Appendix C

Transition Times Considered in Full State Space (Sequel)

Here, we refer to Section 2.2.5 and present the derivation of the metastable transition times $\overline{T}^{\epsilon}_{1\to 2}$ for the situation as illustrated in the right picture of Fig. 2.5. In so doing, we directly affiliate to the achievements from Section 2.2.5.

Situation 2: $V^{(1)}_{\mathrm{bar}}$ strictly monotonically decreasing. In addition, we assume $\lim_{x\to\infty} V^{(1)}_{\mathrm{bar}}(x) = 0$. We demonstrate the problem with the averaged exit rates by choosing a bounded connected domain $D = D(\sigma) = [a, b]$ of the x state space such that $\int_D \bar{\mu}^{(1)}(x)\,\mathrm{d}x \approx 1$, that is, the x trajectory will almost never enter the complement D^c of D. In so doing, we decompose the integral in (2.49) and exploit that the minimum of $V^{(1)}_{\mathrm{bar}}(x)$ in D is attained at the right boundary b of D, that is, $V^{(1)}_{\mathrm{bar}}(b) = \min\{V^{(1)}_{\mathrm{bar}}(x) \mid x \in D(\sigma)\}$. Once more we apply Laplace's method to obtain

$$\begin{aligned}
\mathbf{E}_{\bar{\mu}^{(1)}}[1/\mathcal{T}^{\epsilon}_{1\to 2}(x)] &= \int_{-\infty}^{b} 1/\mathcal{T}^{\epsilon}_{1\to 2}(x)\bar{\mu}^{(1)}(x)\mathrm{d}x + \int_{D^c} 1/\mathcal{T}^{\epsilon}_{1\to 2}(x)\bar{\mu}^{(1)}(x)\mathrm{d}x \\
&\simeq \frac{\sqrt{\omega^{(1)}(b)\omega_0(b)}}{\pi\,(-\partial_x V^{(1)}_{\mathrm{bar}}(b))}\,\frac{1}{Z^{(1)}}\,\exp(-\frac{2}{\sigma^2}V(b, m^{(1)}(b)))\,\frac{\varsigma^2}{\epsilon}\,\exp(-\frac{2}{\varsigma^2}V^{(1)}_{\mathrm{bar}}(b)) \\
&\qquad + \frac{1}{\epsilon}\int_{D^c} 1/\mathcal{T}_{1\to 2}(x)\,\bar{\mu}^{(1)}(x)\,\mathrm{d}x, \qquad \text{(C.1)}
\end{aligned}$$

such that an offset of the boundary b to the right will diminish the second term on the RHS of (C.1). To get a grip on the integral over D^c, let us assume the boundary b to be far away from the accessible part of the state space. As we have $\int_{D^c} \bar{\mu}^{(1)}(x)\mathrm{d}x \approx 0$, the second term on the RHS of (C.1) seems to be negligible. However, because $V^{(1)}_{\mathrm{bar}}(x) \to 0$ as $x \to \infty$, the transition rates for fixed $x \in D$ are faster decreasing asymptotically as the rates for $x \in D^c$. Thus, in the limit of small noise ς (and for fixed $\epsilon = \epsilon^*$), the major contribution to $\mathbf{E}_{\bar{\mu}^{(1)}}[1/\mathcal{T}^{\epsilon^*}_{1\to 2}(x)]$ arises from the integral over D^c, such that $\int_D 1/\mathcal{T}^{\epsilon^*}_{1\to 2}(x)\bar{\mu}^{(1)}(x)\mathrm{d}x$ has asymptotically vanishing contribution.

