NOISY KINKS AND DIFFUSION-LIMITED REACTION

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Java applet:

`http://maths.leeds.ac.uk/Applied/stochastic/nucleation.htm`

EQUATION OF MOTION: CONTINUOUS AND DISCRETIZED SPACE IN 1D

$$\mathrm{d}\mathbf{\Phi}_t(x) = \left(\mathbf{\Phi}_t(x) - \mathbf{\Phi}_t(x)^3 + \partial^2_{xx}\mathbf{\Phi}_t(x)\right)\mathrm{d}t + \sqrt{2KT}\,\mathrm{d}\mathbf{W}_t(x),$$

where $\left\langle \mathrm{d}\mathbf{W}_t(x)\mathrm{d}\mathbf{W}_{t'}(x')\right\rangle = \delta(x-x')\delta(t-t')\mathrm{d}t.$

The numerical version is a system of N SDEs:

$$\begin{array}{cccccccc} & \leftarrow \Delta x \rightarrow & & & & & & \\ \cdots & \times & \times & \times & \times & \cdots & \times \\ & & i-1 & i & i+1 & & N \end{array}$$

At site i :

$$\mathrm{d}\mathbf{\Phi}_t(i) = \left(\mathbf{\Phi}_t(i) - \mathbf{\Phi}_t^3(i) + \tilde{\Delta}\mathbf{\Phi}_t(i)\right)\mathrm{d}t + \sqrt{\frac{2KT}{\Delta x}}\mathrm{d}\mathbf{W}_t(i),$$

where $\tilde{\Delta}\mathbf{\Phi}_t(i) = \Delta x^{-2}\left(\mathbf{\Phi}_t(i+1) + \mathbf{\Phi}_t(i-1) - 2\mathbf{\Phi}_t(i)\right)$

and $\left\langle \mathrm{d}\mathbf{W}_t(i)\mathrm{d}\mathbf{W}_t(i')\right\rangle = \delta_{i-i'}\,\mathrm{d}t$ (independent noises).

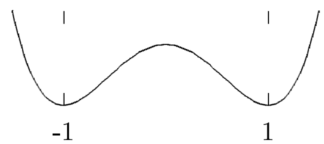
Periodic boundary conditions, $L = N\Delta x \simeq 10^6$, $\beta = 1/KT$.

DOUBLE-WELL POTENTIAL AND ENERGY

The SPDE can be written

$$\mathrm{d}\mathbf{\Phi}_t(x) = \left(-V'(\mathbf{\Phi}_t(x)) + \partial^2_{xx}\mathbf{\Phi}_t(x)\right)\mathrm{d}t + \sqrt{2KT}\mathrm{d}\mathbf{W}_t(x),$$

where $V(\phi) = -\frac{1}{2}\phi^2 + \frac{1}{4}\phi^4$,



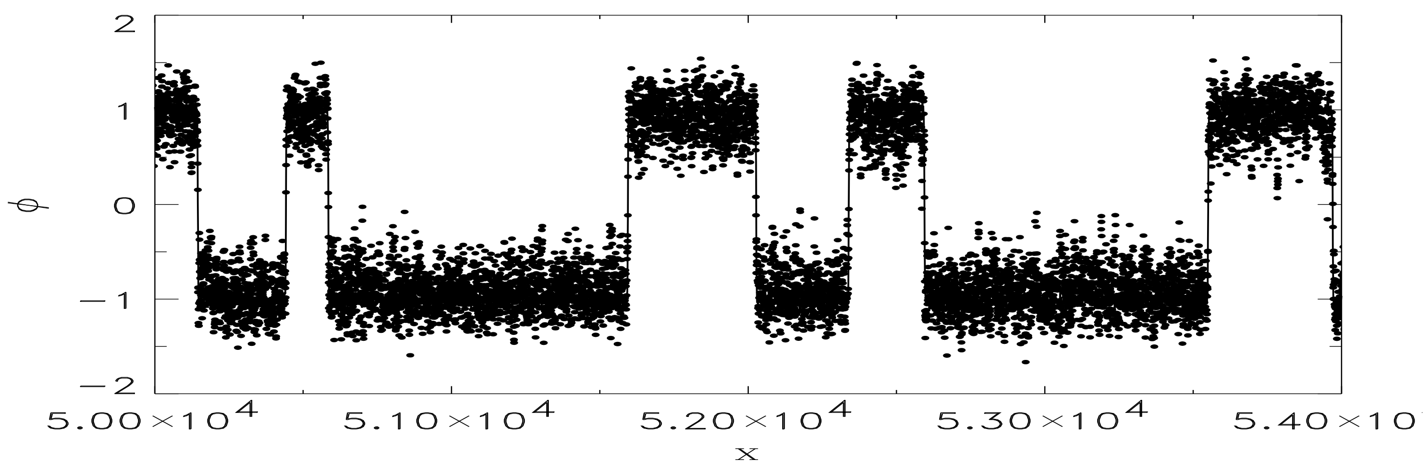
or

$$\mathrm{d}\mathbf{\Phi}_t(x) = -\frac{\delta\mathcal{E}[\mathbf{\Phi}_t]}{\delta\mathbf{\Phi}_t(x)}\mathrm{d}t + \sqrt{2KT}\mathrm{d}\mathbf{W}_t(x),$$

