(r,t) = -\tfrac{1}{2}z_2(t)r^2\frac{\partial P(r,t)}{\partial r} = -\tfrac{1}{2}z_2(t)\left[r\frac{\partial Q(r,t)}{\partial r} - Q(r,t)\right], \tag{25}$$

respectively. Thus, in view of this obvious similarity, we confine ourselves to the one-dimensional case in the present work unless stated otherwise.

The free Brownian motion whose behavior is governed by the following Langevin equation (case (a)):

$$\frac{\mathrm{d}^2x(t)}{\mathrm{d}t^2} + \beta\,\frac{\mathrm{d}x(t)}{\mathrm{d}t} = w(t)\,, \tag{26}$$

where $w(t)$ is the random acceleration arising from collisions of the particle with the surrounding particles of the fluid. Furthermore,

$$\langle w(t)\rangle = 0 \quad \text{and} \quad \langle w(t_1)w(t_2)\rangle = \epsilon\delta(|t_1 - t_2|)\,.$$

It is apparent from eq. (26) that its formal solution is given by

$$x(t) = x_0 + \frac{v_0}{\beta}(1 - e^{-\beta t}) + \frac{1}{\beta}\int_0^t [1 - e^{-\beta(t-t')}]w(t')\,dt'\,. \tag{27}$$

It is obvious that $\langle x(t)\rangle$ in eq. (27) is not constant in general due to the presence of the second term on the right hand side in eq. (27). However, when either $v_0 = 0$ which corresponds to the case where the particle does not move at $t = 0$ or $v_0$ distributes according to Boltzmann's law, we see that $\langle x(t)\rangle = x_0$ whose time-derivative is zero. In the former case, we have

$$\tau(t) = \frac{k_B T}{2m\beta^2}[2\beta t - (1 - e^{-\beta t})(3 - e^{-\beta t})]\,, \tag{28}$$

where we have used the fluctuation-dissipation theorem:

$$\epsilon = 2\beta\frac{k_B T}{m}\,.$$

Whereas, for the latter case,

$$\tau(t) = \frac{k_B T}{m\beta^2}(\beta t - 1 + e^{-\beta t})\,. \tag{29}$$

From eqs. (17) and (18), it follows that the time-dependent diffusion coefficient is given by $d\tau(t)/dt$ which is different in the two cases of eqs. (28) and (29) when $t$ is small. However, as $t$ becomes large, both cases give rise to the identical value of $k_B T/m\beta$ that is nothing but the (time-independent) diffusion coefficient. In other words, the time dependent diffusion coefficient is related to the initial velocity, i.e. inertial effects. In fig. 1, $\tau(t)$ is plotted against $t$ in eq. (29) for $k_B T/m\beta = 1$ and $\beta = 0.1$, 0.5, 1.0, 5.0, and 10.0 from the bottom to the upper curves. The full line represents the asymptotic behaviour for the large $t$, which is given by

$$\tau(t) = \frac{k_B T}{m\beta}t \quad (\text{for large } t)\,. \tag{30}$$

This is the case where inertial effects are neglected. Whereas we note for small $t$ that

$$\tau(t) = \frac{k_B T}{2m}t^2 \quad (\beta t \ll 1)\,. \tag{31}$$

This is the case of $\beta \to 0$ where the particle is *in vacuo* suddenly after $t = 0$ until then it has been in contact with a heat bath which makes the particle be in the thermal equilibrium over velocity. Note that $\tau(t)$ in eq. (31) is independent of $\beta$.

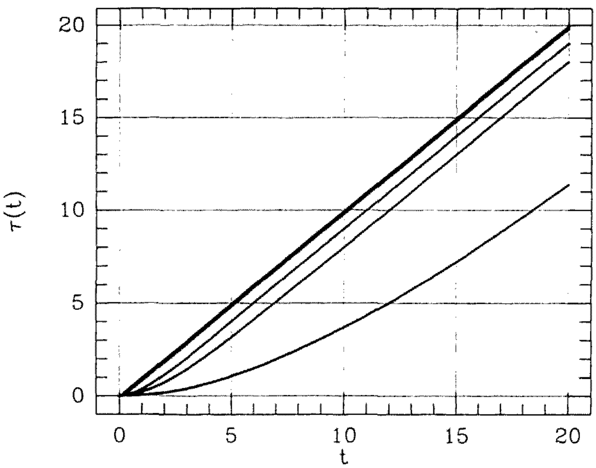


Fig. 1. Plots of $\tau(t)$ vs. $t$ for $(k_B T/m\beta) = 1$ and $\beta = 0.1, 0.5, 1.0$ and $10.0$ from the lower and the upper curves.

