

BREAKING THE CHAIN

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Abstract. We consider the motion of a Brownian particle in \mathbb{R} , moving between a particle fixed at the origin and another moving deterministically away at slow speed $\varepsilon > 0$. The middle particle interacts with its neighbours via a potential of finite range $b > 0$, with a unique minimum at $a > 0$, where $b < 2a$. We say that the chain of particles breaks on the left- or right-hand side when the middle particle is greater than a distance b from its left or right neighbour, respectively. We study the asymptotic location of the first break of the chain in the limit of small noise, in the case where $\varepsilon = \varepsilon(\sigma)$ and $\sigma > 0$ is the noise intensity.

Keywords: first-exit from space-time domains, interacting Brownian particles, asymptotic theory

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1. INTRODUCTION

We are interested in the behaviour of a chain of interacting particles while it is pulled beyond its breaking point. Obvious real world examples would include the tearing of a band of rubber, or a rope, and obvious questions would be how much strain a given chain can endure before breaking, and where the breakpoint will be located once it occurs.

A model for such a chain is given by a collection of interacting Brownian particles i.e. one investigates solutions of the SDE system

$$dx_i(t) = -\frac{\partial H}{\partial x_i}(\mathbf{x}(t)) dt + \sigma dW_i(t), \quad (1.1)$$

where $(W_i)_{1 \leq i \leq N}$ are independent Brownian motions, $\mathbf{x} = (x_1, \dots, x_N) \in \mathbb{R}^N$ is the collection of particle positions, and σ is the (small) noise intensity. The potential energy of the chain is given by

$$H(\mathbf{x}) = \sum_{1 \leq i < j \leq N} U(x_i - x_j) \quad (1.2)$$

for some pair potential U . We now exert strain on this chain of interacting Brownian particles. This is done by solving (1.1) only for $2 \leq i \leq N-1$, fixing $x_1 = 0$ and pulling x_N outwards with (slow) speed ε ; the starting configuration of the chain should be a stable equilibrium, ideally a global minimum configuration of the potential energy. The mathematical questions corresponding to the problems above are then about the expected time of a (still to be defined) breaking event, and its location along the chain. In our case, the potential U will have compact support, on $|x| \leq K$, say, and the breaking event will occur when the distance between two given particles is greater than K .

The model (1.1) is widely used in material science to model the dynamics of crystals, in particular the propagation of cracks. Investigations there are purely numerical, and the main difficulty is the sheer size of the system under consideration. Out of the vast literature on the topic, we only mention [6, 11, 13, 14] and the references therein.

In mathematics, a model of type (1.1) has recently been investigated by T. Funaki [9, 10]. He studies the free motion of a, possibly multi-dimensional, crystal of interacting Brownian particles. In the limit of zero temperature, and under suitable assumptions on U , he shows that if the system is initially rigidly crystallized, then it stays so for macroscopic time, and that the crystal as a whole performs Brownian motion both in the translational and in the rotational degrees of freedom. This is, in some sense, the opposite situation to when the crystal is torn apart by force.

It is clear that in the situation of stretching the chain (1.1) until two particles are more than K apart, we are looking at a first exit problem from a time-dependent domain. Also, although the chain is one-dimensional, the first-exit problem is not, indeed it is $(N - 2)$ -dimensional.

The problem of first-exit from a stationary potential well has been studied in great detail. In [8], the expected exit time from such a well is shown to behave asymptotically like e^{2h/σ^2} , where h is the height of potential well to overcome. This is in agreement with the classical Eyring-Kramers formula [7, 12]. In the multidimensional case, a proof of the expected exit time, with prefactor, has been given only recently [5].

The case of a moving potential well is even more difficult and thus for the time being we settle for a further simplification: we take $N = 3$, and U as a cut-off strictly convex potential. In this case, only x_2 is moving, and so the problem to solve now is the exit of a one-dimensional stochastic process from a time-dependent domain, which still is a rather difficult and interesting topic, and is related to the theory of stochastic resonance [2, 3, 4]. Additionally, while in [2, 3, 4] usually only the exit time distribution is of interest, we will need to know on which side of the domain the exit occurs. This question cannot, to our knowledge, be answered by any previously available results. So we solve it by direct investigation of the SDE, using some of the theory from [1, 2].

Our main result is Theorem 2.1. Roughly speaking, it says that for pulling speed ε and noise level σ both going to zero, the chain will almost surely break on the right hand side if $\varepsilon > \sigma\sqrt{|\ln \sigma|}$, while it will break on either side with probability 1/2 when $\varepsilon < \sigma/\sqrt{|\ln \sigma|}$. This corresponds to the intuition that pulling too fast will just rip off the final particle of the chain, as the noise does not have time to bring the configuration back to an equilibrium. Conversely, pulling very slowly corresponds to an adiabatic situation where the chain is in its local energy minimum all the time and the 1/2 exit probability follows by symmetry. What is surprising is that we obtain this picture with great precision, with both cases separated only by a factor of $|\ln \sigma|$. We do not know what happens in between the two cases specified in Theorem 2.1, although it is likely that the almost-sure law will start to fail before $\sigma = \varepsilon$ due to the fluctuations of Brownian motion. The asymptotic behaviour of the system at this point or, for that matter, at any constellation with $\sigma\sqrt{|\ln \sigma|} \leq \varepsilon \leq \sigma/\sqrt{|\ln \sigma|}$ is an interesting, but probably rather hard, open problem.

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2. THE MODEL AND MAIN RESULT

Three particles x_L , x and x_R in \mathbb{R} interact with each other via a potential, U , of finite range satisfying

(U0) $U \in \mathcal{C}(\mathbb{R})$ with $U(-y) := U(y)$

(U1) $U(y) = 0$ for $|y| \geq b$ and $U \in \mathcal{C}^3((0, b))$

(U2) $b < 2a$, where a is the unique positive number such that $U(a) = \min_{y \geq 0} U(y)$

(U3) There exists $a_0 \in (0, a)$ such that $U''(y) \geq u_0 > 0$ for all $y \in (a_0, b)$

The particle x_L is fixed at the origin and the position of x_R at time $s \geq 0$ is given by $x_R(s) = 2a(1 + \varepsilon s)$, where $\varepsilon > 0$ is a small parameter. We study the behaviour of the middle particle, with position at time s given by x_s . Initially, it has position $x_0 = a$ so that the distance between neighbouring particles is a , which is the energetically-optimal configuration for this potential. The time-dependent potential energy of the particle at position x is given by

$$H(x, \varepsilon s) = U(x) + U(2a(1 + \varepsilon s) - x)$$

which is (1.2) with $N = 3$, $x_1 = x_L = 0$ and $x_3 = x_R = 2a(1 + \varepsilon s)$. The middle particle x moves according to the SDE

$$dx_s = -\frac{\partial H}{\partial x}(x_s, \varepsilon s) ds + \sigma dW_s \quad (2.1)$$

where $x_0 = a$, W_s is a standard Brownian motion and $\sigma > 0$ is the noise intensity. Rescaling time as $t = \varepsilon s$, this is the same in distribution as solving

$$\begin{aligned} dx_t &= -\frac{1}{\varepsilon} \frac{\partial H}{\partial x}(x_t, t) dt + \frac{\sigma}{\sqrt{\varepsilon}} dW_t \\ &= \frac{1}{\varepsilon} (-U'(x_t) + U'(2a(1+t) - x_t)) dt + \frac{\sigma}{\sqrt{\varepsilon}} dW_t \end{aligned} \quad (2.2)$$

