Interrelations of Different Methods for the Determination of Rates: Flux Over Population, Generalized Reactive Flux, the Lowest Eigenvalue and Its Rayleigh Quotient

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The ratio of Kramers’ current carrying stationary probability density and the equilibrium probability density is utilized as smoothed characteristic function in the generalized reactive flux method recently proposed by Borkovec and Talkner [J. Chem. Phys. 92, 5307 (1990)]. Under a certain condition on the potential, as generalized transition state rate Kramers’ phase space diffusion limited rate is obtained. It then represents an upper bound for the true rate. An approximate expression for the plateau value of the generalized reactive flux yields a Rayleigh quotient for the lowest eigenvalue of the considered Fokker-Planck process.

1. Introduction

The generalized reactive flux method [1] primarily aims at the effective numerical simulation of rate constants [2] for those classes of dynamics as e.g. Smoluchowski or jump processes that cannot be tackled by the original reactive flux idea [3]. This goal was achieved by the use of a smoothed characteristic function from which the reactive flux is derived in contrast to a discontinuous one for the original reactive flux method [1]. In this note it will be demonstrated that the same idea may lead to an important improvement of the initial reactive flux rate compared with the transition state rate. For the sake of simplicity this discussion is restricted to the original, one dimensional Kramers’ model [4]. The generalization to higher dimensional models is straightforward. From Kramers’ solution for a current carrying probability density one finds a smoothed characteristic function for which the initial reactive flux rate already yields Kramers’ phase space diffusion limited rate. The initial conditions for the individual transmission factors that lead to the time dependent reactive flux rate, are given by the sources and sinks that render Kramers’ current carrying solution stationary [1, 5]. In order that these initial conditions follow from proper nonnegative probability densities, the nonlinear potential which is obtained from the original potential by subtracting the barrier part must be convex. Under this condition it is sure that Kramers’ rate is an upper bound for the true rate. In an appropriate limit an exact expression for the plateau value is obtained that deviates from the smallest eigenvalue of the considered Fokker-Planck process only by an exponentially small amount. An approximate calculation of the plateau value leads to a Rayleigh quotient for the smallest eigenvalue which is different from previously used ones [5].

2. Kramers’ Model

As a model of a chemical reaction Kramers [4] considered a Brownian particle of mass \( M \) moving in a potential \( U(x) \) with local minima corresponding to an initial reactant and a final product state. The reactant state \( x_0 < 0 \) is separated from the product states \( x_0 > 0 \) by a barrier located at \( x_b = 0 \). The vicinity of the barrier is assumed to be parabolic with curvature \(-\alpha^2\):\n
\[
U(x) \approx -\frac{1}{2} M \alpha^2 x^2 + U(0) \quad \text{for} \ x \text{ near the barrier} \quad (2.1)
\]

Under these conditions Kramers could construct a stationary Fokker-Planck equation in the parabolic vicinity of the barrier:

\[
Lp(x,v) = 0 \quad \text{for} \ x \text{ near the barrier} \quad (2.2)
\]

where the Fokker Planck operator is given by

\[
L = -\frac{\partial}{\partial x} v + \frac{\partial}{\partial v} \left( \frac{U'(x)}{M} + \gamma v \right) + \frac{\gamma k_B T}{M} \frac{\partial^2}{\partial v^2} \quad (2.3)
\]

and where \( \gamma \) denotes the friction rate and \( T \) the temperature of the heat bath causing fluctuations and dissipation.