Although $\tau(t)$ in eq. (28) leads to the same result as that in eq. (30) for large $t$, the short-time limit in eq. (28) gives

$$\tau(t) = \frac{k_B T}{3m}\beta t^3 \quad (\text{for } \beta t \ll 1)\,, \tag{32}$$

from which we see that

$$\lim_{\beta \to 0} \tau(t) \to 0 \tag{33}$$

that is expected from the conditions that the particle does not move at $t = 0, v_0 = 0$ and it is *in vacuo* for $t > 0, \beta = 0$. In other words, eq. (33) means that the particle stays still for $t \geqq 0$.

From eqs. (16)–(18) it follows that the time dependent diffusion coefficients, $(1/2)z_2(t)$ that must be defined in order to take inertial effects into account, for the cases in eqs. (28) and (29) are given by

$$D(1 - e^{-\beta t})^2 \quad \text{and} \quad D(1 - e^{-\beta t})$$

respectively, where $k_B T/m\beta$ is represented by the usual time-independent diffusion coefficient $D$. The former coefficient is always smaller than the latter in short times, which means that the speed of the particle in diffusion in the case of $v_0 = 0$ is slow in comparison of the initial velocity as given by the Maxwell–Boltzman factor.

In the case where there is an absorbing boundary at $x = 0$ and the natural boundary at $x = \infty$, we see that

$$W(x,t) = \frac{1}{2}\sqrt{\frac{1}{\pi\tau(t)}}\left\{\exp\left[-\frac{(x-x_0)^2}{4\tau(t)}\right] - \exp\left[-\frac{(x+x_0)^2}{4\tau(t)}\right]\right\}, \tag{34}$$

where we have assumed that at $t = 0, P(x,0) = \delta(x - x_0)$. Whereas, for the three-dimensional Brownian motion with the absorbing sphere at $r = R$ whose center is located at $r = 0$, and the natural boundary at $r = \infty$, it follows that

$$W(r,t) = \frac{1}{2rr_0}\sqrt{\frac{1}{\pi\tau(t)}}\left\{\exp\left[-\frac{(r-r_0)^2}{4\tau(t)}\right] - \exp\left[-\frac{(r+r_0-2R)^2}{4\tau(t)}\right]\right\}, \tag{35}$$

where we have assumed that $W(r,0) = \delta(r - r_0)/r^2$ at $t = 0$. It should be noted that $W(r,t)$ in eq. (35) is symmetric by interchanging $r$ with $r_0$. Particularly when the initial concentration is uniform in eq. (35), we find that the density at $t$, $\rho(r,t)$ is given by

$$\rho(r,t) = N\int_R^\infty W(r,t)r_0^2\,\mathrm{d}r_0 = N\left[1 - \frac{R}{r}\mathrm{erfc}\frac{(r-R)}{\sqrt{4\tau(t)}}\right]. \tag{36}$$

This is the usual result [7] when inertial effects are ignored in which case $\tau(t) = Dt$ where $D = k_\mathrm{B}T/m\beta$ is the diffusion coefficient. In eq. (36), $N$ is the number of molecules in unit volume, the concentration at $t = 0$. In fig. 2, $\rho(2R,t)/N$ is plotted against $t$ for $\beta = 0.1, 0.5, 1.0, 5.0$, and $10.0$ from the upper to the lower curves for the fixed values of $D/R^2 = 1$. We see that inertial effects indeed give rise to the significant differences at short times in comparison with the case without the effects. From eq. (25), the flux at $r = R$ obtained from eq. (36) is given by

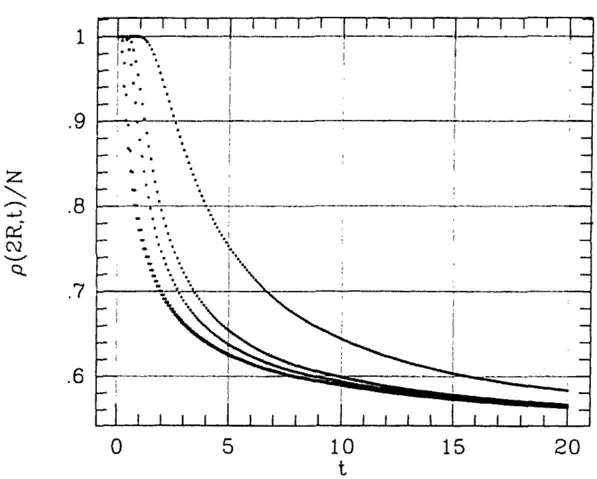


Fig. 2. Plots of $\rho(2R,t)/N$ vs. $t$ for $D/R^2 = 1$ and $\beta = 0.1, 0.5, 1.0, 5.0$ and $10.0$ from the upper to the lower curves.

