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First-passage theory for Brownian motion with an absorbing boundary

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Abstract. We consider the problem of Brownian motion (1 – D) with an absorbing barrier. The approach is the first-passage-time theory recently formulated by us. Explicit results for the position, velocity distribution function are obtained in a high-friction approximation which indicate the usefulness of this approach in determining approximate solutions. An improved approximation, which retains the initial velocity dependence, is then considered, and results obtained which contain much of the qualitative behaviour we would expect to find in the exact solution. Some consequences of the initial velocity dependence in a calculation of the number density are briefly examined.

1. Introduction

The determination of the full position, velocity distribution function for a Brownian particle moving in an environment containing an absorbing barrier has been cited by Wang and Uhlenbeck (1946) as an open problem in the theory of Brownian motion. More recently, Bartlett (1966, 1978) has noted that this situation has remained unchanged. In addition to a considerable intrinsic interest, this problem has application to a number of topical problems, e.g. in the formulation of improved theories of nucleation kinetics (Mou and Lovett 1979) and chemical reaction dynamics (Northrup and Hynes 1978). An orthodox approach to this problem would be based on the Fokker–Planck equation (FPE) with the constraint imposed by the boundary. This, however, presents the difficulty that the boundary condition is specified only for emergent particles, i.e. only for half of the velocity range. We have recently formulated the absorbing-boundary problem in terms of integral equations (Harris 1980), which allows the difficulties associated with the FPE to be avoided.

There are two distinct approaches that our integral equation method is based on. These are closely related in spirit but quite different in detail. The most physical of these is based on the distribution function for first passages to the boundary; we will consider this approach exclusively in what follows. The other approach is based on the distribution function for first turning points (FTP) in the inaccessible part of the physical space. Although less physical, the FTP approach has the advantage that the resulting equation is of the Wiener–Hopf type and thus can be explicitly solved, in principle, by standard methods. Because the technical details involved in obtaining an exact solution are quite complicated, this objective has yet to be realised, and there is still a certain value in considering approximate solutions. Approximations can provide qualitative information and may also prove useful in particular applications, and it is in this regard that the first-passage approach appears to offer certain advantages.

In § 2 we briefly describe the first-passage formulation. In § 3 we consider the high-friction approximation (HFA), which we used earlier (Harris 1980) in the context of the FTP formulation, and obtain the position, velocity distribution function (equation (5)). This result generalises the diffusion theory result for the position distribution function which can be easily found by the method of images. The structure of our approximate result is in agreement with the intuitive expectation (see also the remark by Bartlett (1966, p 168)) that the image 'technique' does not apply in the full one-particle phase space. Interestingly enough, the result found here is not identical to that found using the HFA in the FTP theory except at long times. This is not surprising, since it is well known that a given approximation may lead to different results when used in distinct *exact* theoretical frameworks, e.g. differing results for the equation of state may be found from a given approximation depending on whether the compressibility equation or virial equation is used.

The most obvious shortcoming of the HFA is that the initial velocity dependence is neglected. In § 4 we remedy this defect by considering an improved approximation which includes this dependence in a fairly realistic manner, and again calculate the full position, velocity distribution function using the first-passage approach. We then briefly examine some of the consequences of the dependence on the initial data which our results contain.

2. First-passage formulation

In this section we review the first-passage-time formulation for the problem of one-dimensional Brownian motion with an absorbing boundary. We will denote the Brownian particle position, velocity by $x = q,\ v$, the initial data by $x_0 = q_0,\ v_0$, and consider the case $q_0 > 0$ with the boundary at the origin. $F(x, t; x_0)$ will denote the distribution function which describes the motion in the infinite space (i.e. in the absence of any boundary effects), and $f(x, t; x_0)$ the distribution function for the case of interest with an absorbing barrier at $q = 0$. We can determine f from F by *uniquely* subtracting from the latter the contribution of all those paths which begin at x_0 at $t = 0$, cross the origin at any $t' < t$, and then somehow arrive at x at time t. Since many of these paths will cross the origin several times, care must be taken to count these multiple-crossing paths only once. Let $f'(0, v, t; x_0)$ be the distribution function for first crossing of the origin†. Then, from the Markoff property of Brownian motion in the full x space and the definitions of f, f' and F, the following relationship holds:

$$f(x, t; x_0) = F(x, t; x_0) - \int_0^t \mathrm{d}t' \int_{-\infty}^0 \mathrm{d}v'\, |v'| f'(0, v', t'; x_0) F(x, t - t'; 0, v'). \tag{1}$$

