Evaluation of the rate constant and deposition velocity for the escape of Brownian particles over potential barriers

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Abstract

We analyze the escape of Brownian particles over potential barriers using the Fokker-Planck equation in a similar way to that of Chandrasekhar (Rev. Modern Phys., 1943), deriving a formula for the particle deposition velocity to a surface as a function of the particle response time. For very small particle response times, the particle deposition velocity corresponds to that obtained using a quasi-steady solution of Smoluchowski’s equation and for very large particle response times, the deposition velocity corresponds to that based on the transition state method (E. Wigner, Trans. Faraday Soc., 1938).

1 Introduction

This short paper examines the work of Chandrasekhar [1] on the escape of Brownian particles over potential barriers. It is part of a classic paper that examines a number of stochastic problems using the Fokker-Planck equation for Brownian particles. One of the most important results of his study has been to show under what conditions the Fokker-Planck equation transforms into an advection-gradient diffusion equation commonly referred to as Smoluchowski’s equation. This has a significant bearing on the formula for the release rate of particles over a potential barrier for it is generally assumed that the particle flux out of the well can be obtained from a steady state solution of Smoluchowski’s equation. The general formula for the rate constant for the release of particles from the potential well that Chandrasekhar obtained as a solution of the Fokker-Planck equation, shows that the formula based on Smoluchowski’s equation is one extreme of the solution when the spatial gradient of the forces (per unit mass of the particle) is small compared with the particle response time which in many cases of interest does not apply (see Reeks et al. [3]). The fact that Chandrasekhar obtained a relatively simple formula for the most general result (not restricted by the value of the particle response time) is very important to the analysis we present here.
The situation analyzed by Chandrasekhar is slightly different from the case we wish to consider here where particles from the bulk of the suspending fluid are subject to a potential barrier as they approach a wall where they are finally deposited. It turns out that the analysis is exactly the same as that used by Chandrasekhar, as indeed is the form for the deposition flux. What is different is the way we need to normalize the flux. In the one case when particles are trapped in a well it is the rate constant for escape that we require by dividing the flux by the number of particles in the well whereas in the case of interest, it is the deposition velocity which means we divide the current by the concentration in the bulk or more precisely when referring to the situation in Figure 4.1 to the concentration at the bottom of the potential barrier at A.

With reference to Fig (1.1) we begin with the case analyzed by Chandrasekhar [1] where by Brownian diffusion, particles in a 1-D potential well with minimum potential at A escape over a potential barrier of height \( Q \) at C into the potential well at B. A complete solution can be found by solving the Fokker-Planck equation for the phase space distribution (combined spatial and velocity distribution) for Brownian motion in a conservative field of force. However whilst this can be achieved numerically at least for a 1 D potential, for the case when \( Q \gg \) the kinetic energy of a particle per unit mass, analytical solutions can be found under certain realizable conditions.

2 Rate constant based on Smoluchowski’s equation for advection diffusion.

We refer to Chandrasekhar (1943) [1] and the conditions for which the Fokker-Planck equation reduces to an advection gradient diffusion Eq. (Smoluchowski’s Eq.)

\[
\frac{\partial w}{\partial t} = \nabla \cdot \left( \frac{q}{\beta^2} \nabla w - \frac{K}{\beta} w \right)
\]

(2.1)

where:

- \( \beta \) is the Stokes inverse particle relaxation time

- \( w(x, t) \) is the particle concentration and \( K(x, t) \) the force acting on an individual particle both at position \( x, t \).
• $q = \beta k_B T / m$ is the diffusion coefficient for dispersion in velocity space, $k_B$ is Boltzmann’s constant and $m$ is the particle mass and $T$ the absolute temperature.

It is important to appreciate that Smoluchowski’s equation is only valid if we ignore any changes in time intervals $\sim \beta^{-1}$ or space intervals $\beta^{-1} (k_B T / m)^{1/2}$.

