Breaking the chain and the effect of mass

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Outline of talk

1. Physical motivation.
2. Recap of previous results.
3. Potentials undergoing a bifurcation.
4. The case with mass.

Background

Dynamic force spectroscopy

- The idea is to stretch a molecular bond and see how much force is required for it to break.
- Experiment repeated many times to give a distribution of break forces.
- This can give information about the bond strength and internal dynamics of the molecule, but data needs to be interpreted.
- Theoretical approach is needed.

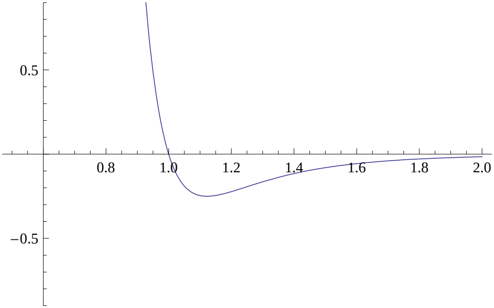
Bond rupture may be viewed as a thermally activated escape from a potential well.

Bond length y_s typically modelled by an SDE of the form

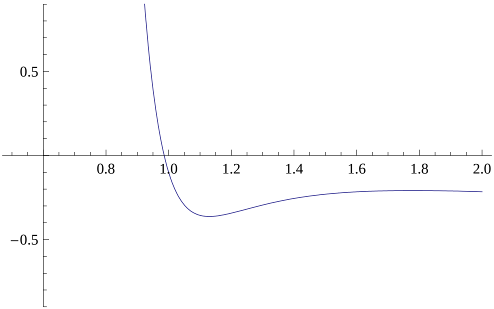
$$\mathrm{d}y_s = (-U'(y_s) + Vs)\mathrm{d}s + \sigma \mathrm{d}W_s, \qquad y_0 = a$$

where a is the minimum of potential U, $\sigma > 0$ the noise intensity and V the loading rate.

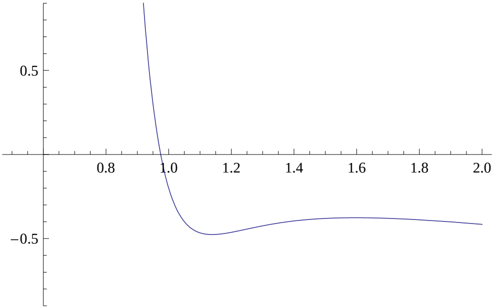
e.g. U is Lennard-Jones potential. At $s = 0$



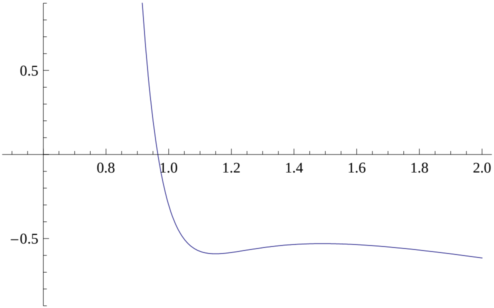
$Vs = 0.1$



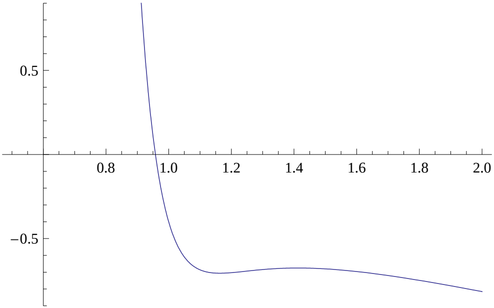
$Vs = 0.2$



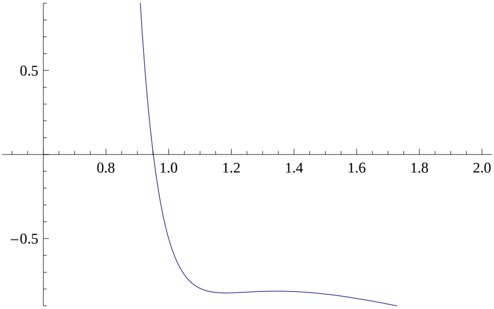
$Vs = 0.3$



$Vs = 0.4$



$Vs = 0.5$



Recall: in the absence of external force, expected time of escape from a potential well given by Eyring-Kramers formula (c.f. Bovier et al, 2004)

$$\mathbb{E}(\tau_{\text{escape}}) \simeq \frac{2\pi}{\sqrt{U''(x)|U''(z)|}} \mathrm{e}^{2(U(z)-U(x))/\sigma^2}$$

Adiabatic approximation assumed: speed of stretching much slower than relaxation time of molecules...

...Eyring-Kramers formula gives instantaneous rate of escape $k(t)$ at time t.

$$\frac{\mathrm{d}}{\mathrm{d}s}P(s) = -k(s)P(s)$$

where $P(s)$ is bond survival probability up to time s.