This phenomenon is observed even more clearly by coupling ς to ϵ through (2.48) with $V^{\text{small}}_{\text{bar}} = V^{(1)}_{\text{bar}}(b)$ and letting $\epsilon \to 0$. As we will see, the averaged transition rates then become a completely useless quantity and cannot represent the effective transition rates from $B^{(1)}$ to $B^{(2)}$. The problem is exemplified by using (C.1) and inserting (2.48). Then we asymptotically have

$$\int_{-\infty}^{b} 1/\mathcal{T}^{\epsilon}_{1\to 2}(x)\bar{\mu}^{(1)}(x) \;=\; \text{ord}((\ln(1/\epsilon))^{-1}) \qquad \longrightarrow 0, \tag{C.2}$$

$$\int_{b}^{\infty} 1/\mathcal{T}^{\epsilon}_{1\to 2}(x)\bar{\mu}^{(1)}(x) \;=\; \text{ord}(\epsilon^{-\delta}(\ln(1/\epsilon))^{-1}) \;\longrightarrow \infty,\; 0<\delta<1. \tag{C.3}$$

Therefore $\mathbf{E}_{\bar{\mu}^{(1)}}[1/\mathcal{T}^{\epsilon}_{1\to 2}(x)] \to \infty$ as $\epsilon \to 0$, which completely contradicts the physical intuition, for the trajectory will almost never reach D^c and concentrate around the minimum of $V(x, m^{(1)}(x))$ instead. The problem of getting falsified values in the case of $\epsilon \to 0$ can be explained by the following consideration: As mentioned above, the derivation of the averaged transition rates according to (2.49) is performed under the assumption that the metastable transitions between $B^{(1)}$ and $B^{(2)}$ happen on a time scale that is longer than the time scale of the slow variable dynamcis' x; for fixed $\epsilon = \epsilon^*$ and $\varsigma \to 0$, we easily observe the transition times for fixed x to exponentially grow which implies the metastable transition times to happen on a time scale longer than the x dynamics; thus, for $\epsilon = \epsilon^*$ and ς small, we obviously can apply formula (2.49) and asymptotically get $\overline{\mathcal{T}}^{\epsilon^*}_{1\to 2} \simeq 1/\,\mathbf{E}_{\bar{\mu}^{(1)}}[1/\mathcal{T}^{\epsilon}_{1\to 2}(x)]$; in contrast, for $\epsilon \to 0$ and $\varsigma = \varsigma(\epsilon)$ given by (2.48) with $V^{\text{small}}_{\text{bar}} = V^{(1)}_{\text{bar}}(b)$ we have to carefully inspect the integrals in (C.2). As we see, (C.3) tends to infinity indicating the existence of points $x \in (b, \infty)$ with $\mathcal{T}^{\epsilon}_{1\to 2}(x) \to 0$ as $\epsilon \to 0$, which in turn prevents the sampling of $\bar{\mu}^{(1)}$ before any transition from $B^{(1)}$ to $B^{(2)}$ happens. Therefore, $\mathbf{E}_{\bar{\mu}^{(1)}}[1/\mathcal{T}^{\epsilon}_{1\to 2}(x)]$ is inappropriate in this case.