This equation is well-defined as long as $2a(1+t) - b < x_t < b$, which is the same condition that ensures the distance between any neighbouring particles is less than b . As soon as this inequality fails, we consider the chain to be broken as there is no longer any interaction between x and one of its neighbours. Let

$$\tau = \inf\{t \geq 0 : x_t \notin (2a(1+t) - b, b)\} \quad (2.3)$$

We say the chain breaks on the left-hand side if $x_\tau = b$ and it breaks on the right-hand side if $x_\tau = 2a(1 + \tau) - b$. The chain necessarily breaks when $t = b/a - 1$, so $\tau \leq b/a - 1$.

Let \mathbb{P} denote the law of the process x_t when started from a at time 0. We also write $f(\sigma) \ll g(\sigma)$ to mean that $f(\sigma)/g(\sigma) \rightarrow 0$ as $\sigma \downarrow 0$.

Theorem 2.1. *Let x_t solve (2.2) and define τ as in (2.3).*

- (1) *(Fast stretching) If $\sigma |\ln \sigma|^{1/2} \ll \varepsilon(\sigma) \ll 1$ then $\mathbb{P}\{x_\tau = b\} \rightarrow 0$ as $\sigma \downarrow 0$.*
- (2) *(Slow stretching) If*

$$\frac{1}{\sigma^{2/3}} \exp\left\{-\frac{1}{\sigma^{2/3}}\right\} \ll \varepsilon(\sigma) \ll \sigma |\ln \sigma|^{-1/2}$$

then $\mathbb{P}\{x_\tau = b\} \rightarrow 1/2$ as $\sigma \downarrow 0$.

- The proof of this theorem will actually yield that when $\sigma |\ln \sigma|^{1/2} \ll \varepsilon(\sigma) \ll 1$, $\mathbb{P}\{x_\tau = b\} < (C\varepsilon/\sigma^2) e^{-c\varepsilon^2/\sigma^2}$.
- The lower bound on ε in (2) arises because our method applies on timescales shorter than that given by the Eyring-Kramers formula (see Introduction), although we expect the result to hold without this lower bound.
- If U is quadratic, then (2) is true without the lower bound on ε . We will comment on this at the end.
- The proof can be extended to the case that the chain is stretched according to some nonlinear function $p(t)$, that is, $x_R(t) = 2a(1 + p(t))$, where $0 < p_0 < p'(t) < p_1$.

- The above bounds on $p(t)$ are critical if we want to define what is fast and slow stretching. As an example of what could go wrong, consider $p(t)$ that is constant after an initial stretch, or even $p \equiv 0$, in which case there is no such thing as fast stretching.

The theorem shows that when the stretching is fast, the chain will almost surely break on the right-hand side as $\sigma \downarrow 0$. This is the same behaviour as in the deterministic case when $\sigma = 0$ (see the following section). However, when the stretching is sufficiently slow, there is an equal probability to break on either side, as when there is no stretching at all.

3. PROOF OF THEOREM 2.1

3.1. Outline. In Section 3.2, we give an alternative formulation of Theorem 2.1 in terms of another stochastic process, leading to the equivalent Theorem 3.1, which will subsequently be proved. In Section 3.3, we isolate the linear part of our new process, bounding the nonlinear part using Proposition 3.2. In Section 3.4, we prove Theorem 3.1 (1). Finally in Section 3.5, we prove Theorem 3.1 (2).

3.2. An alternative formulation. For times $t < \tau$, we can replace U with any potential $\tilde{U} \in \mathcal{C}(\mathbb{R})$ such that $\tilde{U} \in \mathcal{C}^3((0, \infty))$, $\tilde{U}(y) = U(y)$ for $|y| \leq b$, $\tilde{U}(-y) = \tilde{U}(y)$ and $\tilde{U}''(y) \geq u_0 > 0$ for all $|y| > a_0$. Defining $\tilde{H}(x, t) = \tilde{U}(x) + \tilde{U}(2a(1+t) - x)$ we have that for times $t < \tau$, $H(x_t, t) = \tilde{H}(x_t, t)$ and x_t also solves

$$dx_t = -\frac{1}{\varepsilon} \frac{\partial \tilde{H}}{\partial x}(x_t, t) dt + \frac{\sigma}{\sqrt{\varepsilon}} dW_t$$

Let x_t^{det} be the solution of the deterministic equation

$$dx_t^{\text{det}} = -\frac{1}{\varepsilon} \frac{\partial \tilde{H}}{\partial x}(x_t^{\text{det}}, t) dt \quad (3.1)$$

with $x_0^{\text{det}} = a$. This ODE is well-defined as long as $0 < x_t^{\text{det}} < 2a(1+t)$. The deterministic particle, x_t^{det} , will follow the midpoint of the chain, $a(1+t)$, but always lagging behind. In fact, for times $t \gg \varepsilon$, we have by an expansion in ε that its solution can be written as

$$x_t^{\text{det}} = a(1+t) - \frac{a\varepsilon}{2\tilde{U}''(a(1+t))} + \mathcal{O}(\varepsilon^2) \quad (3.2)$$

and so the ODE is well-defined for all $t \in [0, b/a - 1]$. Furthermore, by taking ε sufficiently small we also have in this interval that $a_0 < x_t^{\text{det}} < 2a(1+t) - a_0$, which is useful in view of the strict convexity property of \tilde{U} . If we had used H instead of \tilde{H} in (3.1), then x_t^{det} would not have been defined on the whole interval $[0, b/a - 1]$. Indeed, there is $t < b/a - 1$ such that $2a(1+t) - x_t^{\text{det}} = b$, at which time only \tilde{H} is well-defined.