- For very slow stretching, there is enough time for thermal fluctuations to act at smaller forces. Rupture force scales like $\ln V$.
- For faster stretching, break occurs when potential barrier very low. Rupture force scales like $(\ln V)^{2/3}$

A model of two breakable bonds

Let $\mathbf{x}(s) = (0, x_s, 2a(1+\varepsilon s)) \in \mathbb{R}^3$ denote the positions of three particles.

Only the middle particle is free. It satisfies:

$$\mathrm{d}x_s = -\frac{\partial H}{\partial x}(x_s, \varepsilon s)\mathrm{d}s + \sigma \mathrm{d}W_s$$

with initial condition $x_0 = a$ and time-dependent potential energy given by

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

where U is a pair potential.

Main properties of U:

- U has a unique minimum at $a > 0$
- U has finite range $b > 0$
- $b < 2a$

We will let $\varepsilon = \varepsilon(\sigma)$ and consider behaviour as $\sigma \downarrow 0$.

We rescale time as $t = \varepsilon s$, so that $\mathbf{x}(t) = (0, x_t, 2a(1+t))$ and x_t solves

$$\mathrm{d}x_t = -\frac{1}{\varepsilon}\frac{\partial H}{\partial x}(x_t, t)\mathrm{d}t + \frac{\sigma}{\sqrt{\varepsilon}}\mathrm{d}W_t$$

The chain breaks when its configuration changes from the starting potential minimum to another.

After this, the middle particle only interacts with one of its neighbours.

The chain breaks on the left- or right-hand side if the middle particle no longer interacts with its neighbour on that respective side.

Previous results

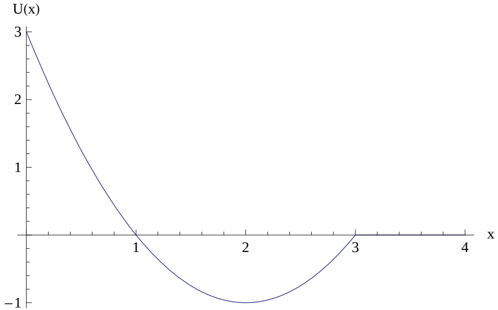
Recall that our potential U has unique minimum at $a > 0$ and finite range $b > 0$, where $b < 2a$. In addition, we will assume:

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

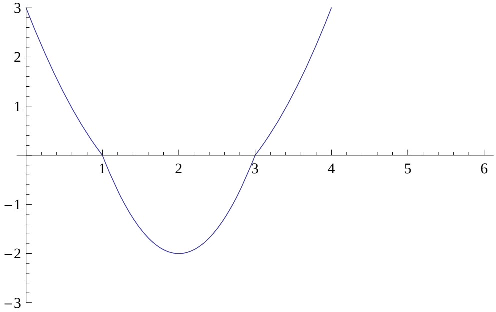
An example of such a potential is a cut-off quadratic given by

$$U(y) = \begin{cases} (|y| - a)^2 - (b - a)^2 & 0 \leqslant |y| \leqslant b \\ 0 & \text{otherwise} \end{cases}$$

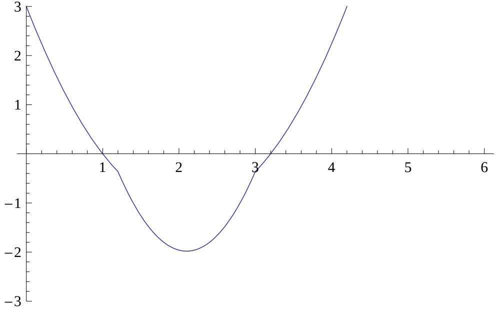
where $b < 2a$, shown below for $a = 2, b = 3$.



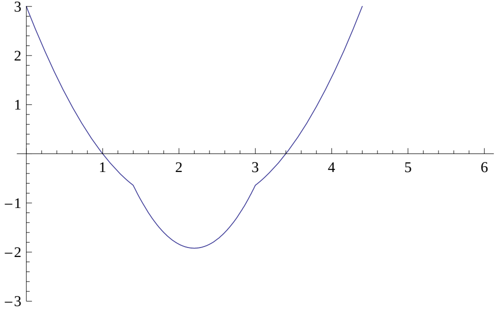
The potential energy $H(x,t) = U(x) + U(2a(1+t) - x)$ when $t = 0$



