Anomalous behavior of the Kramers rate at bifurcations in classical field theories

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Abstract

We consider a Ginzburg–Landau partial differential equation in a bounded interval, perturbed by weak spatio–temporal noise. As the interval length increases, a transition between activation regimes occurs, in which the classical Kramers rate diverges [MS01]. We determine a corrected Kramers formula at the transition point, yielding a finite, though noise-dependent rate prefactor, confirming a conjecture by Maier and Stein [MS03]. For both periodic and Neumann boundary conditions, we obtain explicit expressions for the prefactor in terms of Bessel and error functions.

1 Introduction

Weak noise acting on spatially extended systems can cause a wide range of interesting phenomena. In particular, it can induce rare transitions between states which would be otherwise invariant, e.g. nucleation of one phase within another [Lan67], micromagnetic domain reversal [Née49, Bra93, BNR00], pattern nucleation in electroconvection [CH93], instabilities in metallic nanowires [BSS05], and many others. The rate of such transitions for weak noise intensity ε is in general governed by Kramers' law[1] $\Gamma \simeq \Gamma_0 \exp\{-\Delta W/\varepsilon\}$, where the activation energy ΔW is the energy difference between stable and transition states, and the rate prefactor Γ_0 is related to second derivatives of the system's energy functional at these states [Eyr35, Kra40].

In a series of recent works [MS01, MS03, Ste04], Maier and Stein studied transition rates in a Ginzburg–Landau partial differential equation on a finite interval, perturbed by space-time white noise. They discovered the striking fact that as the interval length approaches a critical value, which depends on the boundary conditions (b.c.), the rate prefactor Γ_0 *diverges*. Although this divergence is reminiscent of the behavior of certain thermodynamic quantities at phase transitions, it has a different origin [Ste05]: It is due to the fact that the Kramers law only takes into account the effect of quadratic terms in the energy functional on thermal fluctuations, while at the critical length some quadratic terms vanish due to a bifurcation, and higher-order terms come into play.

Maier and Stein conjectured [MS01] that the actual rate prefactor at the bifurcation point behaves like $\Gamma_0 \simeq C\varepsilon^{-\alpha}$, for some constants $C, \alpha > 0$. Until recently, Kramers rate theory was not sufficiently sharp to allow for the computation of these constants. Based on a new approach by Bovier *et al* [BEGK04], we developed a method allowing to compute rate prefactors for potentials with nonquadratic transition states [BG08b]. The aim of this Letter is to illustrate the method by determining the constants C and α in the case of the Ginzburg–Landau equation.

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[1]Throughout this Letter, the notation $a \simeq b$ indicates that $\lim_{\varepsilon \to 0} a/b = 1$.

2 Model

Consider a one-dimensional classical field $\phi(x,t)$, subjected to the quartic double-well potential energy function

$$V(\phi) = \frac{1}{4}\phi^4 - \frac{1}{2}\phi^2 \,, \tag{2.1}$$

to diffusion and to weak space–time white noise. Its evolution is given by the stochastic partial differential equation (SPDE)

$$\partial_t \phi(x,t) = \partial_{xx}\phi(x,t) + \phi(x,t) - \phi(x,t)^3 + \sqrt{2\varepsilon}\,\xi(x,t) \,, \tag{2.2}$$

where $\xi(x,t)$ denotes space–time Gaussian white noise, i.e., formally,

$$\mathbb{E}\{\xi(x_1,t_1)\xi(x_2,t_2)\} = \delta(x_1 - x_2)\delta(t_1 - t_2) \,. \tag{2.3}$$

Here we consider the case of a bounded interval $x \in [0,L]$, and either periodic or Neumann b.c. with zero flux, i.e., $\partial_x\phi(0,t) = \partial_x\phi(L,t) = 0$.

