A NEW VARIATIONAL METHOD TO CALCULATE ESCAPE RATES IN BISTABLE SYSTEMS ☆

W. BEZ and P. TALKNER

Institut für Theoretische Physik, Universität Stuttgart, Fed. Rep. Germany

We apply the Rayleigh–Ritz variational principle to the inverse of the Smoluchowsky operator in order to calculate the lowest non-vanishing eigenvalue of the Smoluchowsky equation. In contrast to former variational calculations the new method is very insensitive to the choice of the test function. We obtain the asymptotic expansion of the eigenvalue in the limit of vanishing diffusion.

The motion of a bistable system may be influenced decisively by random perturbations, even when they are small: the decay of the system from the point of instability is initiated by fluctuations and when the system has reached a stable point of the deterministic motion it does not stay there because of fluctuations.

A famous example is a brownian particle moving in a bistable potential [1]. In the high friction limit the motion is described by the Smoluchowsky equation:

$$\partial P(x, t)/\partial t = (\partial/\partial x)[U'(x) + \epsilon\, \partial/\partial x] P(x, t)\,. \qquad (1)$$

$P(x, t)$ is the probability density for the position of the brownian particle at time t. The systematic force acting on the brownian particle is derived from a "viscous potential" $U(x)$ and is given by $-U'(x)$. For a bistable system the potential has two minima. The diffusion ϵ is assumed to be small.

When the particle has reached the bottom of the well it does not stay there as it would in the absence of fluctuations, but can escape over the barrier. The escape rate is closely related to the lowest non-vanishing eigenvalue in the eigenvalue problem associated with the Smoluchowsky equation.

The eigenvalue cannot be expanded in powers of the diffusion because there is an essential singularity for $\epsilon \to 0$. Various methods have been proposed to cope with this essential singularity: WKB and path integral calculations [2–4], projection operators [5], and other methods [6–8] have been used to substantiate and refine Kramers' early calculation of the escape rate [1].

As a particularly simple and successful technique the Rayleigh–Ritz variational principle can be applied to the Smoluchowsky operator. The difficulty in these calculations is that the eigenvalue to be calculated is much smaller than the others. In order to compensate for the smallness one has to have detailed knowledge about the eigenfunction, and choose a test function which approximates the eigenfunction extremely well.

In this paper we apply the variational principle not to the Smoluchowsky operator itself, but to the inverse of it. What was the smallest eigenvalue of the Smoluchowsky operator becomes the largest one of the inverse operator, and the result of the variational calculation depends only weakly on the test function chosen. Therefore the main difficulty of the former variational calculation turns into a major advantage of the new one.

In Kramers' barrier penetration problem one requires natural boundary conditions at infinity:

$$\lim_{x \to \pm\infty} [U'(x) + \epsilon\, \partial/\partial x] P(x, t) = 0\,. \qquad (2)$$

With these boundary conditions the unnormalized stationary solution of the Smoluchowsky equation is

☆ Work supported by the Deutsche Forschungsgemeinschaft.

$$w(x) = \exp[-U(x)/\epsilon] . \tag{3}$$

With the ansatz

$$P(x, t) = w(x)\psi(x)\mathrm{e}^{-\lambda t} , \tag{4}$$

the Smoluchowsky equation is transformed into the eigenvalue problem

$$L\psi_k = -\lambda_k \psi_k , \tag{5}$$

where

$$L = -U'(x)\partial/\partial x + \epsilon\partial^2/\partial x^2 , \tag{6}$$

and the boundary conditions are

$$\lim_{x\to\pm\infty} w(x)\,\partial\psi(x)/\partial x = 0 . \tag{7}$$

The Smoluchowsky operator L is selfadjoint with respect to the scalar product

$$(f, g) = \int_{-\infty}^{\infty} w(x) f(x) g(x)\,\mathrm{d}x , \tag{8}$$

which contains the stationary distribution as a weight function. Therefore the eigenfunctions form a complete set in the space of functions which are square integrable with weight $w(x)$. The scalar product of two functions is the mean value of their product with respect to the stationary distribution.