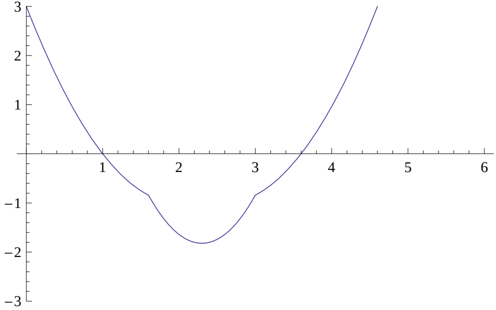
$t = 0.05$



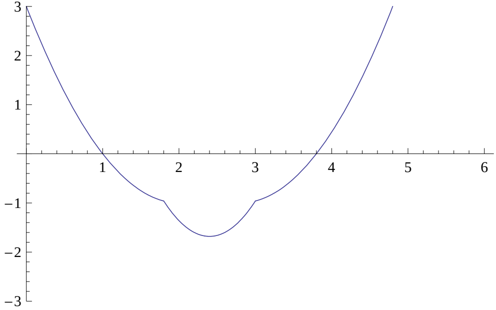
$t = 0.1$



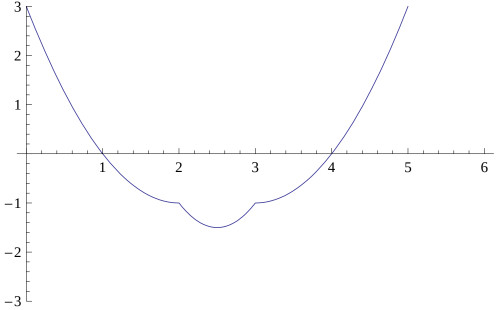
$t = 0.15$



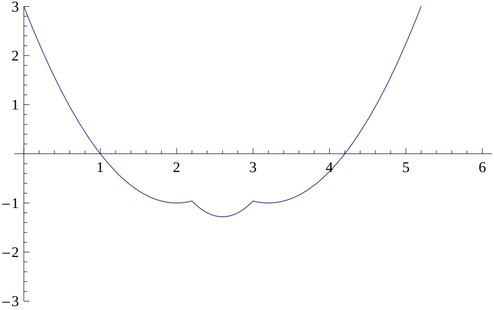
$t = 0.2$



$t = 0.25$



$t = 0.3$



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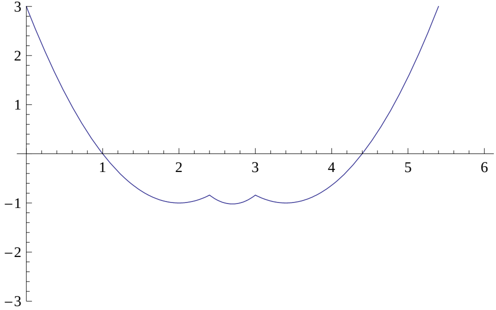
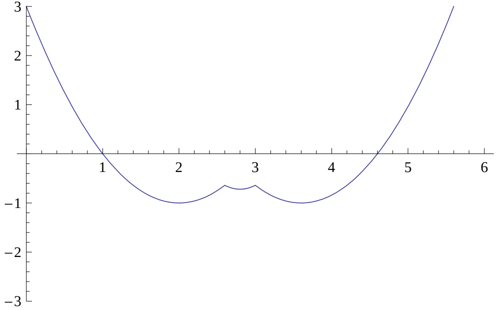
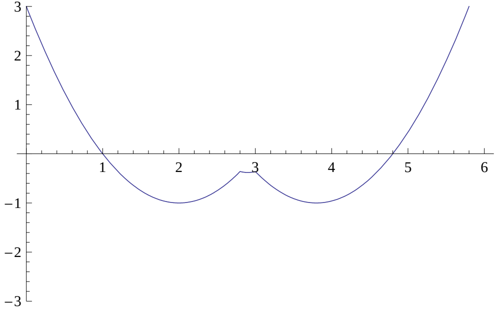


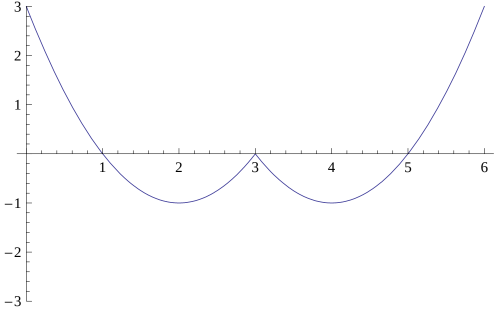
$t = 0.4$



$t = 0.45$



$t = 0.5$



Notation: $f(\sigma) \ll g(\sigma)$ means $f(\sigma)/g(\sigma) \to 0$ as $\sigma \downarrow 0$.