The solution \( p \) is given by the product of a form-function \( \zeta(x,v) \) and the equilibrium Boltzmann distribution \( p_{eq}(x,v) \)

\[
p(x,v) = \zeta(x,v) \ p_{eq}(x,v) \quad (2.4)
\]

where

\[
p_{eq}(x,v) = Z^{-1} e^{-\frac{1}{2} M \left( x^2 + \frac{U(x)}{k_B T} \right)} \quad (2.5)
\]

The form function matches smoothly the equilibrium distribution in the initial well with a vanishing probability density at the product state. It is given by [4]

\[
\zeta(x,v) = \omega_0^2 (M/2\pi \gamma k_B T \lambda_+)^{1/2} \int_{-\infty}^{\infty} e^{-\frac{M \alpha^2 u^2}{2 \gamma k_B T \lambda_+}} \ du \quad (2.6)
\]
where
\[
\lambda_+ = -\frac{\gamma}{2} + \left(\frac{\omega_0^2 + \left(\frac{\gamma}{2}\right)^2}{2}\right)^{1/2}.
\] (2.7)

The stationary solution \( p(x, y) \) carries a probability current over the barrier that follows from
\[
j = \int_{-\infty}^{\infty} dx \, \psi^* \psi \equiv p(x, 0),
\] (2.8)

This flux is maintained by sources and sinks which are given by [1, 5]
\[
S(x, v) = -Lp(x, v)
\] (2.9a)
\[
= \left(\frac{\lambda_+}{2\pi \gamma M k_B T}\right)^{1/2} \nabla \cdot (v - \frac{\lambda_+}{\omega_0}) \cdot e^{-\frac{M d^2}{2 \gamma k_B T} \left(\frac{\lambda_+ v}{\omega_0}\right)^2}.
\] (2.9b)

where \( V(x) \) denotes the nonlinear part of the potential resulting from the full potential \( U(x) \) subtracted by its parabolic contribution (2.1)
\[
V(x) = U(x) + \frac{1}{2} M \omega_0^2 x^2 - U(0)
\] (2.10)

Kramers’ phase space diffusion limited rate \( k_{\text{K}} \) is then readily obtained from the ratio of the flux given by Eq. (2.8) and the population \( n \) of the well
\[
k_{\text{K}} = \frac{j}{n}
\] (2.11)
\[
k_{\text{K}} = \frac{\lambda_+}{\omega_0} \frac{e^{-E_0^2}}{2\pi} = e^{-E_0^2} e^{-E_0^2}
\] (2.12)

where \( E_0 = U(0) - U(x_0) \) denotes the barrier height and
\[
n = \int_{-\infty}^{\infty} dx \, \int_{-\infty}^{\infty} dv \, p(x, v)
\] (2.13)

This result represents a reasonable estimate of the true rate, if all trajectories ejected by the source properly thermalize before eventual thermal fluctuations drive them out of the initial well [1, 5].

We conclude this section by noting that the action of the Fokker Planck operator \( L \) on a product of a function \( f(x, v) \) and the equilibrium distribution can be expressed by another operator \( L^* \) acting solely on \( f \):
\[
L[f p_{\text{eq}}] = p_{\text{eq}} L^* f.
\] (2.14)

The operator \( L^* \) coincides with the backward operator of the time reversed process [7, 8]
\[
L^* = -v \frac{\partial}{\partial x} + \frac{U'(x)}{M} - \gamma v \frac{\partial}{\partial v} + \frac{\gamma k_B T}{M} \frac{\partial^2}{\partial v^2}.
\] (2.15)

Moreover, we note that the operator \( L^* \) is just the adjoint operator of the backward operator \( L^+ \) of the original process with respect of the scalar product defined by the equilibrium expectation value
\[
\langle f | L^* | g \rangle = \langle g | L^* | f \rangle
\] (2.16)

where
\[
\langle f \rangle = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dv \, f(x, v) \, p_{\text{eq}}(x, v)
\] (2.17)

and
\[
L^+ = v \frac{\partial}{\partial x} - \left(\frac{U(x)}{M} + \gamma v \right) \frac{\partial}{\partial v} + \frac{\gamma k_B T}{M} \frac{\partial^2}{\partial v^2}.
\] (2.18)

In the next Sect. we shall discuss the constrained flux method for the classical model.