$$j_r(r,t) = -\frac{z_2(t)}{2} NR\left\{\operatorname{erfc}\left[\frac{1}{\sqrt{4\tau(t)}}(r-R)\right] + r\sqrt{\frac{1}{\pi\tau(t)}}\exp\left[-\frac{(r-R)^2}{4\tau(t)}\right]\right\}. \tag{37}$$

If we put $r = R$ in eq. (37), we see

$$j_r(R,t) = -\frac{z_2(t)}{2} NR\left(1 + \frac{R}{\sqrt{\pi\tau(t)}}\right). \tag{38}$$

Here, we note that in view of eq. (18), and if we use the expression of $\tau(t)$ in eq. (29), it follows that

$$\frac{z_2(t)}{2} = \frac{\mathrm{d}\tau(t)}{\mathrm{d}t} = \frac{k_\mathrm{B}T}{m\beta}(1 - \mathrm{e}^{-\beta t}). \tag{39}$$

It is seen immediately from eq. (38) that if inertial effects are neglected,

$$\lim_{t\to 0} j_r(R,t) \to \infty. \tag{40}$$

But this difficulty is removed in the present case with inertial effects. In fact, eqs. (38) and (39) lead to

$$\lim_{t\to 0} j_r(R,t) \to -\frac{k_\mathrm{B}T}{m} NR\left(1 + R\sqrt{\frac{2m}{\pi k_\mathrm{B}T}}\right). \tag{41}$$

Note that the initial flux does not depend on the friction, $\beta$. In fig. 3, $-j_r(R,t)/NR$ is plotted against $t$ for $\beta = 0.1$, 0.5, 1.0, 5.0, and 10.0 from the lower to the upper curves for the fixed value of $D/R^2 = 1$. We see again that the short-time behaviour is not as simple as that expected from the ordinary diffusion equation without considering inertial effects. The inertial region followed by the asymptotic behavior in eq. (41) and the diffusion controlled region where $j_r(R,t) \approx t^{-1/2}$ are apparent from fig. 3. At this stage, we note in eq. (36) that

$$\lim_{t\to\infty} \rho(r,t) \to N\left(1 - \frac{R}{r}\right). \tag{42}$$

That means that for the case where the initial concentration at $t = 0$ is uniformly distributed, not all the particles can be absorbed by the wall at $r = R$. In fact, the concentration far away from the wall remains the same. The particles near the absorbing sphere are attracted and the rest does not *feel* the wall. It also implies that in the present steady-state case, the equilibrium distribution can depend on the initial distribution. Although $J(x,t)$ in one-dimensional motion can be readily obtained, we will not develope our discussion further, because the diffusion limited reaction is usually treated in the three dimensional space as we have.

In the case of the Brownian motion under the gravitational potential (case (b))

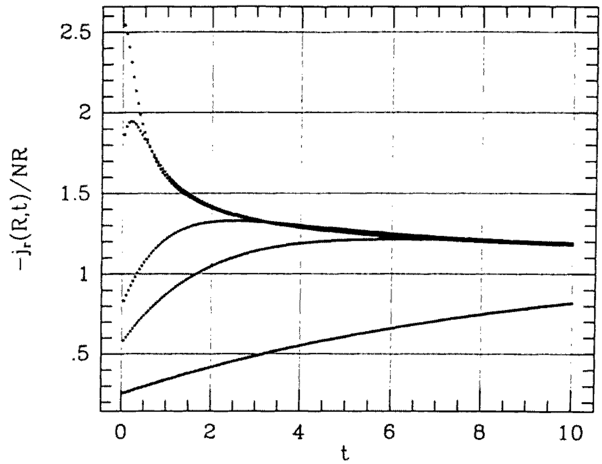


Fig. 3. Plots of $-j_r(R,t)/NR$ vs. $t$ for $D/R^2 = 1$ and $\beta = 0.1, 0.5, 1.0, 5.0$ and $10.0$ from the lower to the upper curves.