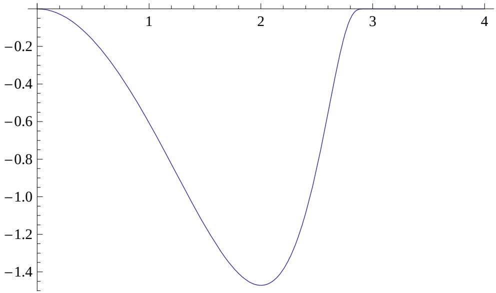
Theorem (A.,Betz)

1. *Fast Stretching*
   If
   $$\sigma|\ln\sigma|^{1/2} \ll \varepsilon(\sigma) \ll 1$$
   then $\mathbb{P}\{$*breaks on left-hand side*$\} \to 0$ *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 $\mathbb{P}\{$*breaks on left-hand side*$\} \to 1/2$ *as* $\sigma \downarrow 0$.

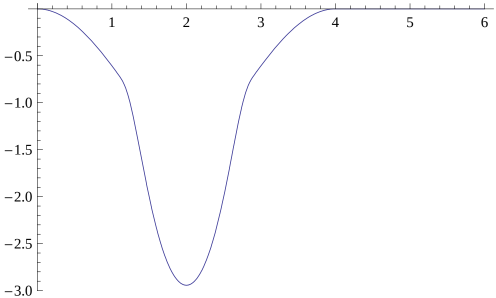
Next step

We want to do the same with U differentiable everywhere.
e.g.

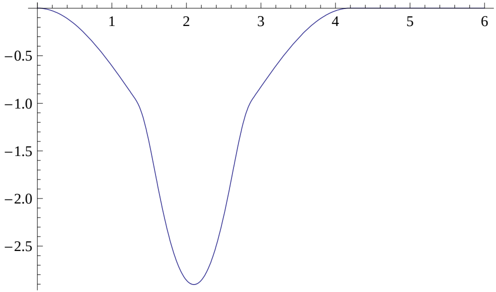
$$U(y) = \begin{cases} -y^2\,\mathrm{e}^{-1/(3-y)} & 0 \leqslant |y| \leqslant 3 \\ 0 & \text{otherwise} \end{cases}$$



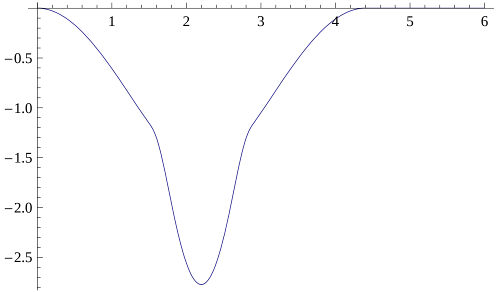
The potential energy $H(x,t) = U(x) + U(2a(1+t) - x)$ when $t = 0$



