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# Transitions between wells and escape by diffusion in a one-dimensional potential landscape

B.U. Felderhof

*Institut für Theoretische Physik A, RWTH Aachen University, Templergraben 55, 52056 Aachen, Germany*

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ABSTRACT

The time-dependence of the occupation probabilities of neighboring wells due to diffusion in one dimension is formulated in terms of a set of generalized rate equations describing transitions between neighboring wells and escape across a final barrier. The equations contain rate coefficients, memory coefficients, and a long-time coefficient characterizing the amplitude of long-time decay. On a more microscopic level the stochastic process is described by a Smoluchowski equation for the one-dimensional probability distribution. A numerical procedure is presented which allows calculation of the transport coefficients in the set of generalized rate equations on the basis of the Smoluchowski equation.



## 1. Introduction

The process of diffusion of a particle in a one-dimensional potential landscape is described by the Smoluchowski equation [1,2]. In earlier work we have studied the escape of a particle from a single well followed by a barrier into free space, where the potential vanishes, for the case where the well and the barrier are parabolic [3]. We found that the time-dependence of the occupation probability of the well could be described accurately by a reduced description involving a single rate equation with memory term and a source term describing long-time exchange with the outer space [4]. The three coefficients in the reduced equation could be determined from the solution of the Smoluchowski equation. Naturally the question arises whether a similar reduced description holds for cases where the Smoluchowski equation cannot be solved analytically, and whether for such cases an efficient method of determination of the coefficients in the reduced equation can be found.

The work was extended to a landscape with two parabolic wells and two parabolic barriers [5]. In this case it was found that the time-dependence of the occupation probabilities of the two wells could be described accurately by a set of two generalized rate equations with memory terms. The coefficients were determined from the analytic solution of the Smoluchowski equation. Again the question arises whether the reduced equations hold for potentials of similar shape, and whether one can determine the coefficients in the equations without knowledge of the complete analytic solution.

The method of Padé approximants, applied to the numerical solution of the Laplace transform of the Smoluchowski equation, turns out to be effective. The behavior in the complex frequency plane of the transform of the probability current into free space determines the number of dominant poles, and consequently the number of required reduced equations. The linear term in the expansion of the transformed current in powers of the square root of frequency determines the value of

*E-mail address:* ufelder@physik.rwth-aachen.de.

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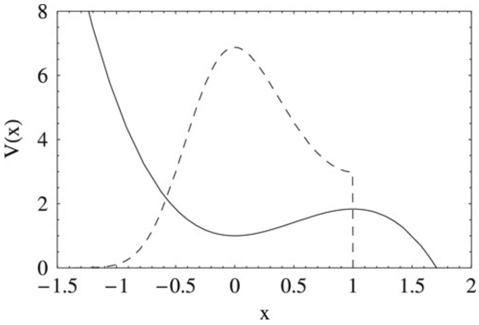


**Fig. 1.** Plot of the potential $V(x)$ given by Eq. (5.1) (solid curve), and of the initial distribution $P(x, 0)$ corresponding to equilibrium to the left of the top of the barrier (multiplied by 8, dashed curve).

the coefficient of the long-time tail in the decay of the total probability of occupation of the potential landscape. It is shown in Section 3 that the coefficient can be found exactly for general shape of the potential. The exact value is used in the Padé approximant method. In Section 5 we show how the method works for the examples of a cubic and a quintic potential.

## 2. Diffusion in a one-dimensional potential

We consider diffusion of a particle in one dimension in a potential $V(x)$, as described by the Smoluchowski equation for the probability distribution $P(x, t)$

$$\frac{\partial P}{\partial t} = D\frac{\partial}{\partial x}\left[\frac{\partial P}{\partial x} + \beta\frac{\partial V}{\partial x}P\right], \tag{2.1}$$

where $D$ is the diffusion coefficient, and $\beta = 1/k_BT$. The function

$$g(x) = \exp[-\beta V(x)] \tag{2.2}$$

is a time-independent solution of Eq. (2.1). We shall consider a class of potentials consisting of $n$ neighboring potential wells separated by potential barriers, with a final barrier separating the last well from open space. For definiteness we assume that the potential tends to $+\infty$ for $x \to -\infty$, that its first minimum is located at $x = 0$, and that the potential vanishes beyond some cutoff point $c > 0$. In Fig. 1 we show an example of such a potential with a single well and a single barrier. It is convenient to write the distribution function as

$$P(x, t) = f(x, t)g(x). \tag{2.3}$$

Then the function $f(x, t)$ satisfies the adjoint Smoluchowski equation

$$\frac{\partial f}{\partial t} = D\left[\frac{\partial^2 f}{\partial x^2} - \beta\frac{\partial V}{\partial x}\frac{\partial f}{\partial x}\right]. \tag{2.4}$$

At a point where the potential and/or its derivative is discontinuous the auxiliary function $f(x, t)$ must be continuous, and its left and right derivative must satisfy the jump condition

$$g(x)\frac{\partial f}{\partial x}\bigg|_{-} = g(x)\frac{\partial f}{\partial x}\bigg|_{+}. \tag{2.5}$$

We note that the right-hand side of Eq. (2.4) can be expressed as $Dg^{-1}\partial/\partial x(g\partial f/\partial x)$. As a result of the above conditions the probability current is continuous.

We define the Laplace transform of the distribution as

$$\hat{P}(x, s) = \int_0^\infty \mathrm{e}^{-st}P(x, t)\,\mathrm{d}t. \tag{2.6}$$

The Laplace transform of Eq. (2.1) takes the form

$$\frac{\partial}{\partial x}\left[\frac{\partial \hat{P}}{\partial x} + \beta\frac{\partial V}{\partial x}\hat{P}\right] - \alpha^2\hat{P} = -\frac{1}{D}P(x, 0), \tag{2.7}$$

where $\alpha = \sqrt{s/D}$. We assume that the initial distribution $P(x, 0)$ vanishes for $x > c$, so that at time $t = 0$ the particle is found with certainty to the left of the exit point $c$. We define the occupation probabilities $p(t)$ and $p_>(t)$ as

$$p(t) = \int_{-\infty}^{c} P(x, t)\,\mathrm{d}x, \qquad p_>(t) = \int_c^\infty P(x, t)\,\mathrm{d}x. \tag{2.8}$$