Effect of Boundary Condition Fluctuations on Smoluchowski Reaction Rates

Dedicated to Lutz Schimansky-Geier, half a century wise

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Abstract. We formulate, solve, and examine an elementary model of gated absorption, where the reactivity of a sphere fluctuates in time, in the context of Smolukowski's diffusion-controlled rate processes. Interest in this problem was stimulated by some experiments on biomolecular rate processes in the 1970s. The model under discussion here was studied by a number of investigators in the 1980s, and interest is renewed by the discovery of resonant activation in the 1990s. We find that the simplest gated reaction process does not exhibit features characteristic of resonant activation, although some interesting nonequilibrium correlations may have a quantitative effect in some situations. We speculate on the possible appearance of resonant activation phenomena in related processes.

1 Introduction

Resonant activation [1] is a nonlinear nonequilibrium phenomenon involving the emergence of correlations between ostensibly independent processes. Consider a stochastically perturbed particle crossing a potential barrier described by a Kramers type activation process [2]. In the overdamped limit when the barrier is high compared to the particle's diffusion coefficient, the typical escape time depends exponentially on the ratio, i.e., \( T_{\text{escape}} \sim e^{V/D} \). Now consider a temporally fluctuating potential barrier where the variations are an externally controlled process so that the particle state does not affect the barrier changes (the set-up is now strictly nonequilibrium). Suppose the barrier fluctuation time scale is \( T_{\text{barrier}} \) and, for simplicity, that the barrier fluctuates between \( V_{\text{min}} \) and \( V_{\text{max}} \) with an average \( \langle V \rangle \). When the barrier fluctuations are slow relative to the longest relevant time scales in the system, so that \( T_{\text{barrier}} \gg T_{\text{max}} \sim e^{V_{\text{max}}/D} \), then the average time to cross the barrier will be the average, \( T_{\text{escape}} \sim \langle e^{V/D} \rangle \), which may be of the order of the longest time \( \sim e^{V_{\text{max}}/D} \). On the other hand when \( T_{\text{barrier}} \ll T_{\text{min}} \sim e^{V_{\text{min}}/D} \) and the barrier fluctuations are fast compared to the barrier crossings, then the particle effectively moves in the average potential and we expect \( T_{\text{escape}} \sim e^{\langle V \rangle /D} < \langle e^{V/D} \rangle \).

These two limiting scales, \( \sim e^{\langle V \rangle /D} \) and \( \sim \langle e^{V/D} \rangle \), might reasonably thought to be the range of possible times for the barrier crossing process. But the phenomena of resonant activation shows otherwise. For some system
configurations it is possible that an even shorter barrier crossing time scale emerges at an intermediate time. Indeed, when $T_{\text{barrier}} \approx T_{\text{min}}$, then $T_{\text{escape}}$ also $\approx T_{\text{min}} \sim e^{V_{\text{min}}/D} < e^{(V)/D} < \langle e^{V/D} \rangle$. What happens is that if the barrier remains “down” long enough for the particle to cross, then it does so in a typical time characteristic of the lowered barrier crossing. Strong correlations between the barrier variations and particle crossing events emerge when these time scales match up, correlations which are absent in either the fast or slow barrier fluctuation regime (see [1]).

This effect and related phenomena have been studied from a great number of points of view ([3]-[12]). Most recently a thorough experimental study [13] both observed resonant activation directly and, moreover, measured the complete escape time distribution for various regimes of barrier fluctuation time scales.

Activated rate processes in nonequilibrium systems like glasses [14] and biomolecules [15] provide ample motivation for considering such complex stochastic dynamical processes. The fluctuating barrier scenario was hypothesised in particular for experiments in the 1970s on the reaction kinetics for hemoglobin rebinding of carbon monoxide and dioxygen [16]. In those experiments the “ligands” carbon monoxide and dioxygen were photodissociated, and then the ensuing diffusion-controlled rebinding process was monitored at a wide range of temperatures and, later, in a range of solvent viscosities [17]. The first attempt at modeling the effect of reaction rate fluctuations in such a diffusion-controlled ligand-to-protein binding process came in 1981 [18], which was soon followed by more intensive and general studies [19], [20]. Those theoretical investigation focused on the effect of surface reactivity fluctuations on Smoluchowski’s diffusion-controlled rate theory ([21]-[23]). A re-examination of this model, with an eye towards the search for interesting phenomena like resonant activation, is the focus of this paper.

In the next section we review the classical Smoluchowski theory in order to recount some of the basic modeling assumptions and introduce notation. Then in section 3 we generalize the model to include random fluctuations in the surface reactivity as a model of a gating process active at a protein surface. We solve the model in the steady state and point out some features of some limiting cases. The final section 4 is a discussion of the results and their implications for the relevance of resonant activation phenomena in complex systems like the protein-ligand binding reaction.

2 Smoluchowski Theory for a Partially Absorbing Sphere

We begin by recalling the classical theory of a partially absorbing sphere (the protein) of radius $R$ at rest in a solvent filled with diffusing particles (ligands) at concentration $C$ far away ([21]-[23]). By “partially absorbing” we mean that the sphere absorbs ligands impinging on the surface at a fixed