Note that $\xi(x,t)$ can be rigorously defined by independent white noises acting on each Fourier mode. For periodic b.c., this leads to setting

$$\phi(x,t) = \frac{1}{\sqrt{L}}\sum_{k=-\infty}^{\infty}\phi_k(t)\,\mathrm{e}^{2\pi\,\mathrm{i}\,kx/L} \tag{2.4}$$

and substituting in (2.2). The resulting system of stochastic differential equations (SDEs) is given by

$$\dot{\phi}_k = -\lambda_k\phi_k - \frac{1}{L}\sum_{k_1,k_2,k_3:\,k_1+k_2+k_3=k}\phi_{k_1}\phi_{k_2}\phi_{k_3} + \sqrt{2\varepsilon}\,\dot{W}_t^{(k)} \,, \tag{2.5}$$

where $\lambda_k = -1 + (2\pi k/L)^2$, and the $W_t^{(k)}$ are by definition independent Wiener processes (see for instance [Jet86] for a discussion of the equivalence of different approaches to SPDEs). In the case of Neumann b.c., setting

$$\phi(x,t) = \frac{1}{\sqrt{L}}\phi_0(t) + \sqrt{\frac{2}{L}}\sum_{k=1}^{\infty}\phi_k(t)\cos(\pi kx/L) \,. \tag{2.6}$$

yields a similar system of SDEs.

With the SPDE (2.2) we associate the energy functional

$$\mathcal{H}[\phi] = \int_0^L \left[\frac{1}{2}(\phi'(x))^2 + V(\phi(x))\right]\mathrm{d}x \,. \tag{2.7}$$

For both periodic and Neumann b.c., the uniform configurations $\phi_\pm \equiv \pm 1$ are stable stationary configurations of the system without noise. Both are minima of the energy functional, of energy $\mathcal{H}[\phi_\pm] = -L/4$. In terms of the Fourier coefficients, for periodic b.c., the potential energy is given by

$$\mathcal{H}[\phi] = \widehat{\mathcal{H}}[\{\phi_k\}] = \frac{1}{2}\sum_{k=-\infty}^{\infty}\lambda_k|\phi_k|^2 + \frac{1}{4L}\sum_{k_1+k_2+k_3+k_4=0}\phi_{k_1}\phi_{k_2}\phi_{k_3}\phi_{k_4} \,, \tag{2.8}$$

and a similar relation can be obtained for Neumann b.c.

The value of the activation energy ΔW for this model is well known [FJL82, MS01]. The Kramers rate prefactor Γ_0, however, has only been determined for parameters L in certain ranges, excluding bifurcation values of the model [MS03].

3 Transition states and activation energy

The activation energy is the potential energy difference between the initial stable state ϕ_- and the transition state ϕ_t. The latter is defined as the configuration of highest energy one cannot avoid reaching, when continuously deforming ϕ_- to ϕ_+ while keeping the energy as low as possible. The transition state is a stationary state of the energy functional, that is, it satisfies $\phi_t''(x) = -\phi_t(x) + \phi_t(x)^3$. In addition, the Hessian operator $\delta^2 \mathcal{H}/\delta\phi^2$ must have a single negative eigenvalue at ϕ_t. The corresponding eigenfunction specifies the direction in which the most probable transition path approaches the transition state.

The shape of ϕ_t depends on whether the bifurcation parameter L is smaller or larger than a critical value, the latter depending on the chosen b.c. [MS01].

Periodic b.c. For $L \leqslant 2\pi$, the transition state is the identically zero function, which has energy zero. The activation barrier has thus value $\Delta W = L/4$.

For $L > 2\pi$, there is a continuous one-parameter family of transition states, of so-called instanton shape, given in terms of Jacobi's elliptic sine by

$$\phi_{\mathrm{inst},\varphi}(x) = \sqrt{\frac{2m}{m+1}} \operatorname{sn}\left(\frac{x}{\sqrt{m+1}} + \varphi, m\right) . \tag{3.1}$$

Here φ is an arbitrary phase shift, and $m \in [0,1]$ is a parameter related to L by

$$4\sqrt{m+1}\,\mathrm{K}(m) = L , \tag{3.2}$$

where $\mathrm{K}(m)$ denotes the complete elliptic integral of the first kind. Note that $m \to 0^+$ as L approaches the critical length 2π from above. Computing the energy of any instanton transition state (3.1), one gets [MS01] the activation barrier

$$\Delta W = \mathcal{H}[\phi_{\mathrm{inst}}] - \mathcal{H}[\phi_-] = \frac{1}{3\sqrt{1+m}}\left[8\,\mathrm{E}(m) - \frac{(1-m)(3m+5)}{1+m}\,\mathrm{K}(m)\right] , \tag{3.3}$$

where $\mathrm{E}(m)$ denotes the complete elliptic integral of the second kind.

