Problem Statement. (Exam 2, 18.366, 2005) Consider a diffusing particle which feels a conservative force, \( f(x) = -\phi'(x) \), in a smooth, symmetric potential, \( \phi(x) = \phi(-x) \), causing a drift velocity, \( v(x) = bf(x) \), where \( b = D/kT \) is the mobility and \( D \) is the diffusion constant. If the particle starts at the origin, then PDF of the position, \( P(x,t) \), satisfies the Fokker-Planck equation,

\[
\frac{\partial P}{\partial t} + \frac{\partial}{\partial x}(v(x)P(x,t)) = D \frac{\partial^2 P}{\partial x^2},
\]

with \( P(x,0) = \delta(x) \). Suppose that the potential has a minimum \( \phi = 0 \) at \( x = 0 \) with \( \phi''(0) = K_0 > 0 \) and two equal maxima \( \phi = E > 0 \) at \( x = \pm x_1 \) with \( \phi''(x_1) = -K_1 < 0 \). Let \( \tau \) be the mean first passage time to reach one of the barriers at \( x = \pm x_1 \) (and then escape from the well with probability 1/2).

1. Derive the general formula

\[
\tau = \frac{1}{D} \int_0^{x_1} dx \int_0^x dy \frac{e^{\phi(x)/kT}}{e^{\phi(x)/kT}}
\]

2. In the low temperature limit, \( kT/E \to 0 \), calculate the leading-order asymptotics of the escape rate, \( R = 1/2\tau \sim R_0(T) \), using the saddle-point method. Verify the classical result of Kramers: \( R_0(T) \propto e^{-E/kT} \).

3. Calculate the first correction to the Kramers escape rate:

\[
R(T) \sim R_0(T) \left( 1 + \frac{kT}{E} \right).
\]

SOLUTION

1. Mean escape time. We have:

\[
\frac{\partial P}{\partial t} = D \frac{\partial^2 P}{\partial x^2} + D \frac{\partial}{kT \partial x} \phi'(x) P(x,t)
\]

where \( P(x,t) = p(x,t|0,0) \) within initial condition at the bottom of the well, \( P(x,0) = \delta(x) \), and absorbing boundary conditions at the exit points, \( P(\pm x_1,t) = 0 \). We can write:

\[
\frac{\partial P}{\partial t} = L_x P
\]

where the spatial operator \( L_x \) can be simplified using an integrating factor:

\[
L_x = D \frac{\partial}{\partial x} \left[ e^{-\phi(x)/kT} \frac{\partial}{\partial x} \left( e^{\phi(x)/kT} \right) \right]
\]

The probability \( S(t) \) of realization which have started at \( x = 0 \) and which have not yet reached \( x = \pm x_1 \) up to time \( t \) is given by:

\[
S(t) = \int_{-x_1}^{x_1} p(x,t|0,0) dx = \int_{-x_1}^{x_1} P(x,t) dx
\]
The distribution function \( f(t) \) for the first passage time is then given by:

\[
f(t) = \frac{\partial}{\partial t} 1 - S(t) = -\frac{\partial S}{\partial t} = -\int_{-x_1}^{x_1} \frac{\partial P}{\partial t} dx
\]

The mean escape time is then given by:

\[
\tau = \int_0^\infty t f(t) dt = \int_{-x_1}^{x_1} g_1(x) dx \quad \text{with} \quad g_1(x) = -\int_0^\infty t \frac{\partial P}{\partial t} dt
\]

Performing an integration by parts (assuming that \( P(x, t) \) decays quickly enough in time that \( \lim_{t \to \infty} t P(x, t) = 0 \)) gives:

\[
g_1(x) = \int_0^\infty P(x, t) dt
\]

By applying the operator \( L_x \) on both sides of this relation, we get:

\[
L_x g_1(x) = \int_0^\infty L_x P(x, t) dt = \int_0^\infty \frac{\partial P}{\partial t} dt = -P(x, 0) = -\delta(x)
\]

where we have used (1). Using the expression (2) for \( L_x \), it is easy to solve:

\[
g_1(x) = \frac{e^{-\phi(x)/kT}}{D} \int_x^{x_1} e^{\phi(y)/kT} \left[ \int_0^y \delta(z) dz \right] dy
\]

Now we can express the mean escape time:

\[
\tau = \int_{-x_1}^{x_1} g_1(x) dx = 2 \int_0^{x_1} g_1(x) dx
\]

\[
= \frac{1}{D} \int_0^{x_1} e^{-\phi(x)/kT} \left[ \int_x^{x_1} e^{\phi(y)/kT} dy \right] dx
\]

Switch the order of integration, to get finally:

\[
\tau = \frac{1}{D} \int_0^{x_1} dx e^{\phi(x)/kT} \int_0^x dy e^{-\phi(y)/kT}
\]