The difficulty of finding an appropriate formulation for the metastable transition times to $B^{(2)}$ is overcome by incorporating the expected exit times from the set $(-\infty, b]$. For vanishing ϵ we expect the following: As long as the process x^ϵ (with $(x^\epsilon, y^\epsilon) \in B^{(1)}$) is restricted to the domain $(-\infty, b)$, no transitions occur, whereas exiting $(-\infty, b]$ asymptotically leads to an instantly happening jump to $B^{(2)}$, for $V^{(1)}_{\text{bar}}(x) < V^{(1)}_{\text{bar}}(b)$ whenever $x > b$. However, as the transition probability depends on the rate $1/\mathcal{T}^{\epsilon}_{2\to 1}(x)$ as well, we have to incorporate the course of $V^{(2)}_{\text{bar}}(x)$ into our considerations. More precise, whenever $\mathcal{T}^{\epsilon}_{1\to 2}(x)/\mathcal{T}^{\epsilon}_{2\to 1}(x) \to \infty$, the transition probability to jump to $B^{(2)}$ (at $x^\epsilon(t) = x$) will asymptotically converge to zero. But this is exactly the case for $V_{\rm bar}^{(2)}(x) < V_{\rm bar}^{(1)}(x)$. In order to modify the effect let us assume for simplicity that $V_{\rm bar}^{(2)}(x)$ is strictly monotonically increasing with $\lim_{x \to -\infty} V_{\rm bar}^{(2)}(x) = 0$. This implies the existence of a point m such that $V_{\rm bar}^{(1)}(m) = V_{\rm bar}^{(2)}(m)$. If we assume $b < x < m$, we obtain $V_{\rm bar}^{(2)}(x) < V_{\rm bar}^{(1)}(x) < V_{\rm bar}^{\rm small} = V_{\rm bar}^{(1)}(b)$, such that the process x^ϵ has to exit the domain $(-\infty, m]$ for an instantly happening jump from $B^{(1)}$ to $B^{(2)}$ in the asymptotic limit $\epsilon \to 0$.

An illustration of the problem is shown in Figure C.1 and Fig. C.2 below. The left side of Fig. C.1 visualizes a possible choice of $V_{\rm bar}^{\rm small} = V_{\rm bar}^{(1)}(b^{(1)}) =$

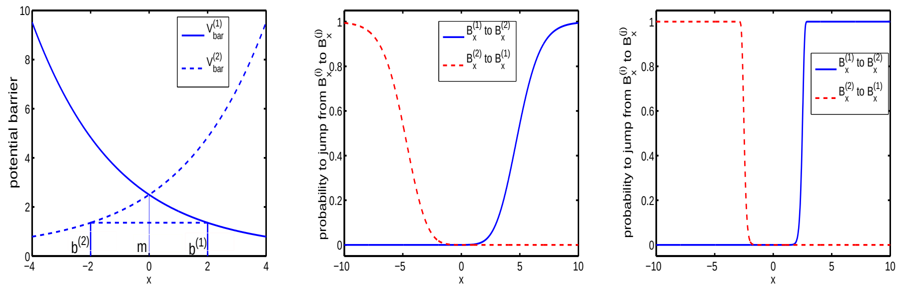

Figure C.1: left: Illustration of $V_{\rm bar}^{(i)}$, $i = 1, 2$ and $b^{(2)} < m < b^{(1)}$; middle: transition probabilities (time step $\mathrm{d}t = 0.01$) corresponding to (2.48) with $V_{\rm bar}^{\rm small} = V_{\rm bar}^{(1)}(b^{(1)})$ and $\epsilon = 10^{-3}$; right: transition probabilities with $\epsilon = 10^{-12}$.

$V_{\rm bar}^{(2)}(b^{(2)})$ with $b^{(1)} = 2 > m = 0$. The picture in the middle shows the transition probabilities $p_{1\to 2} = p_{12}^\epsilon(\mathrm{d}t, x)$, $p_{2\to 1} = p_{21}^\epsilon(\mathrm{d}t, x)$ to jump over the barrier for moderately chosen $\epsilon = 10^{-3}$ and time step $\mathrm{d}t = 1/100$. At the right we illustrate the transition probabilities for very small $\epsilon = 10^{-12}$. We clearly observe that for vanishing ϵ the particle will jump over the barrier once it has reached $b^{(1)}$ and $b^{(2)}$, respectively. In Fig. C.2 the