Neumann b.c. In this case, the identically zero solution forms the transition state for all $L \leqslant \pi$, so that the activation barrier has again value $\Delta W = L/4$.

For $L > \pi$, there are two transition states of instanton shape, given by

$$\phi_{\mathrm{inst},\pm}(x) = \pm\sqrt{\frac{2m}{m+1}} \operatorname{sn}\left(\frac{x}{\sqrt{m+1}} + \mathrm{K}(m), m\right) , \tag{3.4}$$

where the parameter $m \in [0,1]$ is now related to L by

$$2\sqrt{m+1}\,\mathrm{K}(m) = L . \tag{3.5}$$

In this case we have $m \to 0^+$ as L approaches the critical length π from above. The activation energy is simply half the activation energy (3.3) of the periodic case [MS01].

4   Rate prefactor

The rate prefactor Γ_0 is usually computed by Kramers' formula [Eyr35, Kra40]

$$\Gamma_0 \simeq \frac{1}{2\pi} \sqrt{\left| \frac{\det \Lambda_{\mathrm{s}}}{\det \Lambda_{\mathrm{t}}} \right|} |\lambda_{\mathrm{t},0}| \; . \tag{4.1}$$

Here $\Lambda_{\mathrm{s}} = \partial^2 \mathcal{H}/\partial \phi^2[\phi_-]$ denotes the linearized evolution operator at the stable state ϕ_-, $\Lambda_{\mathrm{t}} = \partial^2 \mathcal{H}/\partial \phi^2[\phi_{\mathrm{t}}]$ denotes the linearized evolution operator at the transition state ϕ_{t}, and $\lambda_{\mathrm{t},0}$ denotes the single negative eigenvalue of Λ_{t}.

For instance, for Neumann b.c. and $L \leqslant \pi$, the eigenvalues of $\Lambda_{\mathrm{t}} = -\mathrm{d}^2/\mathrm{d}x^2 + 1$ are given by $\lambda_k = -1 + (\pi k/L)^2$, $k = 0, 1, 2 \ldots$, while the eigenvalues of $\Lambda_{\mathrm{s}} = -\mathrm{d}^2/\mathrm{d}x^2 - 2$ are of the form $\eta_k = 2 + (\pi k/L)^2$. It follows [MS03] that the rate prefactor is given by

$$\Gamma_0 \simeq \frac{1}{2\pi} \sqrt{\prod_{k=0}^{\infty} \frac{2 + (\pi k/L)^2}{|-1 + (\pi k/L)^2|}} = \frac{1}{2^{3/4}\pi} \sqrt{\frac{\sinh(\sqrt{2}L)}{\sin L}} \; . \tag{4.2}$$

The striking point is that this prefactor diverges, like $(\pi - L)^{-1/2}$, as L approaches the critical value π. In fact, this is due to the Kramers formula (4.1) not being valid in cases of vanishing $\det \Lambda_{\mathrm{t}}$. To confirm Maier and Stein's conjecture that the rate prefactor at $L = \pi$ behaves like $C\varepsilon^{-\alpha}$ and determine the constants C and α, we have to derive a corrected Kramers formula valid in such cases. This can be done [BG08b] by extending a technique initially developed by Bovier *et al* [BEGK04], which we outline now.