2. Kramers Mean Escape Rate. We use the saddle-point asymptotics (just Laplace’s method on the real axis, in this case) to evaluate the integrals as \( kT \to 0 \). Factors of \( 1/2 \) arise since the maximum and minimum occur at the endpoints.

\[
\int_0^x e^{-\phi(y)/kT} dy \sim \frac{1}{2} \sqrt{\frac{2\pi kT}{\phi''(0)}} e^{-\phi(0)/kT} = \sqrt{\frac{\pi kT}{2K_0}}
\]

So that:

\[
\int_0^{x_1} dx e^{\phi(x)/kT} \int_0^x dy e^{-\phi(y)/kT} \sim \sqrt{\frac{\pi kT}{2K_0}} \int_0^{x_1} e^{\phi(x)/kT} dx
\]

with:

\[
\int_0^{x_1} e^{\phi(x)/kT} dx \sim \frac{1}{2} \sqrt{\frac{2\pi kT}{\phi''(x_1)}} e^{\phi(x_1)/kT} = \sqrt{\frac{\pi kT}{2K_1}} e^{E/kT}
\]

Escape occurs with probability \( 1/2 \) from either of 2 activation barriers, so

\[
R = \frac{1}{2\tau} = \frac{1}{\tau} \sim R_0(T) = \frac{2D\sqrt{K_0K_1}}{\pi kT} e^{-E/kT} \propto e^{-E/kT}
\]

\footnote{The function \( g_1(x) \) from 10.95 Lecture 11 is denoted \( g_0(x) \) in 18.366 Lecture 18 from 2005, and some of this derivation can also be found in both sets of scribe notes.}
3. First Correction to the Kramers Escape Rate. In the next derivation, we will use the following relation:

\[
\int_{-\infty}^{+\infty} e^{-ax^2+bx^3+cx^4} \, dx \sim \int_{-\infty}^{+\infty} \left( 1 + bx^3 + cx^4 + \frac{b^2 x^6}{2} \right) e^{-ax^2} \, dx
\]

\[
= \sqrt{\frac{\pi}{a}} \left( 1 + \frac{3 c}{4 a^2} + \frac{15 b^2}{16 a^3} \right)
\]

Using saddle-point asymptotics with the previous formula:

\[
\int_0^x e^{-\phi(y)/kT} \, dy \sim \frac{1}{2} \sqrt{\frac{2\pi kT}{\phi''(0)}} \left( 1 - \frac{kT}{8} \frac{\phi''(0)}{[\phi''(0)]^2} + \frac{5kT}{24} \left[ \frac{\phi'''(0)}{[\phi''(0)]^3} \right]^2 \right) e^{-\phi(0)/kT}
\]

Since the well is symmetric, \(\phi''(0) = 0\), we end up with:

\[
\int_0^x e^{-\phi(y)/kT} \, dy \sim \sqrt{\frac{\pi kT}{2K_0}} \left( 1 - \frac{kT M_0}{8 K_0^2} \right)
\]

with \(M_0 = \phi^{(4)}(0)\). The same way:

\[
\int_0^{x_1} e^{\phi(x)/kT} \, dx \sim \frac{1}{2} \sqrt{\frac{2\pi kT}{\phi''(x_1)}} \left( 1 + \frac{kT}{8} \frac{\phi''(x_1)}{[\phi''(x_1)]^2} - \frac{5kT}{24} \left[ \frac{\phi'''(x_1)}{[\phi''(x_1)]^3} \right]^2 \right) e^{\phi(x_1)/kT}
\]

that we write:

\[
\int_0^{x_1} e^{\phi(x)/kT} \, dx \sim \sqrt{\frac{\pi kT}{2K_1}} \left( 1 + \frac{kT M_1}{8 K_1^2} - \frac{5kT L_1^2}{24 K_1^3} \right) e^{E/kT}
\]

with \(L_1 = \phi''(x_1)\) and \(M_1 = \phi^{(4)}(x_1)\). We write then:

\[
\tau \sim \frac{1}{R_0(T)} \left( 1 - \frac{kT M_0}{8 K_0^2} \right) \left( 1 + \frac{kT M_1}{8 K_1^2} - \frac{5kT L_1^2}{24 K_1^3} \right)
\]

\[
\sim \frac{1}{R_0(T)} \left[ 1 + \frac{kT}{8} \left( \frac{M_1}{K_1^2} - \frac{M_0}{K_0^2} - \frac{5 L_1^2}{3 K_1^3} \right) \right]
\]

that is:

\[
R(T) \sim R_0(T) \left[ 1 - \frac{kT}{8} \left( \frac{M_1}{K_1^2} - \frac{M_0}{K_0^2} - \frac{5 L_1^2}{3 K_1^3} \right) \right]
\]

with:

\[
K_0 = \phi''(0) \quad L_1 = \phi''(x_1) \quad M_0 = \phi^{(4)}(0) \quad K_1 = -\phi''(x_1) \quad M_1 = \phi^{(4)}(x_1)
\]