NON-STOKESIAN DAMPING AND THERMALLY ACTIVATED ESCAPE

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There exist in physics and chemistry important rate processes that involve activated escape of a particle over barriers. Examples are chemical reactions, superionic conductors, and ligand migration in proteins. Only those processes which involve a clear separation of timescales of particle and heat bath motion are understood.[1] In what follows, we consider the transport as a passage over a mean potential barrier between two wells. In contrast to Kramers' classic investigation,[1] we consider the rate of motion of the particle to be on the same order as the rate of motion of the excitation field of the heat bath. Applications can be made to the migration of ligands in proteins, impurity diffusion in solids,[2] and chemical reactions on surfaces of insulators that lack fast-moving electrons. The relevant motion in the barrier region must then be modeled by a generalized Langevin equation (we use a unit particle mass) in a phase space (x,u) of coordinate and velocity, respectively,

$$\dot{x} = u$$

and

$$\dot{u} = \omega^2 x - \int_0^t \gamma(t-\tau)u(\tau)\mathrm{d}\tau + \xi(t). \tag{1}$$

Here, ω denotes the barrier frequency obtained by expanding the external potential $\phi(x)$ around its barrier value,

$$\phi(x) = \phi_b - \frac{\omega^2}{2}x^2 + \ldots, \omega^2 > 0, \tag{2}$$

and $\xi(t)$ is the thermal stationary Gaussian random force satisfying the fluctuation-dissipation theorem. Equation 1 completely determines the dynamics of the process within the barrier region. The corresponding conditional probability satisfies a time-convolutionless (but not memory-less) non-Markov master equation of the Fokker-Planck type with a mixed derivative, $\partial^2/\partial x\,\partial u$.[3] The escape rate,

$$\lambda = J_0/n_0, \tag{3}$$

is obtained from the nonequilibrium diffusion current, J_0, which is obtained by injecting particles at the locally stable well, x_0, and removing them at the adjacent well, $x_0' \cdot n_0$ denotes the particle density around x_0. The result for the rate λ reads (ω_0 is the angular frequency at x_0)

$$\lambda = \frac{\omega_0}{2\pi\omega}\left\{\left(\frac{\bar{\gamma}^2}{4} + \bar{\omega}^2\right)^{1/2} - \frac{\bar{\gamma}}{2}\right\} \exp - \frac{[\phi_b - \phi_0]}{kT}, \tag{4}$$

where

$$\bar{\gamma} = -\lim_{t\to\infty}\frac{\dot{a}}{a}, \qquad \bar{\omega}^2 = -\lim_{t\to\infty}\frac{b}{a}, \tag{5}$$

with

$$a(t) = \dot{\rho}(t)(1 + \omega^2\int_0^t \rho(\tau)\mathrm{d}\tau) - \omega^2\rho^2(t) \tag{6a}$$

$$b(t) = \omega^2[\rho(t)\,\ddot{\rho}\,(t) - \dot{\rho}(t)^2]. \tag{6b}$$

The correlation, $\rho(t)$, is defined by the inverse Laplace transform (L^{-1})

$$\rho(t) = L^{-1}(\hat{\rho}(z)) = L^{-1}\left[\frac{1}{z^2 - \omega^2 + z\hat{\gamma}(z)}\right], \qquad \rho(t=0) = 0. \tag{6c}$$

In contrast to the Markov result, the prefactor is determined by the (bare) parameters ω_0 and ω and a "renormalized" quantity,

$$\alpha = \left(\frac{\bar{\gamma}^2}{4} + \bar{\omega}^2\right)^{1/2} - \frac{\bar{\gamma}}{2}. \tag{7}$$

Further, if $\hat{\rho}(z)$ is meromorphic, *i.e.*, if

$$\rho(t) = \sum_{i=1}^{n} C_i t^{m_i} e^{\lambda_i t}, \tag{8}$$

with $\lambda_1 < \lambda_2 < \cdots \lambda_{n-1} < \lambda_n$, and λ_i, and λ_i, m_i is real, then one finds that the limit α is, in fact, equal to the limit

$$\alpha = \lim_{t\to\infty}\frac{\dot{\rho}(t)}{\rho(t)} = \lambda_n > 0, \tag{9}$$

with λ_n being the largest positive pole of $\hat{\rho}(z)$. λ_n is a characteristic function of ω^2 and depends on the details of the damping $\gamma(t)$, but λ_n is not an explicit function of temperature T in the harmonic approximation. A non-Markovian transport over n multiple barriers can thus be conveniently modeled by a set of $(n+1)$ rate equations with corresponding rates determined from (4).

REFERENCES

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