Note that the eigenvalue problem (5) is phrased in terms of the operator L appearing in the *backward* Smoluchowsky equation, not the forward equation (1). Equivalent choices for the eigenvalue problem are also common: one can multiply our eigenfunctions by $w^{1/2}(x)$ and obtain an operator which is selfadjoint in a scalar product with constant weight function [9]. Or, if one multiplies our eigenfunctions with $w(x)$ the resulting operator is the forward Smoluchowsky operator appearing in eq. (1), which is selfadjoint in a scalar product with weight function $w^{-1}(x)$ [10].

The lowest non-vanishing eigenvalue of the Smoluchowsky equation can now be found by applying the Rayleigh–Ritz variational principle to the operator L:

$$\lambda_1 = \min_{\langle\psi\rangle=0} |(\psi, L\psi)|/(\psi, \psi) . \tag{9}$$

The space of test functions has to be restricted to functions with vanishing mean value because the lowest eigenvalue in the unrestricted space is $\lambda_0 = 0$ with eigenfunction $\psi_0(x) = 1$ corresponding to the stationary distribution.

In this form the variational principle has been used many times to calculate the eigenvalue, either applied to the operator L [10–13], or, equivalently, to one of the closely related operators mentioned before. We propose to apply the variational principle to the inverse of the operator L:

$$\lambda_1^{-1} = \max_{\langle\psi\rangle=0} |(\psi, L^{-1}\psi)|/(\psi, \psi) . \tag{10}$$

The space of test functions has to be restricted as before, because the inverse of L can only be defined on the space orthogonal to ψ_0 according to the Fredholm alternative. In the unrestricted space one can still find an operator that is the right inverse of L:

$$\Gamma f(x) = -\epsilon^{-1} \int_0^x w^{-1}(y)\,\mathrm{d}y \int_y^{\infty} w(z) f(z)\,\mathrm{d}z , \tag{11}$$

but is no longer a left inverse. The projection of Γ on the space orthogonal to ψ_0 is the unique inverse of L in this restricted space:

$$L^{-1} = [1 - |\psi_0)(\psi_0|]\,\Gamma\,[1 - |\psi_0)(\psi_0|] . \tag{12}$$

In the variational functional (10) the operator is sandwiched between two functions of the space orthogonal to ψ_0 and therefore Γ can be used in eq. (10) instead of L^{-1}:

$$\lambda_1^{-1} = \max_{\langle\psi\rangle=0} |(\psi, \Gamma\psi)|/(\psi, \psi) . \tag{13}$$

Clearly, both variational calculations (9) and (10) require a small mean square deviation of the test function from the eigenfunction. For the new variational principle (10) this necessary condition is also sufficient while for the old one this requirement is much too weak: it can be shown that the mean square deviation of the derivative of the test function from the derivative of the eigenfunction must be small, too.

The new variational principle is most powerful when the lowest eigenvalue λ_1 is much smaller than the higher ones. This is the case, e.g., in the limit of vanishing diffusion. In this limit the corresponding eigenfunction ψ_1 is almost constant, except in the vicinity of the maximum of the potential $U(x)$ where it changes sign. For simplicity we assume that the potential $U(x)$ is a symmetric function. From the functional (13) we get the expression

$$\lambda_1^{-1} = \frac{\int_0^\infty \mathrm{d}x\, w(x)\psi_1(x) \int_0^x \mathrm{d}y\, w^{-1}(y) \int_y^\infty \mathrm{d}z\, w(z)\psi_1(z)}{\epsilon \int_0^\infty \mathrm{d}x\, w(x)\psi_1^2(x)} \tag{14}$$

for the eigenvalue λ_1 in terms of the eigenfunction ψ_1. The denominator of eq. (14) can be evaluated by the saddle-point method since $\psi_1(x)$ is almost constant where $w(x)$ is sharply peaked. The numerator can also be evaluated by this method because each of the integrands of the three integrals to be evaluated successively factors into a sharply peaked exponential and a slowly varying function. In the first and third integral the sharply peaked factor is the stationary distribution, while in the second one it is the inverse of $w(x)$, which is peaked at the maximum of the potential.