3. The Generalized Reactive Flux Method

After a transient on a microscopic time scale \( \tau_{\text{m}} \), the reaction rate governs the time behavior of the correlation function
\[
C(t) = \frac{\langle f(x, v, t) \theta(-x(t)) \rangle}{\langle f(x, v) \theta(-x) \rangle} \approx e^{-t}.
\] (3.1)

where \( \langle \cdot \rangle \) again denotes the equilibrium average, \( \theta(-x) \) is the step function being unity for negative and zero for positive values of \( x \). In contrast, \( f(x, v) \) is a function that smoothly interpolates from unity in the phase space region of reactants to zero in that of products. In order to avoid back reactions, phase space regions of products must be absorbing.

The time derivative of Eq. (3.1) yields a time-dependent expression:
\[
k(t) = -\frac{dC(t)}{dt} = -\frac{\langle \theta(-x(t)) L^* f(x, v) \rangle}{\langle f(x, v) \theta(-x) \rangle}.
\] (3.2)

In order to obtain this result, one expresses the time dependent part \( \theta(-x(t)) \) formally by
\[
\theta(-x(t)) = e^{k(t) t} \theta(-x)
\] (3.3)

and, after differentiation with respect to \( t \), uses Eq. (2.16).

In a standard way the generalized transition state \( k(0) \) and the transmission coefficient \( \kappa(t) \) are introduced:
\[
k(t) = k(0) \kappa(t)
\] (3.4)

where
\[
k(0) = -\frac{\langle \theta(-x) L^* f(x, v) \rangle}{\langle f(x, v) \theta(-x) \rangle}
\] (3.5)

and
\[
\kappa(t) = \langle \theta(-x(t)) \rangle_+ - \langle \theta(-x(t)) \rangle_-. \] (3.6)
The nonequilibrium initial states \( p_{\pm} \) by which the expectation values \(<\theta(-x(t))>_\pm\) are determined, read

\[
P_{\pm} = \frac{\theta(\mp x) p_{\pm}(x,v) L^* f(x,v)}{<\theta(\mp x) L^* f(x,v)>}.
\]

(3.7)

In order that \( p_+ \) are nonnegative probability densities, the function \( f(x,v) \) has to be properly chosen. The best choice would be the eigenfunction \( \tilde{h}(x,v) \) of \( L^* \) with the smallest eigenvalue \(-\lambda\):

\[
L^* \tilde{h}(x,v) = -\lambda \tilde{h}(x,v).
\]

(3.8)

With this choice, the time dependent rate \( k(t) \) varies exclusively on the long time scale, determined by the inverse rate

\[
k(t) = \lambda e^{-\lambda t}.
\]

(3.9)

Hence, the generalized transition state rate already coincides with the true rate \( \lambda \).

(3.10)

However, the eigenfunction \( \tilde{h} \) and the corresponding eigenvalue \(-\lambda\) are not known exactly.

As an approximation, Kramers' function \( \zeta(x,v) \) suggests itself because first, it shows the desired qualitative behavior and second, approximates the eigenvalue Eq. (3.8) in the important barrier region [cf. Eqs. (2.2), (2.4) and (2.14)]

\[
L^* \zeta(x,v) = 0 \quad \text{for} \quad x \text{ near the barrier}.
\]

(3.11)

With Eqs. (2.5), (2.6), (2.15) and (3.5) we obtain for the generalized transition state rate \( k(0) \) Kramers' phase space diffusion rate (2.12)

\[
k(0) = k_0.
\]

(3.12)

Combining Eqs. (2.5), (2.9), (2.14) with Eq. (3.7) we obtain for the initial distributions \( p_+ \) and \( p_- \) the normalized projection of the source and sink density (2.9) on the reactant and product phase space regions, respectively:

\[
p_{\pm} = \frac{\theta(\mp x) S(x,v)}{\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} d\theta(\mp x) S(x,v)}.
\]

(3.13)

From (2.9b) we immediately find that the functions \( p_{\pm} \) are nonnegative if the nonlinear potential \( V(x) \) defined by Eq. (2.10) is a convex function

\[
V'(x) \geq 0.
\]

(3.14)

Under this condition, the Kramers' form function \( \zeta(x,v) \) is an admissible choice for the reactive flux function \( f(x,v) \).