where

$$\mathcal{E}[f] = \int\left(V(f(x)) + \frac{1}{2}\left(\partial_x f(x)\right)^2\right)\mathrm{d}x.$$

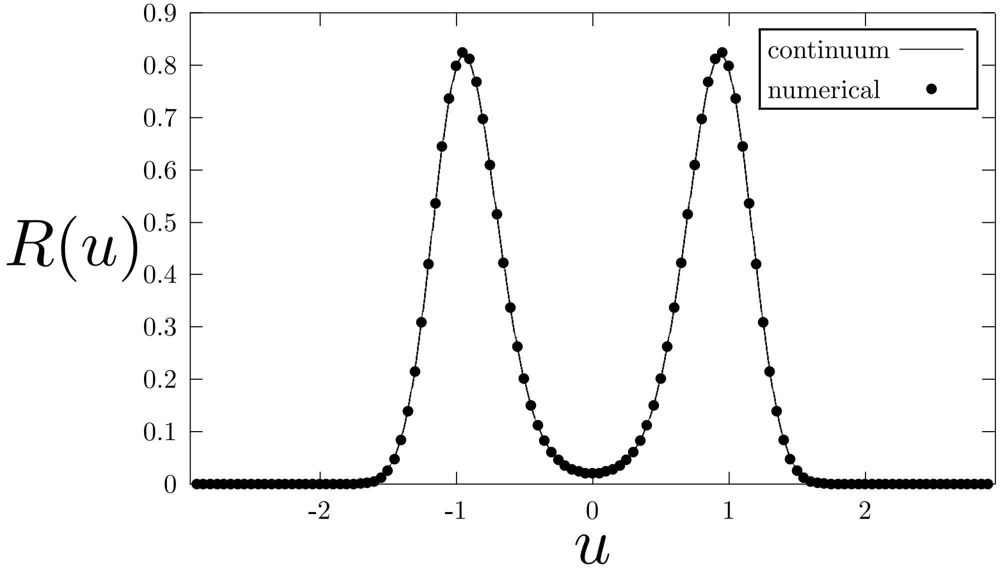
... are localised structures interpolating between the minima of $V(\phi)$



A (noiseless) kink at $x = x_0$,
$\phi^{\mathrm{k}}(x) = \tanh(\frac{x-x_0}{\sqrt{2}})$,
has energy $E_k = \mathcal{E}[\phi^{\mathrm{k}}(x)] = \sqrt{8/9}$.

An antikink at $x = x_0$,
$\phi^{\mathrm{a}}(x) = -\tanh(\frac{x-x_0}{\sqrt{2}})$,
has the same energy as a kink.

STEADY STATE: NON-GAUSSIAN DISTRIBUTION OF FIELD AT A POINT



Steady state density, $R(u) = \frac{\mathrm{d}}{\mathrm{d}u}\mathcal{P}[\mathbf{\Phi}_t(x) < u]$*, for* $\beta = 7$*. The solid line is* $\psi_0(u)^2$*. The dots are obtained from a numerical histogram, run with grid spacing* $\Delta x = 0.2$*.*

- GL and Salman Habib *Stochastic PDEs: convergence to the continuum?* Computer Physics Communications **142** 29 (2001)

Part of a configuration that contains only one kink can be decomposed as

$$\mathbf{\Phi}_t(x) = \phi^{\mathrm{k}}(x - \mathbf{X}_t) + \boldsymbol{\chi}_t(x - \mathbf{X}_t).$$