We also have

$$\begin{aligned} f'(0, v, t; x_0) &= F(0, v, t; x_0) - \int_0^t \mathrm{d}t' \int_{-\infty}^0 \mathrm{d}v'\, |v'| f'(0, v, t'; x_0) \\ &\quad \times F(0, v, t - t'; 0, v'), \qquad v < 0 \\ &= 0, \qquad v > 0. \end{aligned} \tag{2}$$

† Note, the event being described is the first crossing event, which occurs with $v < 0$ for $q_0 > 0$, and not the first crossing with velocity v, despite earlier crossings with $v' \neq v$.

In our earlier work (Harris 1980) we have shown that, for $q>0$, f as determined from equation (1) is equivalent to the solution of the FPE subject to the absorbing-boundary condition that the solution vanishes at $q=0$ for $v>0$.

The presence of the $|v'|$ term in the above equations requires comment: what must be equated are probabilities, which require each distribution function to be multiplied by an element of phase volume prior to the integration. The element $dq'\,dv'$ about the point $0, v'$ has been replaced by $|dq'/dt'|\,dt'\,dv' = |v'|\,dv'\,dt'$, and then all contributions obtained by integrating as shown, with the v' integration restricted to the incoming range. Substitution of $q=0$ into equation (1) reproduces equation (2) for $v<0$; the discontinuity at q, $v=0$ is forced here by the second part of equation (2).

The Laplace transform of equation (2) is a Fredholm equation of the second kind, having an extremely complicated kernel, and as a result is not promising from the point of view of leading to an exact solution. However, as we demonstrate in the following section, this equation does offer some advantages in generating approximate solutions.

3. High-friction approximation

For very large friction coefficient (or at long times) we have $F(x,t;x_0)\to F^\circ(v)n(q,t;q_0)$, where F° is the Maxwellian distribution and n is the solution to the diffusion equation. We have used this approximation earlier (Harris 1980) in the FTP formulation to find f, which requires the full Wiener–Hopf 'machinery' without the benefit of any apparent simplifications. In the present context the solution can be found with considerably less effort, which indicates the potential usefulness of equation (2) in generating good working approximate solutions.

The simplifying feature of the HFA (described above) in the context of equations (1) and (2) is that the f' and F terms are no longer coupled in the velocity integration variable. Thus, if we multiply equation (2) by $|v|$ and integrate over $-\infty<v<0$, we find (after first Laplace transforming)

$$I(s,q_0)\equiv\int_{-\infty}^{0} dv\,|v|f'(v,s;x_0)=\frac{An(0,s;q_0)}{1+An(0,s;0)}, \tag{3}$$

where $A=(kT/2m\pi)^{1/2}$, s is the Laplace variable, and we have suppressed the $q=0$ in the argument of f'. Substituting this back into the transform of equation (2) allows us to directly 'solve' that equation, with the result

$$f'(v,s;x_0)=F^\circ(v)\left(n(0,s;q_0)-\frac{An(0,s;0)n(0,s;q_0)}{1+An(0,s;0)}\right). \tag{4}$$

Either of the preceding two equations with equation (1) gives

$$f(x,s;x_0)=F^\circ\left(n(q,s;q_0)-\frac{n(q,s;-q_0)}{1+A^{-1}(4Ds)^{1/2}}\right) \tag{5}$$

where the identity $n(q,s;0)n(0,s;q_0)=(4Ds)^{-1/2}n(q,s;-q_0)$ has been used in writing the term following the minus sign.