So we may consider the escape of particles from A over the potential barrier at C in terms of quasi-steady concentration and a constant (spatially and time independent) advection diffusion current $j$, implying from Eq. 2.4 that

$$j = q \beta^{-2} \nabla w - \beta^{-1} K w$$

If $K(x)$ is independent of $t$ and derived from a potential $\psi(x)$ such that

$$K = -\nabla \psi$$

$$j = q \beta^{-2} \nabla w - w \beta^{-1} \text{Grad} \psi$$

So integrating between two points $A$ and $B$ we obtain

$$j \cdot \int_A^B \beta \exp(m \psi/k_B T) dx = \frac{k_B T}{m} \exp \left( m \psi/k_B T \right) \bigg|_A^B$$  \hspace{1cm} (2.2)

where we have replaced $q$ by $\beta k_B T / m$. Now let’s determine the rate constant or the probability per unit time that a particle will be escape over the potential barrier at C into potential well around B. We assume that most of the particles are in quasi equilibrium around A and the height of the potential barrier $Q \gg k_B T / m$. This means that to a high degree of approximation, a distribution of velocities very close to Gaussian will exist in the neighborhood of A and that the concentration $w(x)$ in the neighborhood of A will be given by

$$w(x) \approx w_A \exp - m \psi/k_B T$$

where $w_A$ is the concentration of particles at A. We may assume also that $w_A \gg w_B$ and that referring to Eq. (2.2) $w \exp - \beta q^{-1} \psi \big|_A^B \approx w_A$ and so from Eq. (2.2)

$$j = \frac{k_B T}{m} w_A \left( \int_A^B \beta \exp(m \psi/k_B T) dx \right)^{-1}$$

The value of the integral will be largely based on the value of the integrand around C where we can approximate $\psi(x)$ to

$$\psi(x) \cong Q - \frac{1}{2} \omega^2_C (x - x_c)^2$$  \hspace{1cm} (2.3)

so

$$\int_A^B \exp(q \beta^{-1} \psi) dx \cong \exp(Q / k_B T) \int_{-\infty}^{\infty} dx \exp - \omega^2_C (x - x_c)^2 / 2k_B T$$

$$= \exp(Q / k_B T) \left( \frac{2\pi k_B T}{m \omega^2_C} \right)^{1/2}$$
So we have for $j$

$$j = \beta \frac{k_B T}{m} w_A \exp(-Q/k_B T) \left( \frac{2\pi k_B T}{m \omega_C^2} \right)^{-1/2}$$

$$= \beta^{-1} \omega_C \left( \frac{k_B T}{2\pi m} \right)^{1/2} \exp(-Q/k_B T) w_A$$

To obtain a rate constant (probability of a particle of escaping from the potential well in neighborhood of A into potential well at B we need to divide $j$ by the number of particles in the well in the neighborhood of A which we can approximate to

$$N_A = w_A \int_{-\infty}^{\infty} \exp\left(-\frac{1}{2} m \omega_A^2 x^2 / k_B T\right) dx$$

$$= \left( \frac{w_A}{\omega_A} \right) \left( \frac{2\pi k_B T}{m} \right)^{1/2}$$

So finally the rate constant for the release of particles from the potential well at A into the potential well at B is given by

$$P = j/N_A = \left( \frac{\omega_A \omega_C}{2\pi \beta} \right) \exp(-mQ/k_B T)$$

### 3 Rate constant based on the transition state method

We refer to the case where Smoluchowski’s equation does not apply and in particular the case referring to the potential in Fig. (1.1) when $\omega_C/\beta \gg 1$. In other words the particle does not respond at all to any changes that might occur on timescales $\sim \beta^{-1}$ or and changes occur in distances $\sim \beta^{-1} (k_B T/m)$. In terms of particles in the potential well we may safely assume that they are in equilibrium with a concentration in the well that varies as $w_A \exp - m\psi/k_B T$ and a Maxwell distribution of particle velocities $\phi(v)$ independent of $x$ given by