Potential theory.   For simplicity, consider first the case of d-dimensional Brownian motion W_t^x, starting in a point $x \in \mathbb{R}^d$. Given a set $A \subset \mathbb{R}^d$, the expected value $w_A(x) = \mathbb{E}[\tau_A^x]$ of the first time τ_A^x the Brownian path hits A is known [Dyn65] to satisfy the boundary value problem

$$\begin{aligned} \Delta w_A(x) &= 1 & x &\in A^c \; , \\ w_A(x) &= 0 & x &\in A \; . \end{aligned} \tag{4.3}$$

The solution can be written as

$$w_A(x) = \int_{A^c} G_{A^c}(x,y) \, \mathrm{d}y \; , \tag{4.4}$$

where G_{A^c} denotes the associated Green's function, satisfying $\Delta_x G_{A^c}(x,y) = \delta(x-y)$ and the b.c. (for instance, $G_{\mathbb{R}^3}(x,y) = 1/(4\pi\|x-y\|)$). Similarly, let $h_{A,B}(x) = \mathbb{P}\{\tau_A^x < \tau_B^x\}$ denote the probability that the Brownian path starting in x hits the set A before hitting the set B. It satisfies the boundary value problem

$$\begin{aligned} \Delta h_{A,B}(x) &= 0 & x &\in (A \cup B)^c \; , \\ h_{A,B}(x) &= 1 & x &\in A \; , \\ h_{A,B}(x) &= 0 & x &\in B \; . \end{aligned} \tag{4.5}$$

This, however, is also the equation satisfied by the electric potential of a capacitor, with conductors A and B at respective potential 1 and 0. If $\rho_{A,B}(x)$ denotes the surface charge density on the two conductors, we can write

$$h_{A,B}(x) = \int_{\partial A} G_{B^c}(x,y) \rho_{A,B}(y) \, \mathrm{d}y \; . \tag{4.6}$$

The capacity of the capacitor is simply the total charge accumulated on one conductor, divided by the potential difference, which equals one:

$$\text{cap}_A(B) = \int_{\partial A} \rho_{A,B}(y) \, \mathrm{d}y \, . \tag{4.7}$$

The key observation is the following. Let $C = \mathcal{B}_\varepsilon(x)$ be a ball of radius ε around x, and consider the integral $\int_{\partial C} w_A(z)\rho_{C,A}(z) \, \mathrm{d}z$. On one hand, using the expression (4.4) of w_A, symmetry of the Green's function and then (4.6), one sees that this integral is equal to $\int_{A^c} h_{C,A}(y) \, \mathrm{d}y$. On the other hand, as w_A does not vary much on the small ball C [BEGK04], we can replace $w_A(z)$ by $w_A(x)$, and the remaining integral is just the capacity. This yields the relation

$$\Gamma^{-1} = \mathbb{E}[\tau_A^x] = w_A(x) \simeq \frac{\displaystyle\int_{A^c} h_{\mathcal{B}_\varepsilon(x),A}(z) \, \mathrm{d}z}{\text{cap}_{\mathcal{B}_\varepsilon(x)}(A)} \, . \tag{4.8}$$

The interest of this relation lies in the fact that capacities can be estimated by a variational principle. Indeed, the capacity for unit potential difference is equal to the total energy of the electric field,

$$\text{cap}_A(B) = \int_{(A \cup B)^c} \|\nabla h_{A,B}(x)\|^2 \, \mathrm{d}x = \inf_h \int_{(A \cup B)^c} \|\nabla h(x)\|^2 \, \mathrm{d}x \, , \tag{4.9}$$

where the infimum is taken over all twice differentiable functions satisfying the b.c. in (4.5).

If, instead of Brownian motion, we consider the solution of a d-dimensional SDE $\dot{x} = -\nabla \mathcal{H}(x) + \sqrt{2\varepsilon}\, \dot{W}_t$, the above steps can be repeated, provided we replace Δ by the generator $\varepsilon\Delta - \nabla\mathcal{H} \cdot \nabla$ of the equation (the generator is the adjoint of the operator appearing in the Fokker–Planck equation). The above relations remain valid, only with the Lebesgue measure replaced by the invariant measure $\mathrm{e}^{-\mathcal{H}(x)/\varepsilon} \, \mathrm{d}x$. Thus we have

$$\Gamma = \mathbb{E}[\tau_A^x]^{-1} \simeq \frac{\text{cap}_{\mathcal{B}_\varepsilon(x)}(A)}{\displaystyle\int_{A^c} h_{\mathcal{B}_\varepsilon(x),A}(z) \, \mathrm{e}^{-\mathcal{H}(z)/\varepsilon} \, \mathrm{d}z} \, , \tag{4.10}$$

where the capacity can be computed via the Dirichlet form

$$\text{cap}_A(B) = \inf_h \varepsilon \int_{(A \cup B)^c} \|\nabla h(x)\|^2 \, \mathrm{e}^{-\mathcal{H}(x)/\varepsilon} \, \mathrm{d}x \, . \tag{4.11}$$