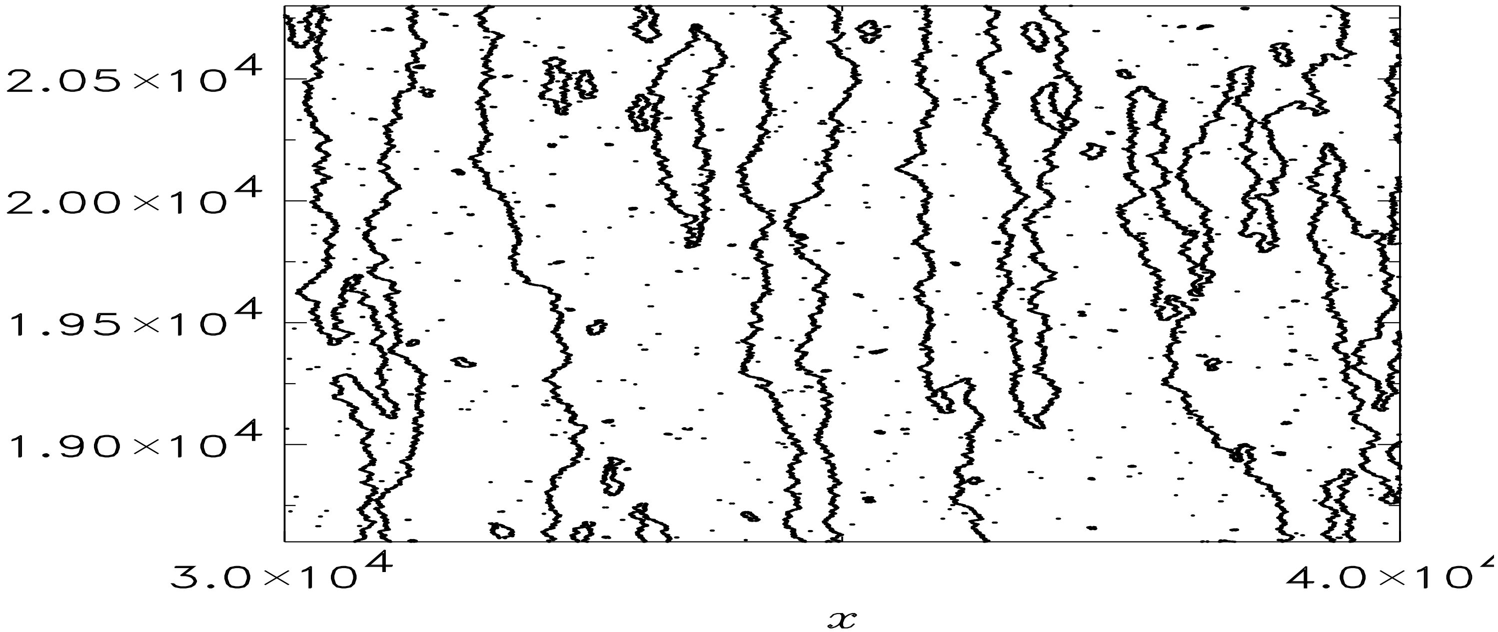
An isolated kink undergoes Brownian motion. Let $D = \lim_{t\to\infty} \frac{1}{2t}\langle {\mathbf{X}_t}^2 \rangle$. One obtains

$$D = \frac{KT}{E_k} + \mathcal{O}((\frac{KT}{E_k})^2).$$

- D.J. Kaup, *Thermal corrections to overdamped soliton motion*, Phys. Rev. B **27** 6787-6795 (1983)

- GL and Franz Mertens *Rice's ansatz for overdamped* ϕ^4 *kinks at finite temperature* Phys. Rev. E **67** 027601 (2003)

A steady-state density of kinks is maintained by a dynamic balance between nucleation and annihilation of kink-antikink pairs.



Part of a numerical spacetime diagram.

EQUILIBRIUM STATE

The density of kinks, ρ_0, is proportional to $\exp(-\beta E_k)$.

Nucleation events occur at random spacetime points with rate

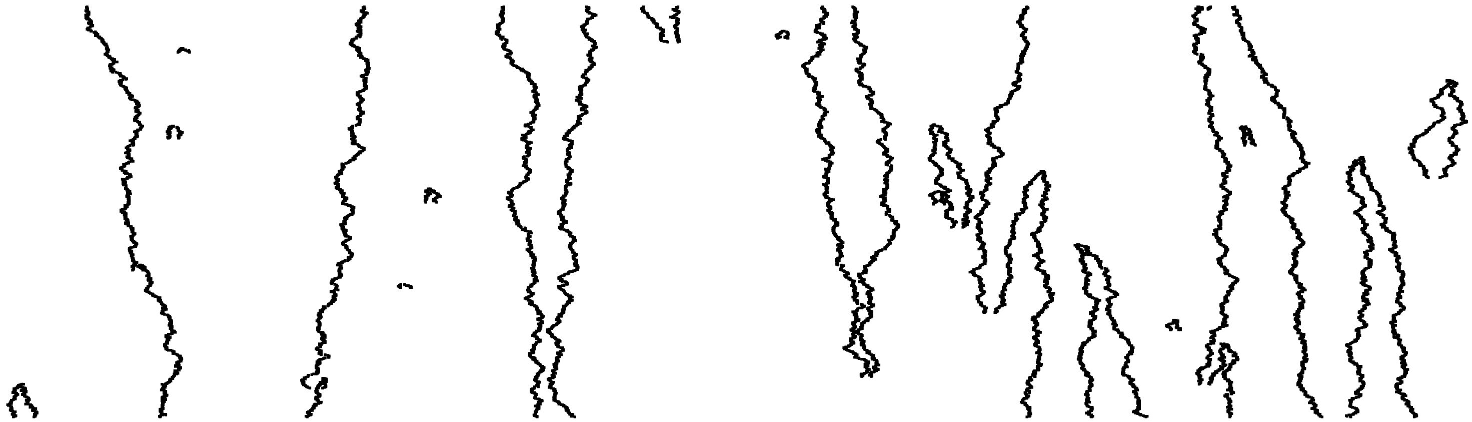
$\Gamma \propto \exp(-2\beta E_k)$.

