Addendum and Erratum:

Escape from a Metastable State [J. Stat. Phys. 42:105-148 (1986)] Peter Hanggi

In this note I update the above article with some relevant material and correct some minor misprints. Following eq. (2.7) one should state more precisely: If U(x) is a **nonlinear** and **nonquadratic** potential field, analytical exact results for (2.7) within the full damping regime are not known. For a parabolic potential field (linear force), $U(x) = (M/2) \omega_0^2 x^2$, the eigenvalues and eigenfunctions are readily obtained (Ref. 41). In particular, the complex-valued eigenvalues read

$$\lambda_{n,m} = -\frac{1}{2}(n+m)\gamma + \frac{1}{2}i[4\omega_0^2 - \gamma^2]^{1/2}(n-m)$$
 $n, m = 0, 1,...$

Approximate, analytical solutions for a bistable potential at intermediate and high friction can be found in: J. F. Gouyet and A. Bunde, J. Stat. Phys. 36:43 (1984); Physica 132A:357 (1985).

In the case of the strongly overdamped (Smoluchowski) case the boundary condition following (2.24) should be corrected to read

$$p_o(x \sim x_1) = \bar{p}(x \sim x_1)$$

For weakly damped systems, the equilibrium probability $\bar{p}(E)$, (2.41), for the energy depends, of course, on the inverse density of states v(E) on the **dimension** of the reaction coordinate x. Equation (2.53c) should be completed by writing for the density of states $\psi(E)$

$$\psi(E) = \int d\Omega \, \delta[E - \mathcal{H}(\mathbf{\Omega})] \equiv 1/\nu(E)$$
 (2.53c)

The multidimensional generalization of (eqs. 2.38, 2.41–2.46, 2.51, 2.52, and 2.62 is then given with v(E) determined from (2.53c). Moreover, it should also be noted that the rate exhibits in the weak friction regime a rather

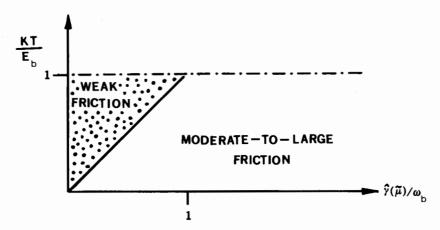


Fig. 1. Regime of validity of the various classical rate expressions as a function of the dimensionless parameters kT/E_b and $\hat{\gamma}(\tilde{\mu})/\omega_b$, with $\tilde{\mu}$ (memory friction) defined in (2.59). Weak-friction results (energy diffusion controlled regime): eqs. 2.43, 2.44, 2.45, 2.46, and 2.48; moderate-to-large friction: eqs. 2.20, 2.49, and 2.58; crossover regime: eqs. 2.46 and 2.64.

interesting sensitivity to the coupling strengths among the degrees of freedom x, modeling the reaction dynamics. Recently, this has been beautifully demonstrated in a study by M. Borkovec, J. E. Straub, and B. J. Berne, "The Influence of Intramolecular Vibrational Relaxation on the Pressure Dependence of Unimolecular Rate Constants", J. Chem. Phys. 85:(in press).

Reference 70b, containing the informative numerical simulation data for escape driven by exponentially correlated Gaussian noise, should be completed as follows: J. E. Straub, M. Borkovec, and B. J. Berne, J. Chem. Phys. 84:1788 (1986). Also, Ref. 109 should be complemented by adding the reference: A. J. Leggett, Phys. Rev. B, 30:1208 (1984). In Ref. 20 we should add: G. Maneke, J. Schroeder, J. Troe, and F. Voss, Ber. Bunsenges. Phys. Chem. 89:896 (1985).

Finally, we present here a rate-phase diagram which summarizes the regime of validity of the various classical rate expressions (Fig. 1).

ACKNOWLEDGMENT

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