The denominator in (4.10) can be easily estimated by saddle-point methods, using the fact that $h_{\mathcal{B}_\varepsilon(x),A}$ is essentially 1 in the basin of attraction of x and 0 in the basin of A. It is equal to leading order to $(2\pi\varepsilon)^{d/2} \, \mathrm{e}^{-\mathcal{H}(x)/\varepsilon} / \sqrt{\det(\delta^2\mathcal{H}/\delta x^2)(x)}$. A good upper bound of the denominator in (4.10) is obtained by inserting a sufficiently good guess for the potential h in (4.11). Assume, e.g., that near a transition state at 0, the energy has the expansion

$$\mathcal{H}(x) = -\frac{1}{2}|\lambda_0|x_0^2 + u(x_1) + \frac{1}{2}\sum_{j=2}^{d-1} \lambda_j x_j^2 + \dots \, , \tag{4.12}$$

where $u(x_1)$ corresponds to the possibly neutral direction in which a bifurcation occurs. Choosing $h(x) = f(x_0)$ where $\varepsilon f''(x_0) - \partial_{x_0}\mathcal{H}(x_0, 0, \dots 0)f'(x_0)$ with appropriate b.c. and
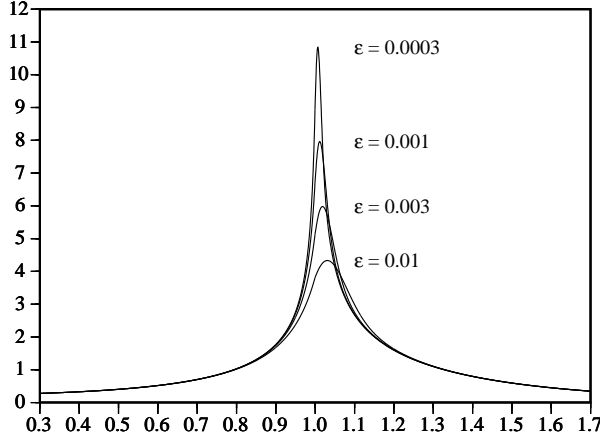
FIGURE 1. Rate prefactor Γ_0 as a function of L/π for Neumann b.c. and different values of noise intensity ε.

substituting in (4.11) yields

$$\operatorname{cap}_A(B) \leqslant \frac{1}{2\pi} \sqrt{\frac{(2\pi\varepsilon)^{d-1}|\lambda_0|}{\lambda_2 \dots \lambda_{d-1}}} \int_{-\infty}^{\infty} \mathrm{e}^{-u(x_1)/\varepsilon} \, \mathrm{d}x_1 \ . \tag{4.13}$$

A matching lower bound for the capacity can be obtained by a slightly more elaborate argument, see [BG08b] for details. If $u(x_1) = \frac{1}{2}\lambda_1 x_1^2$, the integral has value $\sqrt{2\pi\varepsilon/\lambda_1}$ and we recover the usual Kramers formula. However, (4.13) applies to other cases as well, e.g. a quartic $u(x_1)$.

We now return to the SPDE (2.2). We apply the above theory first to a finite-dimensional approximation of the system (2.2), obtained either by truncation of high wave numbers in its Fourier transform (2.5), or by replacing the system by a discrete chain [BFG07a, BFG07b], and then taking the limit. A difficulty is that the error terms will depend on the number of retained modes (see, for instance, [Liu03] for estimates on the convergence rate of the spectral approximations). Thus the results below are for now only formal. The error terms in the capacity can, however, be controlled [BG08a].