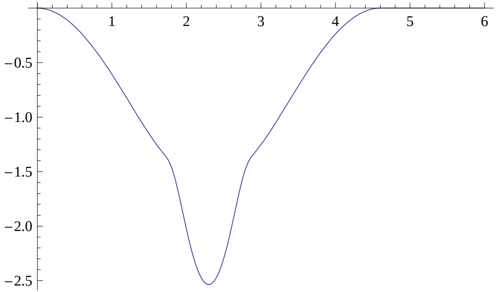
$t = 0.05$



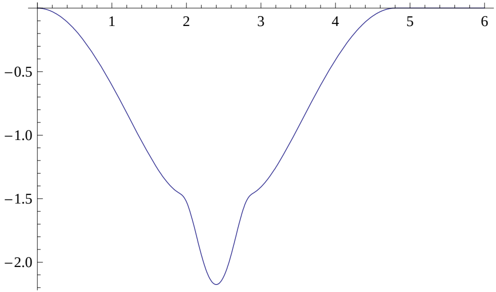
$t = 0.1$



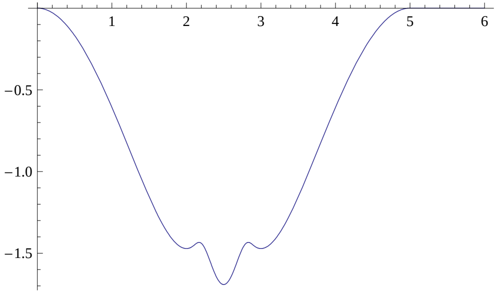
$t = 0.15$



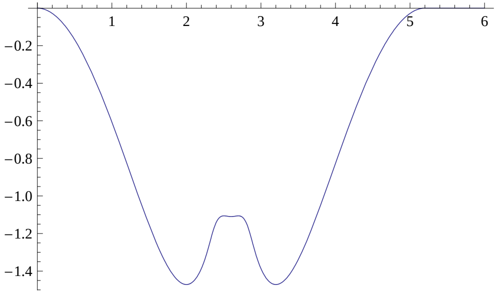
$t = 0.2$



$t = 0.25$



$t = 0.3$



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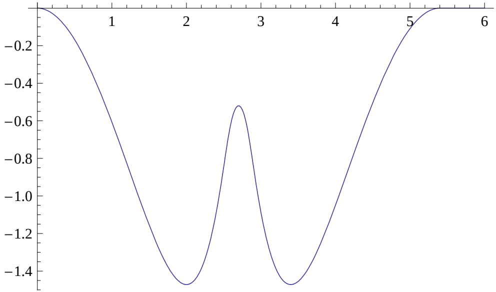
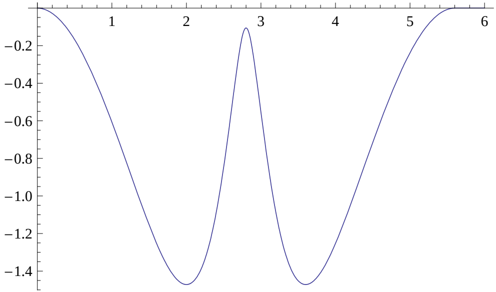
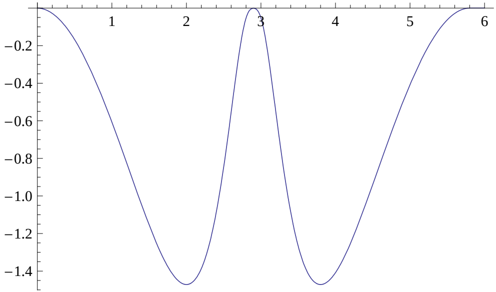


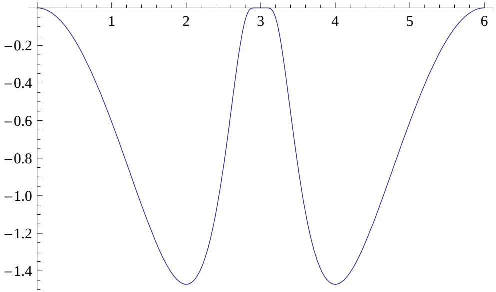
$t = 0.4$



$t = 0.45$



$t = 0.5$



We expect the middle particle to track the midpoint of the chain for $t \leqslant T$, where T is the time of bifurcation.

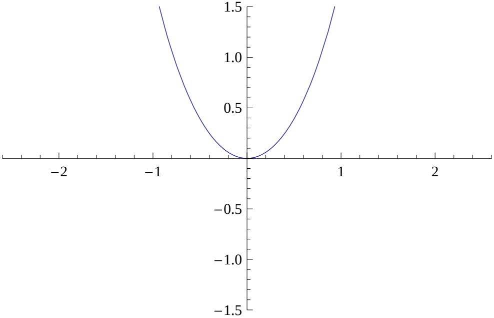
Here, the effective potential H is approximately quadratic.

By changing $t \to t - T$ and $x \to x - a(1+t)$, we will consider instead motion in the potential

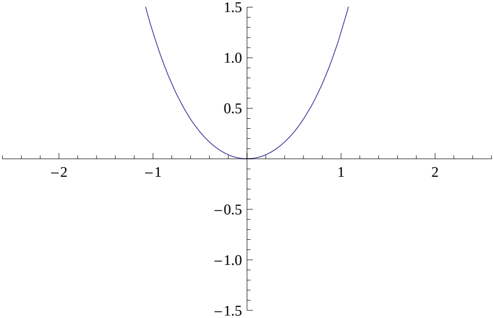
$$H(x,t) = -\frac{1}{2} t\, x^2 + \frac{1}{4} x^4$$

with $x_{-T} = 0$.

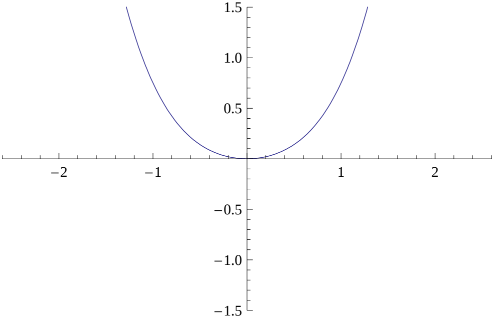
$H(x,t) = -\frac{1}{2}t\,x^2 + \frac{1}{4}x^4$ for $t = -3$