We can now define the deviation process $y_t := x_t - x_t^{\text{det}}$ on the interval $[0, \tau]$, since $\tau \leq b/a - 1$. This solves, with initial condition $y_0 = 0$,

$$\begin{aligned} dy_t &= \frac{1}{\varepsilon} [-\tilde{U}'(x_t) + \tilde{U}'(x_t^{\text{det}}) + \tilde{U}'(2a(1+t) - x_t) - \tilde{U}'(2a(1+t) - x_t^{\text{det}})] dt + \frac{\sigma}{\sqrt{\varepsilon}} dW_t \\ &= \frac{1}{\varepsilon} [A(t)y_t + B(y_t, t)] dt + \frac{\sigma}{\sqrt{\varepsilon}} dW_t \end{aligned} \quad (3.3)$$

where

$$A(t) = -\tilde{U}''(x_t^{\text{det}}) - \tilde{U}''(2a(1+t) - x_t^{\text{det}})$$

and $B(y, t)$ contains the remainder terms. Furthermore, there is a constant $M > 0$ such that $|B(y, t)| \leq My^2$ for all pairs $(y, t) \in \mathcal{D}$, where \mathcal{D} is given in (3.4). We can also

find constants $A_0, A_1 > 0$ such that $-A_1 \leq A(t) \leq -A_0$ for all $t \in [0, b/a - 1]$. This decomposition into linear and nonlinear parts is standard and also used in [1].

For the chain to be unbroken, y_t must satisfy

$$2a(1+t) - b - x_t^{\det} < y_t < b - x_t^{\det}$$

which we write as

$$d_-(t) < y_t < d_+(t)$$

where, using (3.2), we have for times $t \gg \varepsilon$ that

$$d_+(t) = b - x_t^{\det} = b - a(1+t) + \frac{a\varepsilon}{2\tilde{U}''(a(1+t))} + \mathcal{O}(\varepsilon^2)$$

and

$$d_-(t) = 2a(1+t) - b - x_t^{\det} = a(1+t) - b + \frac{a\varepsilon}{2\tilde{U}''(a(1+t))} + \mathcal{O}(\varepsilon^2)$$

The problem is then to study the first exit of the process y_t from the space-time domain, $\mathcal{D} = \mathcal{D}(\varepsilon)$, given by

$$\mathcal{D} = \{(y, t) : d_-(t) < y < d_+(t), 0 \leq t \leq b/a - 1\} \quad (3.4)$$

The stopping time τ given in (2.3) can be written

$$\tau = \inf\{t \geq 0 : (y_t, t) \notin \mathcal{D}\} \quad (3.5)$$

Then $y_\tau = d_-(\tau)$ corresponds to $x_\tau = 2a(1+\tau) - b$, that is, the chain breaking on the right-hand side. Note that $d_+(t) \geq -d_-(t)$ for all $t \in [0, b/a - 1]$ and so the curve $d_-(t)$ crosses zero before $d_+(t)$. This means that in the deterministic case, when $y_t \equiv 0$, the curve $d_-(t)$ is hit before $d_+(t)$ and the chain breaks on the right-hand side.

We can then state Theorem 2.1 as

Theorem 3.1 (Alternative version of Theorem 2.1). *Let y_t solve (3.3) and define τ as in (3.5).*

- (1) *If $\sigma |\ln \sigma|^{1/2} \ll \varepsilon(\sigma) \ll 1$ then $\mathbb{P}\{y_\tau = d_+(\tau)\} \rightarrow 0$ as $\sigma \downarrow 0$.*
- (2) *If*

$$\frac{1}{\sigma^{2/3}} \exp\left\{-\frac{1}{\sigma^{2/3}}\right\} \ll \varepsilon(\sigma) \ll \sigma |\ln \sigma|^{-1/2}$$

then $\mathbb{P}\{y_\tau = d_+(\tau)\} \rightarrow 1/2$ as $\sigma \downarrow 0$.

Note that $\mathbb{P}(x_0 = a) = 1$ implies $\mathbb{P}(y_0 = 0) = 1$.

3.3. Linearisation of y_t . Solving (3.3), we find that the process y_t is given by

$$\begin{aligned} y_t &= \frac{\sigma}{\sqrt{\varepsilon}} \int_0^t e^{\alpha(t,s)/\varepsilon} dW_s + \frac{1}{\varepsilon} \int_0^t e^{\alpha(t,s)/\varepsilon} B(y_s, s) ds \\ &=: y_t^0 + y_t^1 \end{aligned}$$

where

$$\alpha(t, s) = \int_s^t A(u) du$$

satisfies $-A_1(t-s) \leq \alpha(t, s) \leq -A_0(t-s)$. We will also write $\alpha(t) = \alpha(t, 0)$. The term y_t^0 is Gaussian and so is easier to work with than y_t^1 . As long as y_t is not too large, then

y_t^1 can be bounded using that $|B(y, t)| \leq My^2$. For example, if $\sup_{0 \leq s \leq \tau} |y_s| \leq D$, then for any $t \leq \tau$ we have

$$|y_t^1| \leq \frac{1}{\varepsilon} \int_0^t |B(y_s, s)| e^{\alpha(t,s)/\varepsilon} ds \leq \frac{MD^2}{\varepsilon} \int_0^t e^{-A_0(t-s)/\varepsilon} ds = \frac{MD^2}{A_0} (1 - e^{-A_0 t/\varepsilon}) \quad (3.6)$$

If D is small, then the contribution of y_t^1 will be much less than that of y_t^0 . The following proposition tells us when we have this type of bound.

Proposition 3.2. *Let $D = D(\sigma)$ and $\varepsilon = \varepsilon(\sigma)$ be such that $\sigma \ll D \ll 1$ and*

$$\frac{D^2}{\sigma^2} \exp \left\{ -\frac{D^2}{\sigma^2} \right\} \ll \varepsilon \ll 1$$

Then

$$\lim_{\sigma \downarrow 0} \mathbb{P} \left\{ \sup_{0 \leq t \leq \tau} |y_t| \geq D \right\} = 0$$

Remark 1. *The lower bound on ε is related to the fact that we cannot bound y_t on timescales larger than given by the Eyring-Kramers formula. An excursion of size D corresponds to climbing a potential height of $\mathcal{O}(D^2)$, which we expect to occur after a time of order $e^{\mathcal{O}(D^2)/\sigma^2}$.*

To prove this proposition, we will use a lemma which says roughly that the Gaussian term y_t^0 stays with high probability in a corridor of width proportional to its variance. More precisely, the variance of y_t^0 is given by

$$\text{Var}(y_t^0) = \frac{\sigma^2}{\varepsilon} \int_0^t e^{2\alpha(t,s)/\varepsilon} ds = \sigma^2 v(t)$$

where $v(t)$ is a solution of $\varepsilon \dot{v} = 2A(t)v + 1$ with $v(0) = 0$. Following [1], we see that since the right-hand side of this ODE vanishes for $v = -1/(2A(t))$, we can find a particular solution of the form

$$\xi(t) = -\frac{1}{2A(t)} + \mathcal{O}(\varepsilon) \quad (3.7)$$

where the $\mathcal{O}(\varepsilon)$ term is uniform in t . So there are constants $0 < \xi_- < \xi_+$ such that for ε sufficiently small, $\xi_- \leq \xi(t) \leq \xi_+$ for all $t \in [0, b/a - 1]$. The function $\xi(t)$ satisfies $|\xi(t) - v(t)| \leq C e^{2\alpha(t)/\varepsilon}$ and will be used in the following lemma. The advantage of $\xi(t)$ over $v(t)$ is that it is bounded away from zero. The following lemma shows how paths of y_t^0 are concentrated.