$$\phi(v) = \frac{1}{\sqrt{2\pi k_B T/m}} \exp\left(-\frac{v^2}{2k_B T}\right)$$

The region beyond C is such that a particle only responds to the force which attracts it towards B, and there is no diffusion back into A. The potential around B acts as a perfect sink for particles. There is no fluid resistance to the particles motion and effectively the particles motion is such that immediately beyond C refers only to those particles traveling in the $+ve x$ direction. So we can write the current $j$ immediately beyond C as

$$j = w_A \exp - m\psi/k_B T \int_{0}^{\infty} v \phi(v) dv$$

$$= w_A \exp - m\psi/k_B T \left( \frac{k_B T}{2\pi m} \right)^{1/2}$$
So dividing by $N_A$ in Eq.(2.4) gives $P$

$$P = j/N_A = \frac{\omega_A}{2\pi} \exp - m\psi/k_BT \quad (3.3)$$

Unlike the rate constant based on Smoluchowski’s advection diffusion equation, the rate constant $P$ in Eq.(3.3) does not depend on $\omega_C$. The formula is based on what is called the transition state method [2].

4 Rate constant from a solution of the Fokker-Planck equation

Chandrasekhar [1] has evaluated the rate constant by solving the Fokker-Planck equation for Brownian particles in a potential well and obtained a solution that is valid for all $\beta$. The solution necessarily contracts to the formulae previously derived for $\beta^{-1}\omega_C \ll 1, \gg 1$. The same assumption is made that the height of the potential barrier at $C$ in Figure 1.1, $Q \gg k_BT$. We shall briefly outline how the formula is obtained and refer to Chandrasekhar [1] for the precise details. The Fokker-Planck equation for the phase space density $W(v,x,t)$ for diffusion in a conservative field of force $K(x)$ is given for 1D in space by

$$\frac{\partial W}{\partial t} + v \frac{\partial W}{\partial x} + K \frac{\partial W}{\partial v} = \beta v \frac{\partial W}{\partial v} + \beta W + q \frac{\partial^2 W}{\partial v^2} \quad (4.1)$$

where $K = -\partial \psi(x)/\partial x$. The equilibrium solution is

$$W(v,x) = C \exp \left[-m \left(v^2 + 2\psi(x)\right)/2k_BT\right]$$

for which $\psi(0) = 0$ at $A$ in Figure 1.1 and for future reference

$$C = w_A (m/2\pi k_BT)^{1/2} \quad (4.2)$$

As Chandrasekhar points out this cannot be the solution for all $x$ because there would be no diffusion of particles over the potential barrier. For the case we are studying where $Q \gg k_BT$ we would expect the solution to be close to the equilibrium solution at $A$. A solution is therefore sought of the form

$$W(v,x) = C F(v,x) \exp \left[-m \left(v^2 + 2\psi(x)\right)/2k_BT\right] \quad (4.3)$$

where $F(v)$ is very near unity in the neighborhood $A$ at $x = 0$ and for $x \gg x_C$ i.e. in the region of $B$. Chandrasekhar points out that the most sensitive region to calculate the departure from equilibrium in the neighborhood of $C$ where $\psi(x)$ has the form given in Eq.(2.3). So substituting the form for $W(v,x)$ in Eq.(4.3) into the stationary Fokker-Planck equation with $\psi(x)$ given by Eq.(2.3) of the Eq.(4.1) gives the following equation for $F(v,x)$:
\[ v \frac{\partial F}{\partial X} + \omega^2 X \frac{\partial F}{\partial v} = q \frac{\partial^2 F}{\partial v^2} - \beta v \frac{\partial F}{\partial v} \] (4.4)

where we have written \( F \) as a function of \( X = x - x_C \) and \( v \). The solution of this equation satisfying the boundary conditions is

\[ F(\xi) = \left( \frac{a - \beta}{2\pi q} \right)^{1/2} \int_{-\infty}^{\xi} \exp \left[ -(a - \beta) \xi^2 / 2q \right] d\xi \] (4.5)

where \( \xi = v - aX \) and \( a = \left[ (\beta/2)^2 + \omega^2_C \right]^{1/2} + (\beta/2) \). The current at \( C \) is given by

\[ j = \int_{-\infty}^{\infty} W(v, X = 0)vdv \]

which substituting the form for \( W(v, x) \) based on Eq.(4.3) and Eq.(4.5) for \( F(\xi) \) gives

\[ j = C \left( \frac{k_B T}{m} \right) \left[ (a - \beta)/a \right]^{1/2} e^{-mQ/k_B T} \] (4.6)

