A Criterion for the Validity of Kramers' Rate Expression in the Moderate to Large Damping Regime

Peter Talkner, Institut für Physik, Klingelbergstrasse 82, CH-4056 Basel, Switzerland

Abstract: A physical explanation is given for the failure of Kramers' phase space diffusion rate for small damping constants.

In a seminal paper Kramers calculated the escape rate of a Brownian particle out of a metastable well over a potential barrier as the ratio of a probability current at the barrier and the population of the metastable well |1, 2|. In order to maintain a stationary state with a finite probability current the steady flow of probability out of the well must be compensated by replacing escaped particles. Therefore the continuity equation for the probability must contain a source term:

$$- \operatorname{div} \mathbf{J} + S = 0 \tag{1}$$

where $\mathbf{J}$ denotes the probability current density and S the density of sources ($S > 0$) and sinks ($S < 0$). Note that sinks may only be present beyond the barrier. The precise location and strength of the sources within the well does not influence the rate as long as the injected particles first thermalize, i.e. settle down in the well, before they escape eventually. In this communication we shall examine whether this condition is satisfied by the particular current carrying probability density for a Brownian particle of mass M in a metastable potential U (x) at mediate damping strength as has been proposed by Kramers |1|:

$$\rho(x, v) = \left(\frac{M\omega_b^4}{2\pi\gamma k_B T \lambda_+} \right)^{\frac{1}{2}} \int_{x-\lambda_+ v/\omega_b^2}^{\infty} \exp\left\{ - \frac{M\omega_b^4 u^2}{2\gamma\lambda_+ k_B T} \right\} du \; p(x,v) \tag{2}$$

where p (x,v) denotes the Boltzmann distribution at temperature T:

$$p(x,v) = N \exp\left\{ - \left(\tfrac{1}{2} M v^2 + U(x)\right) / k_B T \right\}, \tag{3}$$

γ the damping constant, $M\omega_b^2$ the curvature of the potential at the barrier being located at the origin $x = 0$, and $\lambda_+ = -\gamma/2 + ((\gamma/2)^2 + \omega_b^2)^{1/2}$ the positive eigenvalue of the deterministic motion at the barrier. With the probability current for a Brownian particle |3| we obtain from Eqs. (1), (2) and (3) the densitiy of sources and sinks which renders (2) stationary:

$$S(x, v) = -\left(\frac{\lambda_+}{2\pi\gamma M k_B T}\right)^{\frac{1}{2}} \left(U'(x) + \omega_b^2 x\right) \exp\left\{ -\frac{M\omega_b^4}{2\gamma\lambda_+ k_B T}\left(x - \lambda_+ v / \omega_b^2\right)^2 \right\} \; p(x, v) \tag{4}$$

From this expression one finds that for arbitrary finite values of the damping constant all particles are injected into the deterministic domain of attraction of the well if the temperature is sufficiently low. If, however, at a fixed temperature the damping constant is decreased below a certain value the source emits particles with energies being too large to be thermalized within the well. This clearly indicates the known failure of Kramers' phase space diffusion rate for small damping constants. A simple quantitative measure is given by the mean energy $\langle E \rangle_S$ of the emited particles

$$\langle E \rangle_S - E_b = \frac{1}{2}\left(1 + \gamma\lambda_+ / \omega_b^2\right) k_B T - \frac{1}{2}\Gamma(1 + 2/p)\, \gamma\lambda_+ M \left(k_B T / a\right)^{2/p} \tag{5}$$

where ax^p is the leading nonlinear correction to the parabolic approximation of the potential $U(x)$ at the barrier, where E_b denotes the barrier height, and Γ the gamma function. As long as the mean energy of injected particles is smaller than the barrier energy Kramers' phase space diffusion rate expression is correct while it overestimates the rate if $\langle E \rangle_S - E_b$ becomes comparable with or even larger than the energy loss of the particle on a round trip |1|.

References:

|1| H. A. Kramers, Physica **7**, 284 (1940)

|2| As a review of subsequent work may serve P. Hänggi, J. Stat. Phys. **42**, 105 (1986)

|3| R.L. Stratonovich, Topics in the Theory of Random Noise Vol. 1, Gordon Breach, New York (1963)