The asymptotic expansion of the eigenvalue becomes comes to first order in ϵ

$$\lambda_1 \sim \frac{[U''(1)|U''(0)|]^{1/2}}{\pi} \exp\left(-\frac{U(0)-U(1)}{\epsilon}\right) \times \left[1 + \left(\frac{U^{\mathrm{IV}}(1)}{8[U''(1)]^2} - \frac{U^{\mathrm{IV}}(0)}{8[U''(0)]^2} - \frac{5}{24}\frac{[U'''(1)]^2}{[U''(1)]^3} + \frac{[\psi_1'(1)]^2}{[\psi_1(1)]^2 U''(1)}\right)\epsilon + \dots\right]. \tag{15}$$

We have scaled x so that $x = 1$ for the minimum and $x = 0$ for the maximum of the potential. Up to now we did not need any details of the eigenfunction $\psi_1(x)$, we only made use of the fact that it allows the integrals in eq. (14) to be evaluated by Laplace's method. The leading term of the asymptotic expansion turns out to be independent of any details of the eigenfunction. The next term depends on the ratio $\psi_1'(1)/\psi_1(1)$. This ratio can be calculated from the relation

$$\psi_1'(1) = (\lambda_1/\epsilon) w^{-1}(1) \int_1^\infty \mathrm{d}x\, w(x)\psi_1(x)\,, \tag{16}$$

which follows from the eigenvalue problem (5) by applying Γ from the left and taking the derivative. From eq. (16) the ratio $\psi_1'(1)/\psi_1(1)$ can be evaluated by the saddle-point method. As ϵ goes to zero it vanishes faster than any power of ϵ and therefore does not contribute in the multiplying power series of the asymptotic expansion (15). Therefore the asymptotic expansion of the eigenvalue λ_1 simplifies to

$$\lambda_1 \sim \frac{[U''(1)|U''(0)|]^{1/2}}{\pi} \exp\left(-\frac{U(0)-U(1)}{\epsilon}\right) \times \left[1 + \left(\frac{U^{\mathrm{IV}}(1)}{8[U''(1)]^2} - \frac{U^{\mathrm{IV}}(0)}{8[U''(0)]^2} - \frac{5}{24}\frac{\cancel{[U'''(1)]^2}}{[U''(1)]^3}\right)\epsilon + \dots\right]. \tag{17}$$

Note that we were able to derive the asymptotic expansion with very little knowledge about the eigenfunction. We only needed to know that the integrals appearing in eqs. (14) and (16) can be evaluated by the saddle-point method. Everything else was done by the operator Γ.

In fact the same result could have been obtained by simply using the step function as a test function in the functional (14). In contrast, in the old variational principle (9) the step function yields infinity, because the mean square deviation of the derivatives of the test function and the eigenfunctions diverges. Our result for the escape rate (which is one half of the eigenvalue λ_1 for symmetric potentials) coincides with the one derived in ref. [15]. In a future publication we will apply our new variational method to calculate the rate constant in multistable systems with process-depending diffusion.

We would like to thank Professor W. Weidlich, Professor U. Weiss and Dr. H. Grabert for useful discussions. We thank Dr. M. San Miguel for drawing our attention to ref. [15].

References

[1] H.A. Kramers, Physica 7 (1940) 284.
[2] H. Tomita, A. Ito and H. Kidachi, Prog. Theor. Phys. 56 (1976) 786.
[3] B. Caroli, C. Caroli and B. Roulet, J. Stat. Phys. 21 (1979) 415.
[4] U. Weiss and W. Häffner, in: Functional integration: theory and application, eds. J.P. Antoine and E. Tirapegui (Plenum, New York, 1980).
[5] W. Weidlich and H. Grabert, Z. Phys. B36 (1980) 283.
[6] R. Landauer and J.A. Swanson, Phys. Rev. 121 (1961) 1668.
[7] N.G. van Kampen, J. Stat. Phys. 17 (1977) 71.
[8] M. Mangel, J. Chem. Phys. 72 (1980) 6606.
[9] H. Risken, Z. Phys. 251 (1972) 231.
[10] R.L. Stratonovich, Topics in the theory of random noise, Vol. 1 (Gordon and Breach, New York, 1963).

[11] H. Risken, Z. Phys. 186 (1965) 85.
[12] H.K. Janssen, Z. Phys. 270 (1974) 67.
[13] R.S. Larson and M.D. Kostin, J. Chem. Phys. 69 (1978) 4821.
[14] A. Schenzle and H. Brand, Opt. Commun. 31 (1979) 401.
[15] O. Edholm and O. Leimar, Physica 98A (1979) 313.