Since, as for the original reactive flux, for proper nonnegative \( p_{\pm} \) the expectation values fulfill the obvious inequalities

\[
0 \leq <\theta(-x(t))>_\pm \leq <\theta(-x(t))>_+ \leq 1
\]

(3.15)

for any admissible choice of \( f(x,v) \) the generalized reactive flux rate is an upper bound for the true rate

\[
k(0) \geq k.
\]

(3.16)

From the above consideration we find that a sufficient condition for the Kramers rate to be a bound for the true rate, is the convexity of the nonlinear potential. This is certainly too strong a condition. For example, for a cubic potential \( U(x) = \frac{M_0 a}{2} x^2 / 2 - ax^3 / 3, a > 0 \) one can modify Kramers' form function for positive values of \( x \) such that one obtains proper probability densities \( p_+ \) without a change of Kramers rate. Consequently, still in cases where \( V(x) \) is not convex, the Kramers rate may be an upper bound.

Recently, Pollak et al. [9] obtained the weaker condition that \( V(x) \) must be nonnegative in order that \( k_0 \) be an upper bound.

4. The Plateau Value

The time dependence of the reactive flux rate is determined by the propagator \( e^{tH_0} \) see Eqs. (3.2), (3.3), and results finally in an exponential decay proportional to \( e^{-\lambda t} \), where \(-\lambda\) is the smallest eigenvalue of \( L^* \) and, with Eq. (2.16) also of \( L^+ \). In order to compensate for this decay, one may multiply the reactive flux rate (3.5) by \( e^{\lambda t} \). Then, in the limit \( t \rightarrow \infty \), one obtains for the plateau value \( k_{pl} \) of the reactive flux rate

\[
k_{pl} = \lim_{t \rightarrow \infty} k(t) e^{\lambda t}
\]

(4.1)

\[
= -\frac{<h(x,v) L^* f(x,v)> <\tilde{h}(x,v) \theta(-x)>}{<f(x,v) \theta(-x)>}
\]

where the fact is used that \( e^{(L^* + \lambda)} \) in the limit \( t \rightarrow \infty \) projects onto the eigenspace of \( L^+ \) belonging to the smallest eigenvalue \(-\lambda\):

\[
\lim_{t \rightarrow \infty} e^{(L^* + \lambda)t} = P_{\lambda}.
\]

(4.2)

The projection operator \( P_{\lambda} \) may in the usual way be constructed from the right - and left - eigenvectors of \( L^* \):

\[
L^+ \tilde{h}(x,v) = -\lambda \tilde{h}(x,v)
\]

(4.3a)

\[
L^* \tilde{h}(x,v) = -\lambda \tilde{h}(x,v)
\]

(4.3b)

where

\[
<h(x,v) \tilde{h}(x,v)> = 1
\]

(4.3c)

and where we have used that \( L^+ \) and \( L^* \) are adjoint to each other [see Eq. (2.16)]. Since \( L^+ \) and \( L^* \) are further connected by time reversal [compare Eqs. (2.15), (2.18)] \( h \) and \( \tilde{h} \) are also connected by the time reversal transformation:

\[
h(x,v) = h(x,-v).
\]

(4.4)
Using Eqs. (2.16) and (4.3a) one obtains from Eq. (4.1) for the plateau value \( k_{pl} \)

\[
k_{pl} = \lambda \frac{\langle f(x,v) h(x,v) \rangle \langle \tilde{h}(x,v) \theta(-\lambda) \rangle}{\langle f(x,v) \theta(-\lambda) \rangle}.
\]  

(4.5)

All three factors \( \langle f(x,v) h(x,v) \rangle \), \( \langle \tilde{h}(x,v) \theta(-\lambda) \rangle \), and \( \langle f(x,v) \theta(-\lambda) \rangle \) deviate from the population of the well only by factors of order \( 1 - e^{-E_b/k_BT} \). Hence, as one expects, the plateau value of the reactive flux rate coincides up to exponentially small corrections with the smallest eigenvalue of the Fokker Planck operator.