the constant acceleration $-g$ is added to the right hand side in the Langevin equation (26) as given by

$$\frac{\mathrm{d}^2 x(t)}{\mathrm{d}t^2} + \beta \frac{\mathrm{d}x(t)}{\mathrm{d}t} = -g + w(t)\,. \tag{43}$$

The formal solution of eq. (43) is given by

$$x(t) = x_0 + \frac{v_0}{\beta}(1 - \mathrm{e}^{-\beta t}) - \frac{g}{\beta^2}(\beta t - 1 + \mathrm{e}^{-\beta t}) + \frac{1}{\beta}\int_0^t [1 - \mathrm{e}^{-\beta(t-t')}] w(t')\,\mathrm{d}t'\,. \tag{44}$$

From this equation, we see immediately that $x(t)$ is the Gaussian random variable. We can solve the diffusion equation exactly for the case where the initial velocity is distributed according to the Maxwell law for which

$$Z_1(t) = x_0 - \frac{g}{\beta^2}(\beta t - 1 + \mathrm{e}^{-\beta t}) \tag{45}$$

and

$$Z_2(t) = 2\frac{D}{\beta}(\beta t - 1 + \mathrm{e}^{-\beta t})\,. \tag{46}$$

We find the diffusion equation in the form of eq. (14), but in view of eqs. (45) and (46), it becomes

$$\frac{\partial W(x,t)}{\partial t} = D(1 - \mathrm{e}^{-\beta t})\left[\frac{\partial^2 W(x,t)}{\partial x^2} + c\frac{\partial W(x,t)}{\partial x}\right], \tag{47}$$

where

$$c=\frac{g}{\beta D}\,.$$

Note that in eq. (47) we can take into account $z_1(t)$, because it happens to give the identical time-dependent form to $z_2(t)$ so that we need not consider the moving boundaries as we shall see later. As in the case of the free Brownian motion, inertial effects plays an important role in short times, and they slow down the dynamics in the initial stage.

With the same $\tau(t)$ as in eq. (29), we can write eq. (47) as

$$\frac{\partial W(x,\tau)}{\partial\tau}=\frac{\partial^2 W(x,\tau)}{\partial x^2}+c\frac{\partial W(x,\tau)}{\partial x}\,. \tag{48}$$

The solution of eq. (48) with the reflecting boundary at $x=0$ is then given by (see p. 57 of Chandrasekhar [8]

$$\begin{aligned}W(x,t)=&\frac{1}{2}\sqrt{\frac{1}{\pi\tau(t)}}\left\{\exp\left[-\frac{(x-x_0)^2}{4\tau(t)}\right]\right.\\&\left.+\exp\left[-\frac{(x+x_0)^2}{4\tau(t)}\right]\right\}\exp\left[-\frac{c}{2}(x-x_0)-\frac{c^2}{4}\tau(t)\right]\\&+\frac{c}{2}\mathrm{e}^{-cx}\,\mathrm{erfc}\left(\frac{x+x_0-c\tau(t)}{2\sqrt{\tau(t)}}\right).\end{aligned} \tag{49}$$

As in case (a), inertial effects make the dynamics slow at the initial stage.

It should be stressed again that although the case of harmonic potential gives the Gaussian $x(t)$, we cannot use the present procedure, because $\mathrm{d}/\mathrm{d}x$ and $x$ arising from the potential do not commute. Also, we see that the Boltzmann transport equation with the collision term of Bhatnager, Gross and Krook with $f(x)=0$ leads to an integral equation for non-Gaussian $W(x,t)$ which makes MS considerably more complicated [6].

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## References

[1] J. Crank, *The Mathematics of Diffusion* (Clarendon Press, Oxford, 1975).
[2] H.S. Carslaw and J.C. Jaeger, *Conduction of Heat in Solids* (Clarendon Press, Oxford, 1959).

[3] M.C. Wang and G.E. Ulenbeck, Rev. Mod. Phys. 17 (1945) 323.
[4] D.F. Calef and J.M. Deutch, Ann. Rev. Phys. Chem. 34 (1983) 493.
[5] S. Harris, J. Chem. Phys. 78 (1983) 4698, where other references can be found.
[6] A. Morita, J. Chem. Phys. 96 (1992) 3678.
[7] S.A. Rice, *Diffusion-Limited Reactions* (Elsevier, Amsterdam, 1985).
[8] S. Chandrasekhar, Rev. Mod. Phys. 15 (1943) 1.