Neumann b.c. The potential energy along the normalized eigenvector in the bifurcating direction $v_1(x) = \sqrt{2}\cos(\pi x/L)$ is

$$u(\phi_1) = \mathcal{H}[\phi_1 v_1] = L\left[\frac{1}{2}\lambda_1\phi_1^2 + \frac{3}{8}\phi_1^4 + \dots\right] \ . \tag{4.14}$$

Evaluating the integral in (4.13), we find [BG08b] that for $L \leqslant \pi$ the corrected Kramers prefactor to leading order is given by

$$\Gamma_0 = \frac{1}{2^{3/4}\pi} \sqrt{\frac{\lambda_1}{\lambda_1 + \sqrt{3\varepsilon/4L}}} \Psi_+\left(\frac{\lambda_1}{\sqrt{3\varepsilon/4L}}\right) \sqrt{\frac{\sinh(\sqrt{2}L)}{\sin L}} \ , \tag{4.15}$$

where $\lambda_1 = -1 + (\pi/L)^2$ and Ψ_+ is a universal scaling function, given in terms of the modified Bessel function of the second kind $K_{1/4}$ by

$$\Psi_+(\alpha) = \sqrt{\frac{\alpha(1+\alpha)}{8\pi}} \, \mathrm{e}^{\alpha^2/16} K_{1/4}\left(\frac{\alpha^2}{16}\right) \ . \tag{4.16}$$

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For $L \ll \pi$, since $\Psi_+(\alpha)$ tends to 1 as $\alpha \to \infty$, we recover to leading order the rate (4.2). For $\pi - L$ of order $\sqrt{\varepsilon}$, however, the correction terms come into play, and the factor $\sqrt{\lambda_1}$ in the numerator of (4.15) counteracts the divergence of the prefactor (4.2). In particular, we have

$$\lim_{L \to \pi^-} \Gamma_0 \simeq \frac{\Gamma(1/4)}{2(3\pi^7)^{1/4}} \sqrt{\sinh(\sqrt{2}\,\pi)}\, \varepsilon^{-1/4} . \tag{4.17}$$

For $L > \pi$, the rate prefactor is harder to compute, because the transition states are not uniform. The computation can nevertheless be done [MS03] with the help of a method due to Gel'fand, with the result

$$\Gamma_0 \simeq \frac{1}{\pi} |\mu_0| \sqrt{\frac{\sinh(\sqrt{2}\,L)}{\sqrt{2}\,|(1-m)\,\mathrm{K}(m) - (1+m)\,\mathrm{E}(m)|}} , \tag{4.18}$$

where $\mu_0 = 1 - \frac{2}{m+1}\sqrt{m^2 - m + 1}$ is the negative eigenvalue of Λ_t, and m is related to L by (3.5). As $L \to \pi^+$ (that is, $m \to 0^+$), this expression again diverges, namely like $(L-\pi)^{-1/2}$. Proceeding as above, we find [BG08b] that the corrected prefactor is obtained by multiplying (4.18) by

$$\frac{1}{2} \sqrt{\frac{\mu_1}{\mu_1 + \sqrt{3\varepsilon/4L}}}\, \Psi_- \left(\frac{\mu_1}{\sqrt{3\varepsilon/4L}} \right) . \tag{4.19}$$

Here Ψ_- is again a universal scaling function, given in terms of modified Bessel functions of the first kind $I_{\pm 1/4}$ by

$$\Psi_-(\alpha) = \sqrt{\frac{\pi \alpha(1+\alpha)}{32}}\, \mathrm{e}^{-\alpha^2/64} \left[I_{-1/4}\left(\frac{\alpha^2}{64} \right) + I_{1/4}\left(\frac{\alpha^2}{64} \right) \right] , \tag{4.20}$$

which converges to 2 as $\alpha \to \infty$, and μ_1 is the *second* eigenvalue of Λ_t. We can in fact avoid the computation of this eigenvalue. Indeed, near the bifurcation a local analysis shows that $\mu_1 = -2\lambda_1 + \mathcal{O}(\lambda_1^2) = 3m + \mathcal{O}(m^2)$, while further away from the bifurcation, the quotient in (4.19) is close to 1. One can thus replace μ_1 by $3m$ in (4.19), only causing a multiplicative error $1 + \mathcal{O}(\varepsilon^{1/4})$. The resulting behavior of the prefactor Γ_0 as L crosses the critical value π is shown in Fig. 1.