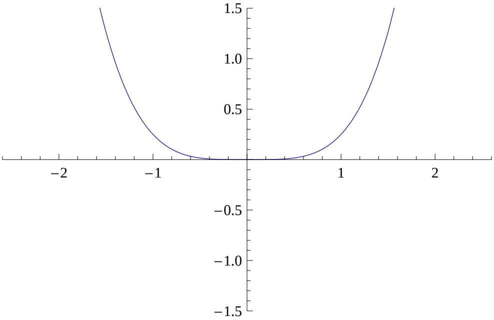
$t = -2$



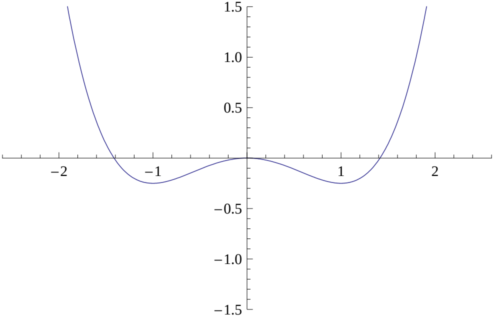
$t = -1$



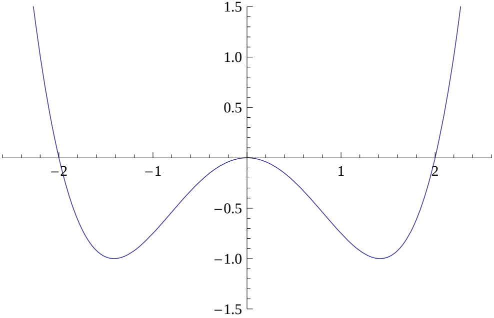
$t = 0$



$t = 1$



$t = 2$



Now we are considering the following SDE instead:

$$\mathrm{d}x_t = \frac{1}{\varepsilon}(t\,x_t - x_t^3 + \varepsilon)\,\mathrm{d}t + \frac{\sigma}{\sqrt{\varepsilon}}\,\mathrm{d}W_t, \qquad x_{-T} = 0$$

(N.B. We choose $+\varepsilon$ in drift term)

For $\varepsilon > \sigma^2$, we know:

for times $-\sqrt{\varepsilon} \leqslant t \leqslant \sqrt{\varepsilon}$,

$$\mathbb{E}(x_t) \approx \sqrt{\varepsilon} \text{ and } \sqrt{\mathrm{Var}(x_t)} \approx \sigma\varepsilon^{-1/4}$$

This suggests that $\varepsilon = \sigma^{4/3}$ is the critical scaling.

We will prove that this is indeed the case.

Proof: Fast stretching ($\varepsilon \gg \sigma^{4/3}$) will follow easily from above calculation.

For slow stretching ($\sigma^2 < \varepsilon \ll \sigma^{4/3}$), consider the SDE

$$\mathrm{d}\tilde{x}_t = \frac{1}{\varepsilon}(t\,\tilde{x}_t - \tilde{x}_t^3)\,\mathrm{d}t + \frac{\sigma}{\sqrt{\varepsilon}}\,\mathrm{d}W_t$$

This is like our equation, but without the $+1$ drift term.

Nils Berglund and Barbara Gentz considered SDEs of this form.

We aim to show that the $+1$ term does not affect the sample paths greatly during the bifurcation.

For $t \geqslant \sqrt{\varepsilon}$, dynamics of $\tilde{x}_t$ dominated by diffusion as long as

$$|\tilde{x}_t| < \frac{\sigma}{\sqrt{2t}}$$

It is shown that $\tilde{x}_t$ typically exits the slightly larger strip

$$\mathcal{S} = \left\{ (x, t) : t \geqslant \sqrt{\varepsilon},\ |x| < \frac{2\sigma\sqrt{|\log \sigma|}}{\sqrt{2t}} \right\}$$

by times of order $\sqrt{\varepsilon \log(\sqrt{\log \sigma})}$

We know that, almost surely, for all $t \geqslant -T$

$$\tilde{x}_t \leqslant x_t \leqslant \tilde{x}_t + \int_{-T}^{t} \mathrm{e}^{(t^2-s^2)/2\varepsilon} \, \mathrm{d}s$$

When $\varepsilon \ll \sigma^{4/3}$, the integral remains sufficiently small for $t \leqslant \sqrt{\varepsilon \log(\sqrt{\log \sigma})}$ so that when $\tilde{x}_t$ leaves $\mathcal{S}$, x_t is still close.

Next: The drift term outside $\mathcal{S}$ dominates the diffusion and pushes paths of $\tilde{x}_t$ further away from the origin.

To show this, a comparison argument is used with solutions of a linear SDE:

$$\mathrm{d}x_t^\kappa = \frac{1}{\varepsilon}\kappa t\, x_t^\kappa \,\mathrm{d}t + \frac{\sigma}{\sqrt{\varepsilon}}\,\mathrm{d}W_t$$

for suitable $\kappa > 0$. The same argument works with paths of x_t, but a different initial condition for the linear SDE is needed to compensate for the $+1$ term.

By times of order $\sqrt{\varepsilon|\log\sigma|}$, paths of both $\tilde{x}_t$ and x_t will have fallen into one of the two wells.

The effect of mass

This is joint work with Martin Hairer.

So far we have only considered overdamped motion i.e. first-order dynamics.

Consider now

$$\begin{aligned} \mathrm{d}x_t &= v_t \, \mathrm{d}t \\ \varepsilon^{\beta} \mathrm{d}v_t &= -v_t \, \mathrm{d}t + \frac{1}{\varepsilon}(t \, x_t - x_t^3 + \varepsilon) \, \mathrm{d}t + \varepsilon^{\alpha} \, \mathrm{d}W_t \end{aligned}$$

with $x_{-T} = 0$, $v_{-T} = 0$, where $\beta > -1$ and $\alpha > -1/2$.