The above result has the same general structure as our earlier result based on the FTP formulation, and at long times (small s) or high friction (small D) goes over into an obvious generalisation of the diffusion equation result. (Note, at short times the diffusion equation boundary condition $n(0,t;q_0)=0$ is not satisfied for $n=\int dv\,f$ as determined by equation (5).) For use in applications, equation (5) offers an advantage over our previous result in that it is easily inverted. Thus we see that, from the point of view of providing *approximate* solutions, equation (2) offers decided advantages over the FTP formulation.

4. Superposition approximation

Our main objective in this section is to generalise the HFA and assess in a qualitative way the effects arising from the dependence of f on the full initial data. One way of doing this is to replace F by a time-weighted superposition of distribution functions which give both the correct initial and long-time behaviour. A choice which satisfies the above criteria is

$$F(x, t; x_0) = [\mathrm{e}^{-t/\tau}\delta(v - v_0) + (1 - \mathrm{e}^{-t/\tau})F^{\circ}(v)]n(q, t; q_0), \tag{6}$$

which is exact at $t = 0$ and as $t \to \infty$, and reduces to the HFA for $\tau \propto \zeta^{-1}$ and large ζ with ζ the friction coefficient. The coordinate dependence in the above approximation has been chosen for technical reasons to avoid the problems of dealing with a delta function, which would be preferable, in the first term. Despite some shortcomings at small times, the above approximation still provides a fairly realistic approximation to F, and has the virtue of allowing an analytic solution for f to be found which contains a significant amount of structure and is a marked improvement over the HFA result, equation (5).

With only minor modifications, the procedure of the preceding section can be followed here. Substituting equation (6) into equation (2), multiplying by $|v|$, and integrating over $-\infty < v < 0$ leads to a generalisation of equation (3):

$$I(s, x_0) = \left[\frac{H(-v_0)|v_0|n(0, \sigma; q_0)}{1 + |v_0|/(4D\sigma)^{1/2}} + \left(\frac{m}{2\pi kT}\right)^{1/2}(n(0, s; q_0) - n(0, \sigma; q_0))\right]$$
$$\times \mathscr{I}\left((4D\sigma)^{-1/2}, \frac{m}{2kT}\right)$$
$$\times \left[1 + \left(\frac{m}{2\pi kT}\right)^{1/2}(n(0, s; 0) - n(0, \sigma; 0))\mathscr{I}\left((4D\sigma)^{-1/2}, \frac{m}{2kT}\right)\right]^{-1}. \tag{7}$$

Here we have used $\sigma = s + \tau^{-1}$, $H(y)$ is the standard Heaviside function, and the dependence of I on both q_0 and v_0 is indicated. The quantity $\mathscr{I}(a, b)$ is defined as

$$\mathscr{I}(a, b) \equiv \int_{-\infty}^{0} \mathrm{d}v\, |v| \frac{\mathrm{e}^{-bv^2}}{1 + a|v|}, \tag{8}$$

and, although the integral is not given explicitly in any of the standard tables, it can be written in terms of standard tabulated functions. We evaluate $\mathscr{I}$ in the Appendix, and consider it as known in what follows. Substituting equations (6) and (7) into equations (2) then determines f':

$$f'(v, s; x_0) = [F(0, v, s; x_0) - I(s, x_0)(n(0, s; 0) - n(0, \sigma; 0))][1 + |v|(4D\sigma)^{-1/2}]^{-1}. \tag{9}$$

In the limit $\tau \to 0$ the above result reduces to the corresponding HFA result, equation (4).