Since, however, the exact eigenfunctions \( h \) and \( \tilde{h} \) are unknown, one can try to evaluate the expression (4.1) for the plateau value of the reactive flux with the help of an appropriate pair of test functions \( h_0(x,v) \) and \( h_0(x,v) \), that one may choose consistently with the reactive flux function \( f(x,v) \):

\[
h_0(x,v) = \frac{\tilde{f}(x,v)}{\langle f(x,v) \tilde{f}(x,v) \rangle} \]  

(4.6)

where [see Eq. (4.4)]

\[
\tilde{f}(x,v) = f(x,-v)
\]  

(4.7)

and where the normalization is given by Eq. (4.3c). \( \tilde{h}(x,v) \) follows immediately with Eq. (4.4). For the plateau value \( k_{pl} \) one then obtains a Rayleigh quotient for the smallest eigenvalue of \( L^* \):

\[
k_{pl} = \frac{\langle f(x,v) L^* \tilde{f}(x,v) \rangle}{\langle f(x,v) \tilde{f}(x,v) \rangle}.
\]  

(4.8)

This expression is different from previously suggested forms of the Rayleigh quotient [6], as it contains two different test functions for the left and right eigenvectors which are related by time reversal, rather than only one of these. Only in cases with strict detailed balance [7, 10] where the operators \( L^* \) and \( L^* \) coincide the classical Rayleigh quotient for a self-adjoint eigenvalue problem is recovered from Eq. (4.8).

If one chooses for \( f(x,v) \) again Kramers’ function \( \zeta(x,v) \) one finds from Eqs. (2.6), (4.6) and (4.8) for a symmetric potential for the plateau value

\[
k_{pl} = k_B \left\{ 1 - \frac{l_0}{8 M \omega_0} U^{(0)}(0) + O(l_0^2) \right\}
\]  

(4.9)

where

\[
l_0 = \frac{k_B T}{M \omega_0} \frac{\gamma^2}{\gamma^2 + (2 \omega_0)^2}.
\]  

(4.10)

Possible temperature corrections to the Gaussian approximation of the well population are neglected. For \( \gamma \to \infty \) \( k_{pl} \) goes over to the Smoluchowski rate with its leading temperature corrections [11], whereas the expression (4.9) fails to give the correct behavior for small friction constants \( \gamma \), because then the Kramers form function does not adequately approximate the eigenfunction \( \tilde{h}(x,v) \).

Conclusions

In this note the generalized reactive flux method is applied to the original Kramers’ model. It is shown that under the condition of a convex nonlinear potential Kramers’ phase space diffusion rate may be obtained as a generalized transition state rate. It is then an upper bound for the exact rate. Further, it is demonstrated that the crucial modification of the reactive flux function from a discontinuous to a smooth characteristic function does not change the plateau value of the time dependent reactive flux rate which is given by the lowest eigenvalues of the Fokker Planck operator. The Rayleigh quotient that follows from the expression for the plateau value allows for the nonselfadjointness of the backward operator as it contains two different test functions.

The generalization of the demonstrated method to higher dimensional systems with detailed balance is straightforward. In principle, the generalized reactive flux method may also be applied to problems without detailed balance. The main problem then consists in the determination of a stationary state corresponding to the thermal equilibrium state.

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References

[8] D. Ryter, J. Stat. Phys. 49, 751 (1987); there extensive use of the duality between \( L^* \) and \( L^* \) is made in order to calculate rates in the regime of weak and moderate noise by means of eigenvalues.

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