N.B. we have chosen $\sigma = \varepsilon^{\alpha+1/2}$.

If all terms were differentiable, this could be written as

$$\varepsilon^\beta \ddot{x}_t = -\dot{x}_t + \frac{1}{\varepsilon}(t\,x_t - x_t^3 + \varepsilon) + \varepsilon^\alpha \dot{W}_t, \qquad x_{-T} = 0,\ \dot{x}_{-T} = 0$$

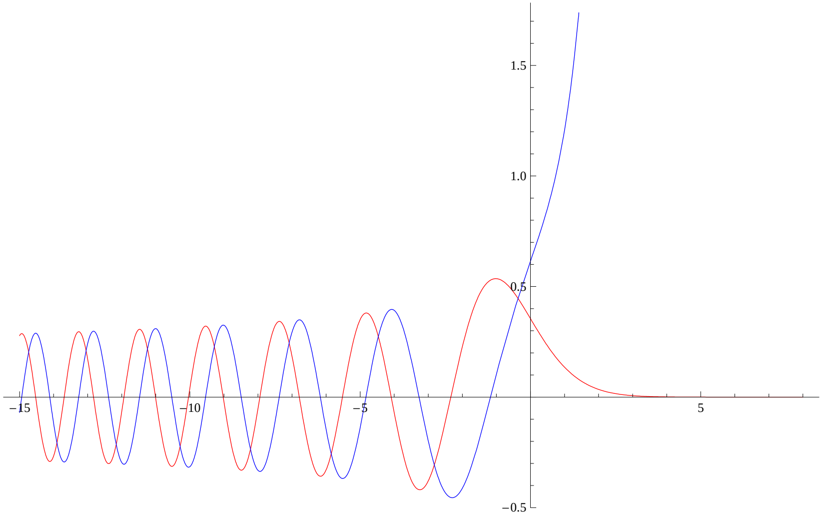
First step: Consider just

$$\varepsilon^\beta \ddot{x}^0_t = -\dot{x}^0_t + \frac{1}{\varepsilon}(t\,x^0_t + \varepsilon) + \varepsilon^\alpha \dot{W}_t, \qquad x^0_{-T} = 0,\ \dot{x}^0_{-T} = 0$$

This can be solved explicitly.

The solution involves Airy functions, $\mathrm{Ai}(t)$ and $\mathrm{Bi}(t)$: these are linearly independent solutions to $\ddot{x} - t\,x = 0$.

$\mathrm{Ai}(x)$ and $\mathrm{Bi}(x)$



$$
\begin{aligned}
x^0(t) =& \pi\varepsilon^{(1-2\beta)/3}\times \\
& \times \left(-\mathrm{Ai}(t(\varepsilon,\beta)) \int_{-T}^{t} \mathrm{e}^{-\frac{1}{2}(t-s)\varepsilon^{-\beta}}\,\mathrm{Bi}(s(\varepsilon,\beta))h(s)\,\mathrm{d}s + \right. \\
& \left. + \mathrm{Bi}(t(\varepsilon,\beta)) \int_{-T}^{t} \mathrm{e}^{-\frac{1}{2}(t-s)\varepsilon^{-\beta}}\,\mathrm{Ai}(s(\varepsilon,\beta))h(s)\,\mathrm{d}s\right)
\end{aligned}
$$

where $h(s) = 1 + \varepsilon^{\alpha}\dot{W}_s$ and

$$
t(\varepsilon,\beta) = \varepsilon^{-(1+\beta)/3}\left(t + \frac{1}{4}\varepsilon^{1-\beta}\right)
$$

Theorem (A., Betz, Hairer)

If either

- $\beta \geqslant 0$ *and* $\alpha > 1/4$
- $-1 < \beta < 0$ *and* $\alpha > (1+\beta)/4$

then

$$\lim_{\varepsilon \downarrow 0} \mathbb{P}\{\lim_{t \to \infty} x_t^0 = +\infty\} = 1$$

while for either

- $\beta \geqslant 0$ *and* $\alpha < 1/4$
- $-1 < \beta < 0$ *and* $\alpha < (1+\beta)/4$

then

$$\lim_{\varepsilon \downarrow 0} \mathbb{P}\{\lim_{t \to \infty} x_t^0 = -\infty\} = \lim_{\varepsilon \downarrow 0} \mathbb{P}\{\lim_{t \to \infty} x_t^0 = +\infty\} = 1/2$$

The main part of the proof is to show that as $\varepsilon \downarrow 0$, we have

$$\lim_{t\to\infty} \frac{\mathbb{E}(x_t^0)}{(\mathrm{Var}(x_t^0))^{1/2}} \sim \varepsilon^{-\alpha+\frac{1}{4}(1+\min\{\beta,0\})}$$

The analysis deals with four cases:

1. $\beta \geqslant 1$
2. $1/2 < \beta < 1$
3. $0 \leqslant \beta \leqslant 1/2$
4. $-1 < \beta < 0$

It can be shown that $x_t^0 \to \pm\infty$, in which case the sign of the exponent above is enough to prove the theorem.