Substituting for f' in equation (1) then leads to the desired result:

$$f(x, s; x_0) = F(x, s; x_0) - H(-v)n(q, \sigma; 0)|v|[F(0, v, s; x_0) - I(s, x_0)F^\circ(v)(n(0, s; 0) - n(0, \sigma; 0))][1 + |v|(4D\sigma)^{-1/2}]^{-1} - I(s, x_0)F^\circ(v)(n(0, s; 0) - n(0, \sigma; 0)). \quad (10)$$

The above result is quite complex, and we will limit ourselves here to some comments on those qualitative features which distinguish it from the HFA result, equation (5). The most significant difference is due to the presence of the Heaviside function, which indicates a discontinuity at $v = 0$. This is the same behaviour we would expect to find in the exact solution. The physical basis for this is the removal of particles at the boundary, an affect which is most pronounced near the boundary. At short and intermediate times a non-trivial velocity dependence is apparent; the initial velocity dependence persists for these same times and also contains discontinuities. An interesting aspect of the initial velocity dependence is how this affects the number density, which we must now define as

$$n(q, s; q_0) = \int \mathrm{d}v_0 \, f(v_0) \int \mathrm{d}v \, f(x, s; x_0), \quad (11)$$

with $f(v_0)$ the initial velocity distribution function. The diffusion equation result, n_D, should correspond to the choice $f(v_0) = F^\circ(v_0)$. For comparison we also consider $n^\pm$, corresponding to $f(v_0) = 2H(\pm v)F^\circ(v_0)$, for which we find

$$n^\pm(q, s; q_0) = n(q, s; q_0) - \tilde{\mathscr{I}}\left((4D\sigma)^{-1/2}, \frac{m}{2kT}\right)\left(\frac{n(q, s; -q_0)}{(4DS)^{1/2}} \mp n(q, s; 0)n(0, \sigma; q_0)\right), \quad (12)$$

where $\tilde{\mathscr{I}}(a, b) = b^{1/2}\mathscr{I}(a, b)[1 + b^{1/2}(n(0, s; 0) - n(0, \sigma; 0))\mathscr{I}(a, b)]^{-1}$.

We see that $n_D = \frac{1}{2}(n^+ + n^-)$ will differ in detail from both n^+ or n^- except in the limit as each becomes zero. Although we do not think that the present results, based on the simple approximation of equation (6), warrant quantitative comparisons, we do think that they suggest that improvements to the diffusion equation theory for the absorbing-boundary problem are well motivated. More rigorous work in this direction is currently in progress.

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Appendix

We wish to evaluate

$$\mathscr{I}(a, b) = \int_{-\infty}^{0} \mathrm{d}v \, |v| \frac{\mathrm{e}^{-bv^2}}{1 + a|v|} = \frac{1}{a^2} \int_0^\infty \mathrm{d}y \, y \frac{\mathrm{e}^{-cy^2}}{1 + y}, \quad (A1)$$

with $c = b/a^2$.

This integral does not appear in the standard tables; a change of variable allows us to write the integral in terms of the Laplace transform of $(1+t^{1/2})^{-1}$, which is also not given in the standard tables for these transforms. Since

$$a^2\mathcal{I} = \left(\frac{\pi}{4c}\right)^{1/2} - \int_0^\infty \mathrm{d}y \frac{\mathrm{e}^{-cy^2}}{1+y}, \tag{A2}$$

we have (Abramowitz and Stegun 1965, p 302)

$$a^2\mathcal{I} = \left(\frac{\pi}{4c}\right)^{1/2} - \mathrm{e}^{-c}\left(\pi^{1/2}\int_0^{c^{1/2}} \mathrm{d}x\, \mathrm{e}^{x^2} - \frac{E_i(c)}{2}\right), \tag{A3}$$

which can be written in terms of the error function for complex argument, $W(z)$, as

$$a^2\mathcal{I} = \left(\frac{\pi}{4c}\right)^{1/2} - \frac{\pi \mathrm{i}}{2}(W(c^{1/2}) - \mathrm{e}^{-c}) + \frac{E_i(c)}{2}\mathrm{e}^{-c}. \tag{A4}$$

Both $W(z)$ and $E_i(z)$ are standard tabulated functions, hence $\mathcal{I}$ is determined. Despite appearances, $\mathcal{I}$ is always real, since $W(c^{1/2}) - \mathrm{e}^{-c}$ is always pure imaginary.

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