Lemma 3.3 (Berglund, Gentz [1, 2]). *If $H^2 > 2\sigma^2$ then for any $t \in [0, b/a - 1]$, we have*

$$\mathbb{P} \left\{ \sup_{0 \leq s \leq t} \frac{|y_s^0|}{\sqrt{\xi(s)}} \geq H \right\} = C_{H/\sigma}(t, \varepsilon) e^{-H^2/2\sigma^2} \quad (3.8)$$

with

$$C_{H/\sigma}(t, \varepsilon) \leq 2e \left[\frac{|\alpha(t)|}{\varepsilon} \frac{H^2}{\sigma^2} [1 + \mathcal{O}(\varepsilon)] \right]$$

Remark 2. *In order to get a meaningful bound in (3.8), we need H to satisfy $\sigma \ll H$, which is exactly what we assumed for D in Proposition 3.2. Below, we will use Lemma 3.3 with $H = D/\sqrt{\xi_+} + \mathcal{O}(D^2)$.*

This lemma is proved by partitioning the interval $[0, t]$ and applying on each subinterval the inequality

$$\mathbb{P} \left\{ \sup_{0 \leq s \leq t} \left| \int_0^s \varphi(u) dW_u \right| \geq \delta \right\} \leq 2 \exp \left\{ -\frac{\delta^2}{2 \int_0^t \varphi(u)^2 du} \right\}$$

which is valid for deterministic Borel-measurable functions $\varphi : [0, t] \rightarrow \mathbb{R}$.

Proof of Proposition 3.2. Consider the stopping time given by

$$\tau(h) = \inf\{t \geq 0 : |y_t| \geq h\sqrt{\xi(t)}\}$$

where $\xi(t)$ is given in (3.7). If we can find h such that $h\sqrt{\xi(t)} \leq D$ for all $t \in [0, b/a - 1]$ then

$$\begin{aligned} \mathbb{P} \left\{ \sup_{0 \leq t \leq \tau} |y_t| \geq D \right\} &\leq \mathbb{P} \{ \tau(h) < \tau \} \\ &= \mathbb{P} \left\{ \sup_{0 \leq t \leq \tau \wedge \tau(h)} \frac{|y_t|}{\sqrt{\xi(t)}} \geq h \right\} \end{aligned}$$

As was noted above, $\xi(t) \leq \xi_+$ and so choosing $h = D/\sqrt{\xi_+}$ gives $h\sqrt{\xi(t)} \leq D$. For $0 \leq t \leq \tau \wedge \tau(h)$, we have $|y_t| \leq D$ and so $|y_t^0| \leq MD^2/A_0$. Therefore, since $\tau \leq b/a - 1$,

$$\sup_{0 \leq t \leq \tau \wedge \tau(h)} \frac{|y_t|}{\sqrt{\xi(t)}} \leq \sup_{0 \leq t \leq b/a-1} \frac{|y_t^0|}{\sqrt{\xi(t)}} + \frac{MD^2}{A_0\sqrt{\xi_-}}$$

and we have

$$\begin{aligned} \mathbb{P} \left\{ \sup_{0 \leq t \leq \tau \wedge \tau(h)} \frac{|y_t|}{\sqrt{\xi(t)}} \geq \frac{D}{\sqrt{\xi_+}} \right\} \\ \leq \mathbb{P} \left\{ \sup_{0 \leq t \leq b/a-1} \frac{|y_t^0|}{\sqrt{\xi(t)}} \geq D \left(\frac{1}{\sqrt{\xi_+}} - \frac{MD}{A_0\sqrt{\xi_-}} \right) \right\} \end{aligned}$$

We can apply Lemma 3.3 with $H = D(1/\sqrt{\xi_+} - MD/(A_0\sqrt{\xi_-})) = D(1/\sqrt{\xi_+} + \mathcal{O}(D))$:

$$\begin{aligned} \mathbb{P} \left\{ \sup_{0 \leq t \leq b/a-1} \frac{|y_t^0|}{\sqrt{\xi(t)}} \geq D \left(\frac{1}{\sqrt{\xi_+}} - \frac{MD}{A_0\sqrt{\xi_-}} \right) \right\} \\ \leq 2e \left[C_1 \frac{D^2}{\varepsilon\sigma^2} (1 + \mathcal{O}(D + \varepsilon)) \right] \exp \left\{ -C_2 \frac{D^2}{\sigma^2} (1 + \mathcal{O}(D)) \right\} \end{aligned}$$

for constants $C_1, C_2 > 0$, from which the result follows. \square

3.4. Fast stretching. In this case, we show that the chain is stretched so fast that the process y_t is almost surely never greater than $d_+(b/a - 1)$ in absolute value. Note that the curve $d_+(t)$ is decreasing: its derivative is given by

$$d_+'(t) = -\frac{d}{dt} x_t^{\det} = \tilde{U}'(x_t^{\det}) - \tilde{U}'(2a(1+t) - x_t^{\det})$$

and the right-hand side is negative. This is because $\tilde{U}''(y) \geq u_0 > 0$ for $|y| > a_0$ and $a_0 < x_t^{\det} < 2a(1+t) - x_t^{\det}$ for $t > 0$, which can be seen from (3.2). Since the curve $d_+(t)$ is decreasing, this means that it cannot have ever been hit by the process y_t and so the chain must have broken on the right-hand side (Fig 1). This is contained in the following proposition.

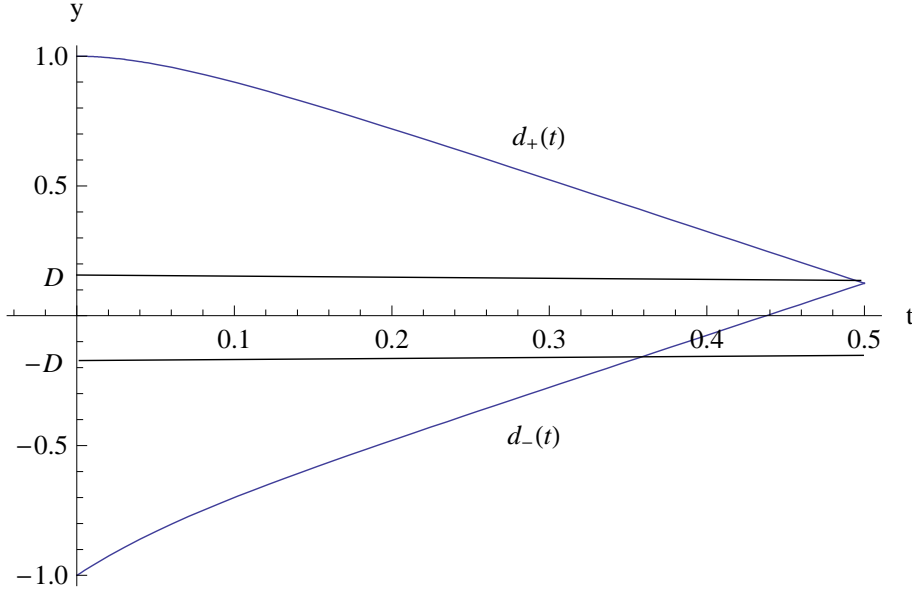


Figure 1: When the chain is pulled sufficiently fast, the process y_t is unlikely to leave the corridor of width $D = d_+(b/a - 1)$, so must hit $d_-(t)$ first (shown here for $U(y) = y^2 - 4y + 3$ and $\varepsilon = 0.25$).