Next: Back to the full potential,

$$\varepsilon^{\beta}\ddot{x}_t = -\dot{x}_t + \frac{1}{\varepsilon}(t\,x_t - x_t^3 + \varepsilon) + \varepsilon^{\alpha}\dot{W}_t$$

by which we mean

$$\begin{aligned} \mathrm{d}x_t &= v_t\,\mathrm{d}t \\ \varepsilon^{\beta}\mathrm{d}v_t &= -v_t\,\mathrm{d}t + \frac{1}{\varepsilon}(t\,x_t - x_t^3 + \varepsilon)\,\mathrm{d}t + \varepsilon^{\alpha}\,\mathrm{d}W_t \end{aligned}$$

Want to show that for suitably large β, sample paths behave as in the overdamped case.

Consider the equations for $t \in [-T, t_1]$, where $t_1 > 0$ is independent of ε.

Theorem (A., Betz, Hairer)

Let $\beta > 2$ *and* $\alpha > 0$. *Then*

$$\lim_{\varepsilon \downarrow 0} \mathbb{P}\{x_t \leqslant \xi_t - \varepsilon^{\beta} V_t \text{ for all } t \in [-T, t_1]\} = 1$$

where ξ_t *solves*

$$\mathrm{d}\xi_t = \frac{1}{\varepsilon}(t\xi_t - \xi_t^3 + C\varepsilon)\,\mathrm{d}t + \varepsilon^{\alpha}\,\mathrm{d}W_t$$

for some $C > 0$ *independent of* ε *and*

$$V_t = \varepsilon^{\alpha-\beta} \int_{-T}^{t} \mathrm{e}^{-(t-s)\varepsilon^{-\beta}}\,\mathrm{d}W_s$$

Proof: Let (X, V) solve

$$\mathrm{d}X_t = V_t \, \mathrm{d}t$$
$$\varepsilon^\beta \mathrm{d}V_t = -V_t \, \mathrm{d}t + \varepsilon^\alpha \, \mathrm{d}W_t$$

Then

$$X_t = \varepsilon^\alpha W_t - \varepsilon^\beta V_t$$

where

$$V_t = \varepsilon^{\alpha-\beta} \int_{-T}^{t} \mathrm{e}^{-(t-s)\varepsilon^{-\beta}} \, \mathrm{d}W_s$$

Let $y_t = x_t - X_t$ and $z_t = v_t - V_t$. Then (y, z) solve

$$\dot{y}_t = z_t$$
$$\varepsilon^\beta \dot{z}_t = -z_t + \frac{1}{\varepsilon} g(t, y_t + X_t)$$

where $g(t, y_t + X_t) \; := \; t(y_t + X_t) - (y_t + X_t)^3 + \varepsilon$, so that

$$z_t = \varepsilon^{-(1+\beta)} \int_{-T}^{t} \mathrm{e}^{-(t-s)\varepsilon^{-\beta}} g(s, y_s + X_s) \mathrm{d}s$$
$$\leqslant \frac{1}{\varepsilon} g(t, y_t + X_t) + C$$

and so

$$\dot{y}_t \leqslant \frac{1}{\varepsilon} g(t, y_t + X_t) + C$$

Since $x_t = y_t + X_t$, this leads us to $x_t \leqslant \eta_t$, where

$$\mathrm{d}\eta_t = \frac{1}{\varepsilon}(t\eta_t - \eta_t^3 + C\varepsilon)\,\mathrm{d}t + \varepsilon^\alpha\,\mathrm{d}W_t - \varepsilon^\beta\,\mathrm{d}V_t$$

Using that $\varepsilon^\beta V_t \leqslant C\varepsilon^{\alpha+\beta/2}$ and by the assumptions on α and β, we can then show that $\eta_t \leqslant \xi_t - \varepsilon^\beta V_t$, where

$$\mathrm{d}\xi_t = \frac{1}{\varepsilon}(t\xi_t - \xi_t^3 + C\varepsilon)\,\mathrm{d}t + \varepsilon^\alpha\,\mathrm{d}W_t$$

as required.

Outlook

Smaller β, where overdamped approximation no longer valid. Need new approach.

Large noise: $-1/2 < \alpha \leqslant 0$. Possible approach to show that the invariant measure, for any given t, is reached faster than rate at which potential changes.

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