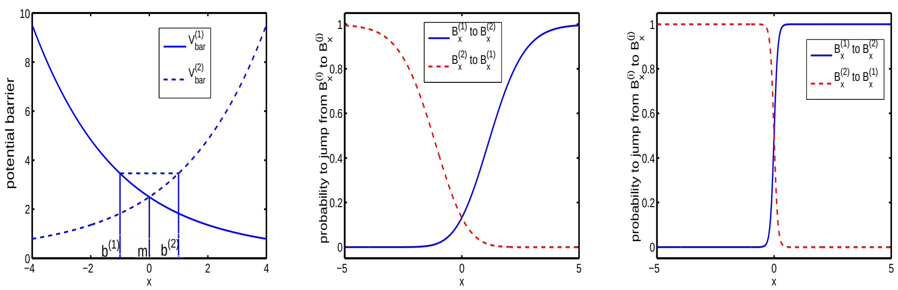

Figure C.2: Same as Figure C.1, but this time $b^{(1)} < m < b^{(2)}$.

situation is contrary: The picture at the left illustrates the choice of $V_{\rm bar}^{\rm small} = V_{\rm bar}^{(1)}(b^{(1)}) = V_{\rm bar}^{(2)}(b^{(2)})$ where this time $b^{(1)} = -1 < m = 0$ and thus $b^{(2)} > m$.

The transition probabilities for $\epsilon = 10^{-12}$ at the right-hand side reveal

$$p_{1\to 2} = p_{12}^{\epsilon}(\mathrm{d}t, x) \approx 0 \quad \text{for } x < m, \qquad p_{2\to 1} = p_{12}^{\epsilon}(\mathrm{d}t, x) \approx 1 \quad \text{for } x > m.$$

The model for the experiments is chosen from Section 2.3 with potential given in (2.57).

Summarisingly, under the assumption of strictly monotonic decrease of $V_{\text{bar}}^{(1)}$ with $\lim_{x\to\infty} V_{\text{bar}}^{(1)}(x) = 0$, and strictly monotonic increase of $V_{\text{bar}}^{(2)}$ with $\lim_{x\to-\infty} V_{\text{bar}}^{(2)}(x) = 0$ we obtain the following: Denote $m \in \mathbf{R}$ the point with $V_{\text{bar}}^{(1)}(m) = V_{\text{bar}}^{(2)}(m)$. Our result in the limit $\epsilon \to 0$ comprise the Smoluchowski dynamics $x^{(i)}(t)$ for $i = 1, 2$ that correspond to the potentials $V\big(x, m^{(i)}(x)\big)$, respectively. For simplicity we assume that $V(x, m^{(i)}(x))$ has one local minimum, for $i = 1, 2$ respectively, and agree $V(x_*^{(i)}, m^{(1)}(x_*^{(i)})) = \min\{V\big(x, m^{(i)}(x)\big) \mid x \in \mathbf{R}\}$ such that $x_*^{(1)} < m < x_*^{(2)}$. Now, we choose $\varsigma = \varsigma(\epsilon)$ to be defined by (2.48) with $V_{\text{bar}}^{\text{small}} = V_{\text{bar}}^{(1)}(b^{(1)})$ and $b^{(1)} \in (x_*^{(1)}, \infty)$ and denote $b^{(2)}$ the uniquely determined point x with $V_{\text{bar}}^{\text{small}} = V_{\text{bar}}^{(2)}(x)$. Finally, we define the expected exit time from the set D over the process $x^{(i)}(t)$ with starting point x_* by $\mathbf{E}_{x_*}[\tau_D(x^{(i)}(t))]$ for $i = 1, 2$. Now, we are in position to explicitly present the metastable transition times by the precise asymptotics in the limit of vanishing ϵ:

$$\begin{aligned} \overline{\mathcal{T}}_{1\to 2}^{\epsilon} &\simeq \mathbf{E}_{x_*^{(1)}}[\tau_{D^{(1)}}(x^{(1)}(t)], \\ \overline{\mathcal{T}}_{2\to 1}^{\epsilon} &\simeq \mathbf{E}_{x_*^{(2)}}[\tau_{D^{(2)}}(x^{(2)}(t)], \end{aligned}$$

where $D^{(1)} = (-\infty, \max(b^{(1)}, m)]$ and $D^{(2)} = [\min(b^{(2)}, m), \infty)$.