Proposition 3.4. *Let $\sigma |\ln \sigma|^{1/2} \ll \varepsilon(\sigma) \ll 1$. Then*

$$\lim_{\sigma \downarrow 0} \mathbb{P} \left\{ \sup_{0 \leq t \leq \tau} |y_t| \geq d_+(b/a - 1) \right\} = 0$$

Proof. Apply Proposition 3.2 with $D = d_+(b/a - 1) = a\varepsilon / (2\tilde{U}''(b/a - 1)) + \mathcal{O}(\varepsilon^2)$. \square

3.5. Slow stretching. The strategy is as follows. Suppose we are given D such that

$$\lim_{\sigma \downarrow 0} \mathbb{P} \left\{ \sup_{0 \leq t \leq \tau} |y_t| \geq D \right\} = 0$$

Then we can assume that $|y_t^1| \leq MD^2/A_0$ for all $t < \tau$, since all other cases have zero probability in the limit. To simplify notation, we will write this last inequality as $|y_t^1| \leq D^2$. For all $t < \tau$ we may then assume

$$y_t^0 - D^2 \leq y_t \leq y_t^0 + D^2 \tag{3.9}$$

Let \mathbb{Q}^{t_0, y_0} denote the law of y_t^0 when started from y_0 at time t_0 . Then by (3.9),

$$P_L \leq \{y_\tau = d_+(\tau)\} \leq P_U$$

where

$$P_L = P_L(D) = \mathbb{Q}^{0,0} \{y_t^0 - D^2 \text{ hits } d_+(t) \text{ before } d_-(t)\}$$

and

$$P_U = P_U(D) = \mathbb{Q}^{0,0} \{y_t^0 + D^2 \text{ hits } d_+(t) \text{ before } d_-(t)\}$$

The aim of this section is to show that given $\varepsilon(\sigma)$, we can pick $D(\sigma)$ such that P_L and P_U tend to $1/2$, which gives the result. The proof of each limit is similar, so we will show

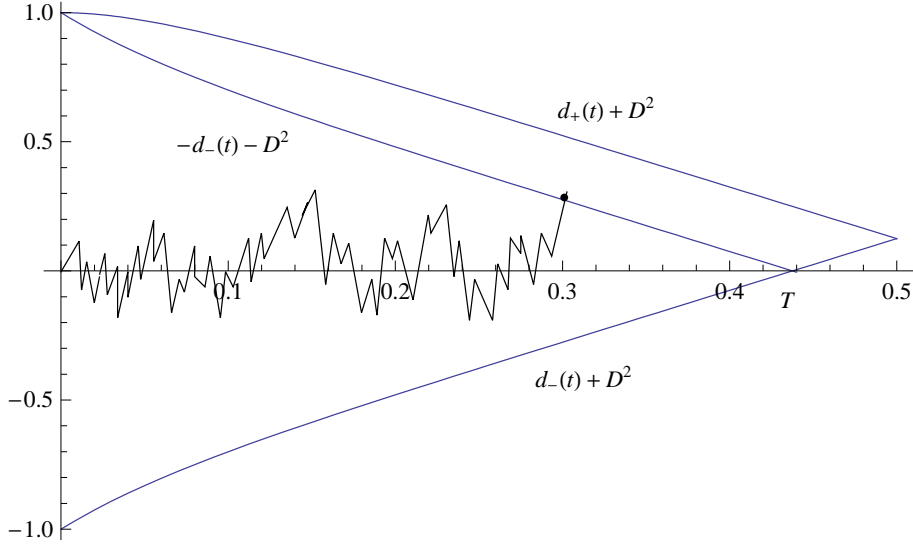


Figure 2: When the chain is stretched slowly, we show that conditional probability of hitting the curve $d_+(t) + D^2$ before $d_-(t) + D^2$, when started from $-d_-(t) - D^2$, goes to one as $\sigma \downarrow 0$.

the details for P_L only. Note that P_L can be written

$$P_L = \mathbb{Q}^{0,0}\{y_t^0 \text{ hits } d_+(t) + D^2 \text{ before } d_-(t) + D^2\}$$

Define the stopping time

$$\tau_L = \tau_L(D) = \inf\{t \geq 0 : |y_t^0| \geq -d_-(t) - D^2\}$$

and note that $\tau_L \leq T$, where $T = \inf\{t \geq 0 : -d_-(t) - D^2 = 0\}$. By symmetry,

$$\mathbb{Q}^{0,0}\{y_{\tau_L}^0 = -d_-(\tau_L) - D^2\} = \mathbb{Q}^{0,0}\{y_{\tau_L}^0 = d_-(\tau_L) + D^2\} = \frac{1}{2}$$

We must show that if $y_{\tau_L}^0 = -d_-(\tau_L) - D^2$ then almost surely y_t^0 hits $d_+(t) + D^2$ soon after as $\sigma \downarrow 0$ (see Fig 2).

In the following two lemmas, we establish upper and lower bounds for τ_L . The upper bound is needed in order that y_t^0 , when started from $-d_-(t) - D^2$, is much closer to $d_+(t) + D^2$ than to $d_-(t) + D^2$. If τ_L is too close to T then this is not the case and y_t^0 is more likely to exit in the “wrong direction”. The lower bound is required since we cannot expect the conditional probability of hitting $d_+(t) + D^2$, when started from $-d_-(t) - D^2$, to be close to one if it is unlikely that y_t^0 has even reached $-d_-(t) - D^2$.