Periodic b.c. For $L \leqslant 2\pi$, the transition state is uniform, and the computations are analogous to those in the previous case. The eigenvalues at the stable and transition states are now given by $\lambda_k = -1 + (2\pi k/L)^2$ and $\eta_k = 2 + (2\pi k/L)^2$ with $k \in \mathbb{Z}$, and are thus double except for $k = 0$. This implies that the integral in (4.13) is to be replaced by a double integral over the subspace of the two bifurcating modes [BG08a]. The result is

$$\Gamma_0 \simeq \frac{1}{2\pi} \frac{\lambda_1}{\lambda_1 + \sqrt{3\varepsilon/4L}}\, \widetilde{\Psi}_+ \left(\frac{\lambda_1}{\sqrt{3\varepsilon/4L}} \right) \frac{\sinh(L/\sqrt{2})}{\sin(L/2)} , \tag{4.21}$$

where the scaling function $\widetilde{\Psi}_+$ is now given in terms of the error function by

$$\widetilde{\Psi}_+(\alpha) = \sqrt{\frac{\pi}{8}}(1+\alpha)\, \mathrm{e}^{\alpha^2/8} \left[1 + \mathrm{erf}(-2^{-3/2}\alpha) \right] . \tag{4.22}$$

As $\widetilde{\Psi}_+$ converges to 1 as $\alpha \to \infty$, for $2\pi - L \gg \sqrt{\varepsilon}$, we recover the usual Kramers prefactor, which diverges as $(2\pi - L)^{-1}$ as $L \to 2\pi^-$. However, as L approaches 2π, the correction terms come into play and we get

$$\lim_{L \to 2\pi^-} \Gamma_0 \simeq \frac{\sinh(\sqrt{2}\pi)}{\sqrt{3}\,\pi}\, \varepsilon^{-1/2} \ . \tag{4.23}$$

For $L > 2\pi$, we again have to deal with a non-uniform transition state ϕ_{t}. An additional difficulty stems from the fact that transition states form a continuous family, so that the Hessian at ϕ_{t} always admits one vanishing eigenvalue. This eigenvalue can be removed by a regularization procedure due to McKane and Tarlie [MT95], which has been applied in the case of an asymmetric potential in [Ste04]. The computations are similar in the symmetric case [Ste], and yield a rate prefactor per unit length

$$\frac{\Gamma_0}{L} \simeq \frac{|\mu_0|}{(2\pi)^{3/2}} \sqrt{\frac{2m(1-m)\sinh^2(L/\sqrt{2})}{(1+m)^{5/2}|\mathrm{K}(m) - \frac{1+m}{1-m}\mathrm{E}(m)|}} \varepsilon^{-1/2} \ , \tag{4.24}$$

with $4\sqrt{m+1}\,\mathrm{K}(m) = L$ and the same μ_0 as for Neumann b.c. The factor $\varepsilon^{-1/2}$ reflects the fact that nucleation can occur anywhere in space [Ste04]. The prefactor now converges to a finite limit as $L \to 2\pi^+$, which differs, however, by a factor 2 from (4.23). This apparent discrepancy is solved by applying the corrected Kramers formula, which shows that (4.24) has to be multiplied by a factor

$$\Phi\left(\frac{3m}{2\sqrt{3\varepsilon/L}}\right) \tag{4.25}$$

where $\Phi(x) = \frac{1}{2}[1 + \mathrm{erf}(x/\sqrt{2})]$. The resulting rate prefactor is indeed continuous at $L = 2\pi$.

5 Conclusion

We have presented a new method allowing the computation of the Kramers rate prefactor in situations where the transition state undergoes a bifurcation. In contrast with the quadratic case, the prefactor is no longer independent of the noise intensity ε to leading order, but diverges like $C\varepsilon^{-\alpha}$, where α is equal to $1/4$ times the number of vanishing eigenvalues. The constant C can in fact be computed in a full neighborhood of the bifurcation point, and involves universal functions, depending only on the type of bifurcation. A similar non–Arrhenius behavior of the prefactor has been observed in irreversible systems [MS96], but there it has an entirely different origin, namely the development of a caustic singularity in the most probable exit path.

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