Using the formula in for \( N_A \) in Eq.(2.4) and the value \( C = \) the rate constant \( P \) is given by

\[ P = j / N_A = (\omega_A / 2\pi \omega_c) \left\{ \left[ \beta^2 / 4 + \omega^2_C \right]^{1/2} - \beta / 2 \right\} e^{-mQ/k_B T} \]

Note that for \( \omega_C / \beta \gg 1 \), \( P \) contracts to the transition state approximation Eq.(3.3) and when \( \omega_C / \beta \ll 1 \) \( P \) contracts to the advection gradient diffusion approximation Eq.(2.5).

5 Depositation velocity for escape of Brownian particles over potential barriers.

In the previous section we considered the case where all the particles were contained in a potential well. The height of the potential barrier \( Q \gg k_B T / m \) the thermal energy /unit particle mass which meant that most of the particles were located in the neighborhood of the minimum potential at \( A \) and were in thermal equilibrium. We used the number of particles in the well as a normalizing factor in the sense that the flux of particles escaping from the well was directly proportional to the number of particles in the well at any instant of time. So the ratio \( j / N_A \) was a constant in time and defined a rate constant \( P \) or equivalently the probability per unit time of a particle in the potential well at \( A \) of escaping over the potential barrier at \( C \) and into the potential well at \( B \). \( P^{-1} \) is therefore typical of the lifetime of particles in the potential well around \( A \).
We want now to consider a slightly different situation depicted in Figure 4.1 corresponding to particles being deposited at a wall at B by diffusion but having to overcome a potential barrier at C before reaching the wall. The particles reach A from the left by Brownian diffusion from a region where the external force acting on the particles is zero. We may assume that in steady state the flux at A scales on the concentration \( w_A \) so \( j = k_d w_A \). The formula for the deposition velocity \( k_d \) is straightforward to obtain since it is readily obtained from the expression for \( j \) we have obtained from the various cases we reconsidered before (there is no need to divide by the number of particles in the well to obtain the rate constant.) So from the expression for \( j \) given in Eq.(4.6) and substituting the value of \( C \) in Eq.(4.2) we have

\[
k_d = \frac{j}{w_A} = \left( \frac{k_B T}{2 \pi m} \right)^{1/2} \left[ (a - \beta)/a \right]^{1/2} e^{-mQ/k_B T}
\]

\[
= \omega_C^{-1} \left( \frac{k_B T}{2 \pi m} \right)^{1/2} \left( \left( \frac{\beta}{2} \right)^2 + \omega_C^2 \right)^{1/2} e^{-mQ/k_B T}
\]

(5.1)

So for the value of \( k_d \) based on the transition state method for which \( (\omega_C/\beta \gg 1) \) we have from Eq.(5.1)

\[
k_d = \left( \frac{k_B T}{2 \pi m} \right)^{1/2} e^{-mQ/k_B T} \quad (\omega_C/\beta) \gg 1
\]

and for \( (\omega_C/\beta \ll 1) \) (based on Smoluchowski’s equation)

\[
k_d = \frac{\beta}{2} \left( 1 + \left( \frac{2\omega_C}{\beta} \right)^2 \right)^{1/2} \omega_C^{-1} \left( \frac{k_B T}{2 \pi m} \right)^{1/2} e^{-mQ/k_B T}
\]

\[
= \frac{\beta}{2 \omega_C} \left[ 4\omega_C^2 \right] \left( \frac{k_B T}{2 \pi m} \right)^{1/2} e^{-mQ/k_B T}
\]

\[
k_d = \left( \frac{\omega_C}{\beta} \right) \left( \frac{k_B T}{2 \pi m} \right)^{1/2} e^{-mQ/k_B T}
\]

Figure 4.1: Potential Barrier for particles depositing at a wall
References

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