Lemma 3.5. *Let $\varepsilon = \varepsilon(\sigma)$, $f = f(\sigma)$ and $D = D(\sigma)$ be such that $\varepsilon \ll \sigma$, $f(\sigma) \ll 1$ and $D^2 \ll \sigma$. Then*

$$\lim_{\sigma \downarrow 0} \mathbb{Q}^{0,0} \left\{ \tau_L \leq \frac{b}{a} - 1 - \frac{\sigma f(\sigma)}{a} \right\} = 1$$

Proof. To prove this upper bound for τ_L , we use a simple fixed-time estimate. Let $t = b/a - 1 - \sigma f(\sigma)/a$. If f is such that $t \geq T$, then the upper bound is trivial. Otherwise

$$\begin{aligned} \mathbb{Q}^{0,0}\{\tau_L \leq t\} &\geq \mathbb{Q}^{0,0}\{|y_t^0| \geq -d_-(t) - D^2\} \\ &= \frac{2}{\sqrt{2\pi\text{Var}(y_t^0)}} \int_{-d_-(t)-D^2}^{\infty} \exp\left\{-\frac{x^2}{2\text{Var}(y_t^0)}\right\} dx \\ &= \frac{2}{\sqrt{\pi}} \int_{(-d_-(t)-D^2)/\sqrt{2\text{Var}(y_t^0)}}^{\infty} e^{-z^2} dz \end{aligned}$$

where

$$\frac{-d_-(t) - D^2}{\sqrt{2\text{Var}(y_t^0)}} \leq \frac{f(\sigma) - D^2/\sigma + \mathcal{O}(\varepsilon/\sigma)}{\sqrt{1/A_1 + \mathcal{O}(\varepsilon^n)}}, \quad n \geq 1$$

This last inequality follows since $\text{Var}(y_t^0) \geq \sigma^2(1 - e^{2A_1 t/\varepsilon})/A_1$. The right-hand side goes to zero as $\sigma \downarrow 0$. \square

Lemma 3.6. *Let $f = f(\sigma)$, $\varepsilon = \varepsilon(\sigma)$ and $D = D(\sigma)$ be such that $1 \ll f(\sigma) \ll 1/\sigma$,*

$$f(\sigma)^2 \exp\{-f(\sigma)^2\} \ll \varepsilon \ll \sigma \quad (3.10)$$

and $D^2 \ll \sigma$. Then we have

$$\lim_{\sigma \downarrow 0} \mathbb{Q}^{0,0} \left\{ \tau_L \geq \frac{b}{a} - 1 - \frac{\sigma f(\sigma)}{a} \right\} = 1$$

Proof. We will use Lemma 3.3. First note that there is $c_1 > 0$ such that for $\varepsilon(\sigma)$ sufficiently small,

$$-d_-(t) \geq b - a(1+t) - c_1\varepsilon$$

holds for all t . Putting $t_1 = b/a - 1 - \sigma f(\sigma)/a$, we get

$$\inf_{0 \leq t \leq t_1} (-d_-(t)) \geq \sigma f(\sigma) - c_1\varepsilon$$

Now put $H = (\sigma f(\sigma) - c_1\varepsilon - D^2)/\sqrt{\xi_+} > 0$. Then

$$H\sqrt{\xi(t)} \leq H\sqrt{\xi_+} = \sigma f(\sigma) - c_1\varepsilon - D^2 \leq \inf_{0 \leq t \leq t_1} (-d_-(t) - D^2)$$

Therefore,

$$\begin{aligned} \mathbb{Q}^{0,0}\{\tau_L < t_1\} &\leq \mathbb{Q}^{0,0} \left\{ \sup_{0 \leq t \leq t_1} \frac{|y_t^0|}{\sqrt{\xi(t)}} \geq \inf_{0 \leq t \leq t_1} \frac{-d_-(t) - D^2}{\sqrt{\xi(t)}} \right\} \\ &\leq \mathbb{Q}^{0,0} \left\{ \sup_{0 \leq t \leq t_1} \frac{|y_t^0|}{\sqrt{\xi(t)}} \geq H \right\} \end{aligned}$$

Now we apply Lemma 3.3 to show that the right-hand side of this inequality tends to 0 as $\sigma \downarrow 0$, which gives the result. \square

Suppose that there is $f_+(\sigma)$ satisfying $1 \ll f_+(\sigma) \ll \min(\sigma/D^2, \sigma/\varepsilon)$. Then we can apply Lemmas 3.5 and 3.6 to $1/f_+(\sigma)$ and $f_+(\sigma)$, respectively. This tells us that

$$\lim_{\sigma \downarrow 0} \mathbb{Q}^{0,0} \left\{ \frac{b}{a} - 1 - \frac{\sigma f_+(\sigma)}{a} \leq \tau_L \leq \frac{b}{a} - 1 - \frac{\sigma}{a f_+(\sigma)} \right\} = 1 \quad (3.11)$$

The next proposition has three parts. Together, they show that if y_t^0 starts from $-d_-(t) - D^2$ for suitable times t^* as given in (3.11), then it hits $d_+(t) + D^2$ in a small interval $[t^*, t^* + \Delta]$ afterwards and does not hit the lower curve $d_-(t) + D^2$ in this time.

Recall that $T = \inf\{t \geq 0 : -d_-(t) - D^2 = 0\}$ is an upper bound for τ_L .

Proposition 3.7. *Let $f_+ = f_+(\sigma)$, $\Delta = \Delta(\sigma)$, $\varepsilon = \varepsilon(\sigma)$ and $D = D(\sigma)$ be chosen so that*

$$1 \ll f_+(\sigma) \ll \sqrt{\varepsilon/\Delta} \ll \min(\sigma/D^2, \sigma/\varepsilon) \ll 1/\sigma \quad (3.12)$$

Then for every f such that $1/f_+(\sigma) \leq f(\sigma) \leq f_+(\sigma)$ and $t^ := b/a - 1 - \sigma f(\sigma)/a$, we have*

- (1) $[t^*, t^* + \Delta] \subset [0, T]$ for σ sufficiently small.
- (2) $\lim_{\sigma \downarrow 0} \mathbb{Q}^{t^*, -d_-(t^*) - D^2} \{y_t^0 \geq d_+(t) + D^2 \text{ for some } t \in [t^*, t^* + \Delta]\} = 1$
- (3) $\lim_{\sigma \downarrow 0} \mathbb{Q}^{t^*, -d_-(t^*) - D^2} \left\{ \inf_{t^* \leq t \leq t^* + \Delta} y_t^0 < 0 \right\} = 0$

Remark 3. *Note that (1) and (3) together guarantee that y_t^0 does not hit $d_-(t) + D^2$ in the interval $[t^*, t^* + \Delta]$.*

Proof. (1) Since $f(\sigma) \leq f_+(\sigma) \ll 1/\sigma$, we have $t^* > 0$. As in the proof of Lemma 3.6, for sufficiently small ε we have the uniform bound

$$-d_-(t) - D^2 \geq b - a(1+t) - c_1\varepsilon - D^2$$

If $t < b/a - 1 - (c_1\varepsilon + D^2)/a$ then the right-hand side is positive and $t < T$. Note that

$$\begin{aligned} t^* + \Delta &= \frac{b}{a} - 1 - \frac{\sigma f(\sigma)}{a} + \Delta \\ &= \frac{b}{a} - 1 - \frac{\sigma f(\sigma) - a\Delta}{a} \end{aligned}$$

If $\sigma f(\sigma) - a\Delta > c_1\varepsilon + D^2$ for sufficiently small σ then $t^* + \Delta < T$. Since $\Delta \ll \varepsilon$ and $f_+(\sigma) \ll \min(\sigma/D^2, \sigma/\varepsilon)$, which follow from (3.12), and since $f(\sigma) \geq 1/f_+(\sigma)$, this is indeed satisfied.

(2) We show that y_t^0 hits $d_+(t) + D^2$ in the interval $[t^*, t^* + \Delta]$, which is the same as the process $e^{-\alpha(t)/\varepsilon} y_t^0$ hitting the curve $e^{-\alpha(t)/\varepsilon} (d_+(t) + D^2)$. The latter will be more convenient to show, since it will lead to a probability involving a Gaussian martingale, for which the reflection principle can be applied. The process y_t^0 , when started from $-d_-(t^*) - D^2$ at time t^* , is given by

$$y_t^0 = -e^{\alpha(t, t^*)/\varepsilon} (d_-(t^*) + D^2) + \frac{\sigma}{\sqrt{\varepsilon}} \int_{t^*}^t e^{\alpha(t, s)/\varepsilon} dW_s \quad (3.13)$$

from which we deduce that

$$\begin{aligned} e^{-\alpha(t)/\varepsilon} y_t^0 &= -e^{-\alpha(t^*)/\varepsilon} (d_-(t^*) + D^2) + \frac{\sigma}{\sqrt{\varepsilon}} \int_{t^*}^t e^{-\alpha(s)/\varepsilon} dW_s \\ &=: -e^{-\alpha(t^*)/\varepsilon} (d_-(t^*) + D^2) + z_t^0 \end{aligned} \quad (3.14)$$

For all $t \in [t^*, t^* + \Delta]$, we have

$$e^{-\alpha(t)/\varepsilon} (d_+(t) + D^2) \leq e^{-\alpha(t^* + \Delta)/\varepsilon} (d_+(t^*) + D^2)$$

Define $h(t^*, \Delta) := e^{-\alpha(t^* + \Delta)/\varepsilon} (d_+(t^*) + D^2) + e^{-\alpha(t^*)/\varepsilon} (d_-(t^*) + D^2)$ and note that it is positive. Then if

$$\sup_{t^* \leq t \leq t^* + \Delta} z_t^0 \geq h(t^*, \Delta)$$

we must have that $z_t^0 \geq e^{-\alpha(t)/\varepsilon} (d_+(t) + D^2) + e^{-\alpha(t^*)/\varepsilon} (d_-(t^*) + D^2)$ for some $t \in [t^*, t^* + \Delta]$, which is equivalent to $y_t^0 \geq d_+(t) + D^2$. By the reflection principle applied to z_t^0 , we have

$$\begin{aligned} \mathbb{Q}^{t^*, -d_-(t^*) - D^2} \left\{ \sup_{t^* \leq t \leq t^* + \Delta} z_t^0 \geq h(t^*, \Delta) \right\} &= 2\mathbb{Q}^{t^*, -d_-(t^*) - D^2} \{z_{t^* + \Delta}^0 \geq h(t^*, \Delta)\} \\ &= \frac{2}{\sqrt{\pi}} \int_L^\infty e^{-z^2} dz \end{aligned}$$

where $L = h(t^*, \Delta) / \sqrt{2\text{Var}(z_{t^* + \Delta}^0)}$. If we can show that $L \rightarrow 0$ as $\sigma \downarrow 0$, then we will be done. We have

$$0 \leq \frac{h(t^*, \Delta)}{\sqrt{2\text{Var}(z_{t^* + \Delta}^0)}} = \frac{e^{-\alpha(t^* + \Delta, t^*)/\varepsilon} (d_+(t^*) + D^2) + d_-(t^*) + D^2}{\sqrt{2e^{2\alpha(t^*)/\varepsilon} \text{Var}(z_{t^* + \Delta}^0)}} \quad (3.15)$$

where

$$2e^{2\alpha(t^*)/\varepsilon} \text{Var}(z_{t^* + \Delta}^0) = \frac{2\sigma^2}{\varepsilon} \int_{t^*}^{t^* + \Delta} e^{-2\alpha(s, t^*)/\varepsilon} ds \geq \frac{\sigma^2}{A_0} (e^{2A_0\Delta/\varepsilon} - 1)$$

which means that

$$\frac{e^{-\alpha(t^* + \Delta, t^*)/\varepsilon} (d_+(t^*) + D^2) + d_-(t^*) + D^2}{\sqrt{2e^{2\alpha(t^*)/\varepsilon} \text{Var}(z_{t^* + \Delta}^0)}} \leq \frac{e^{A_1\Delta/\varepsilon} (d_+(t^*) + D^2) + d_-(t^*) + D^2}{\sigma \sqrt{(e^{2A_0\Delta/\varepsilon} - 1)/A_0}}$$

Using Taylor expansions for the exponential terms, we see from (3.12) that the right-hand side tends to zero as $\sigma \downarrow 0$.

(3) Since the distribution of y_t^0 , when started at 0, is symmetric about $y = 0$, y_t^0 satisfies a reflection principle about this line (see Appendix of [1]) and we have

$$\mathbb{Q}^{t^*, -d_-(t^*) - D^2} \left\{ \inf_{t^* \leq t \leq t^* + \Delta} y_t^0 < 0 \right\} = 2\mathbb{Q}^{t^*, -d_-(t^*) - D^2} \{y_{t^* + \Delta}^0 < 0\} \quad (3.16)$$

where we recall from (3.13) that the conditional process is given by

$$y_t^0 = -e^{\alpha(t, t^*)/\varepsilon} (d_-(t^*) + D^2) + \frac{\sigma}{\sqrt{\varepsilon}} \int_{t^*}^t e^{\alpha(t, s)/\varepsilon} dW_s$$

Therefore,

$$2\mathbb{Q}^{t^*, -d_-(t^*) - D^2} \{y_{t^* + \Delta}^0 \leq 0\} = \frac{2}{\sqrt{\pi}} \int_{-\infty}^U e^{-z^2} dz$$

where

$$U = \frac{e^{\alpha(t^* + \Delta, t^*)/\varepsilon} (d_-(t^*) + D^2)}{\sqrt{2\text{Var}(y_{t^* + \Delta}^0)}} \leq \frac{d_-(t^*) - D^2}{\sigma \sqrt{(e^{2A_1\Delta/\varepsilon} - 1)/A_1}}$$

Note that U is negative, since $t^* < T$, and this inequality comes from the bound

$$2e^{-2\alpha(t^* + \Delta, t^*)/\varepsilon} \text{Var}(y_{t^* + \Delta}^0) \leq \sigma^2 (e^{2A_1\Delta/\varepsilon} - 1)/A_1$$

Again using Taylor expansions and (3.12), we see that the upper bound for U goes to $-\infty$ as $\sigma \downarrow 0$. \square

Now we are ready to complete the proof of Theorem 3.1 (2). First we suppose that $\sigma^2 |\ln \sigma| \ll \varepsilon \ll \sigma |\ln \sigma|^{-1/2}$. Then we can pick D such that $\sigma^2 |\ln \sigma| \ll D^2 \ll \varepsilon$ and it follows that

$$\frac{D^2}{\sigma^2} \exp \left\{ -\frac{D^2}{\sigma^2} \right\} \ll \varepsilon$$

This means we can apply Proposition 3.2 to show $|y_t|$ remains bounded by D almost surely as $\sigma \downarrow 0$. By the upper bound on ε , we can then choose f_+ such that $|\ln \sigma|^{1/2} \ll f_+(\sigma) \ll \sigma/\varepsilon$, in which case

$$f_+(\sigma)^2 \exp \{ -f_+(\sigma)^2 \} \ll \varepsilon$$

Now we apply Lemmas 3.5 and 3.6 to $1/f_+$ and f_+ , respectively, to show that we only need to consider hitting times of $-d_-(t) - D^2$ of the form $t^* = b/a - 1 - \sigma f(\sigma)/a$, where $1/f_+(\sigma) \leq f(\sigma) \leq f_+(\sigma)$. Then we can find $\Delta(\sigma)$ such that

$$1 \ll f_+(\sigma) \ll \sqrt{\varepsilon/\Delta} \ll \sigma/\varepsilon$$

and since $\sigma/\varepsilon = \min(\sigma/D^2, \sigma/\varepsilon)$, this is precisely (3.12) so we can apply Proposition 3.7 to show that the conditional probability of hitting $d_+(t) + D^2$ before $d_-(t) + D^2$ goes to one.

Now suppose that

$$\frac{1}{\sigma^{2/3}} \exp \left\{ -\frac{1}{\sigma^{2/3}} \right\} \ll \varepsilon \leq C \sigma^2 |\ln \sigma|$$

where $C > 0$ is some constant. Pick D such that both $\sigma^2 |\ln \sigma| \ll D^2 \ll \sigma^{4/3}$ and

$$\frac{1}{\sigma^{2/3}} \exp \left\{ -\frac{1}{\sigma^{2/3}} \right\} \ll \frac{D^2}{\sigma^2} \exp \left\{ -\frac{D^2}{\sigma^2} \right\} \ll \varepsilon \quad (3.17)$$

hold. We can apply Proposition 3.2 to bound $|y_t|$ by this choice of D . Letting $f_+(\sigma) = D/\sigma$, we can, by (3.17), apply Lemmas 3.5 and 3.6 to $1/f_+$ and f_+ , respectively. Then, since $D^2 \ll \sigma^{4/3}$, we can find $\Delta(\sigma)$ such that

$$1 \ll f_+(\sigma) = D/\sigma \ll \sqrt{\varepsilon/\Delta} \ll \sigma/D^2$$

where now $\sigma/D^2 = \min(\sigma/D^2, \sigma/\varepsilon)$. Then Proposition 3.7 holds and we are done.

We end this paper by commenting on the case of a quadratic potential U , where Theorem 3.1 (2) holds for all ε such that $\varepsilon \ll \sigma |\ln \sigma|^{-1/2}$. For such potentials, there is no nonlinear term, y_t^1 , and $D \equiv 0$. We just have to show that y_t^0 has probability 1/2 to hit $d_+(t)$ before $d_-(t)$. For this we consider the conditional probability to hit $d_+(t)$ when starting from $-d_-(t)$. If we define the analogue of τ_L as $\tilde{\tau}_L = \inf\{t \geq 0 : |y_t^0| \geq -d_-(t)\}$ then when $\varepsilon \ll \sigma^2$ we can show this conditional probability goes to one with only an upper bound for $\tilde{\tau}_L$. Since we do not need to bound $|y_t^0|$, no lower bound on ε is required. For $\sigma^2 \ll \varepsilon \ll \sigma |\ln \sigma|^{-1/2}$, a lower bound on $\tilde{\tau}_L$ is needed to show the conditional probability goes to one, but this holds for such ε without additional assumptions.

REFERENCES

- [1] N. Berglund, B. Gentz: *Noise-induced Phenomena in Slow-Fast Dynamical Systems: A Sample-Paths Approach*, Springer (2006)
- [2] N. Berglund, B. Gentz: *Pathwise description of dynamic pitchfork bifurcations with additive noise*, Probab. Theory Relat. Fields **122**, No. 3, 341-388 (2002)
- [3] N. Berglund, B. Gentz: *Beyond the Fokker-Planck equation: pathwise control of noisy bistable systems*, J. Phys. A: Math. Gen. **35**, 2057-2091 (2002)
- [4] N. Berglund, B. Gentz: *A sample-paths approach to noise-induced synchronization: stochastic resonance in a double-well potential*, Ann. Appl. Probab. **12**, 1419-1470 (2002)

- [5] A. Bovier, M. Eckhoff, V. Gaynard, M. Klein: *Metastability in reversible diffusion processes I. Sharp asymptotics for capacities and exit times*, J. Eur Math. Soc. **6**, 399-424 (2004)
- [6] Donald L. Ermark and J.A. McCammon: *Brownian dynamics with hydrodynamic interactions* J. Chem. Phys. **69**, 1352 (1978)
- [7] H. Eyring: *The activated complex in chemical reactions*, J. Chem. Phys. **3**, 107-115 (1935)
- [8] M. Freidlin, A. Wentzell: *Random Perturbations of Dynamical Systems*, Springer-Verlag (1984)
- [9] T. Funaki: *Zero Temperature Limit for Interacting Brownian Particles. I. Motion of a Single Body*, Ann. Probab. **32**, 1201-1227 (2004)
- [10] T. Funaki: *Zero Temperature Limit for Interacting Brownian Particles. II. Coagulation in One Dimension*, Ann. Probab. **32**, 1228-1246 (2004)
- [11] W. F. van Gunsteren, H. J. C. Berendsen: *Algorithms for brownian dynamics*, Molecular Physics **45**, 637-647 (1982)
- [12] H. A. Kramers: *Brownian motion in a field of force and the diffusion model of chemical reactions*, Physica **7**, 284-304 (1940)
- [13] Juan J. de Pablo, Fernando A. Escobedo: *Molecular simulations in chemical engineering: Present and future* AIChE Journal **48**, 2716-2721 (2002)
- [14] N. Wagner, B. Holian and A.F. Voter: *Molecular-dynamics simulations of two-dimensional materials at high strain rates*, Phys. Rev. A **45**, 8457 - 8470 (1992)

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