The mean lifetime, τ, of a kink satisfies $\rho_0 = \Gamma\tau$.

Thus the mean lifetime of a kink is proportional to $\exp(\beta E_k)$.

- M. Büttiker and T. Christen, Phys. Rev. E **58**, 1533 (1998)

DIFFUSION-LIMITED REACTION: SIMPLE MODEL OF THE DYNAMICS



1. Pairs of particles are nucleated at random times and positions at rate Γ with separation b;

2. Once born, particles diffuse independently with diffusivity D;

3. Particles annihilate on collision.

Exact results

Choose an arbitrary reference point 0 and let

$r(x,t) \equiv \{\text{probability that the number of particles between } 0 \text{ and } x \text{ at time } t \text{ is even}\}$.

At any $t > 0$, $\quad r(0,t) = 1, \quad \lim_{x\to\infty} r(x,t) = \frac{1}{2}$

and $\lim_{\Delta x\to 0} r(\Delta x, t) = 1 - \rho(t)\Delta x$,

where $\rho(t)$ is the mean number of particles per unit length at time t.

Thus

$$\rho(t) = -\lim_{x\to 0^+} \frac{\partial}{\partial x} r(x,t).$$

- T. O. Masser and D. ben-Avraham, Phys. Rev. E **63** 6108 (2001)

- Salman Habib, Katja Lindenberg, GL and Carmen Molina-París. J. Chem. Phys. **115** 73-89 (2001)

LINEAR PDE FOR $r(x,t)$

$$\frac{\partial}{\partial t} r(x,t) = \begin{cases} 2D\frac{\partial^2}{\partial x^2} r(x,t) + 2x\Gamma(1-2r(x,t)) & x \le b; \\ 2D\frac{\partial^2}{\partial x^2} r(x,t) + 2b\Gamma(1-2r(x,t)) & x > b. \end{cases}$$

$$\lim_{t\to\infty} r(x,t) = r_{\mathrm{e}}(x) = \begin{cases} \frac{1}{2}\left[c_1 \mathrm{Ai}\left(\left(\frac{2\Gamma}{D}\right)^{\frac{1}{3}} x\right) + c_2 \mathrm{Bi}\left(\left(\frac{2\Gamma}{D}\right)^{\frac{1}{3}} x\right) + 1\right] & x \le b; \\ \frac{1}{2}\left[c_3 \exp(-(\frac{2\Gamma b}{D})^{\frac{1}{2}} x) + 1\right] & x > b. \end{cases}$$

The constants c_1, c_2 and c_3 are fixed by requiring $r_{\mathrm{e}}(0) = 1$ and imposing continuity of $r_{\mathrm{e}}(x)$ and $\frac{\mathrm{d}}{\mathrm{d}x} r_{\mathrm{e}}(x)$ at $x = b$.

$$\rho_0 = \left(\frac{\Gamma}{4D}\right)^{\frac{1}{3}} \frac{|\mathrm{Ai}'(0)|}{\mathrm{Ai}(0)} \left(\frac{\mathrm{Bi}'(\varepsilon) + \sqrt{3}\mathrm{Ai}'(\varepsilon) + \varepsilon(\mathrm{Bi}(\varepsilon) + \sqrt{3}\mathrm{Ai}(\varepsilon))}{\mathrm{Bi}'(\varepsilon) - \sqrt{3}\mathrm{Ai}'(\varepsilon) + \varepsilon(\mathrm{Bi}(\varepsilon) - \sqrt{3}\mathrm{Ai}(\varepsilon))}\right), \quad \text{where} \quad \varepsilon = \left(\frac{2\Gamma}{D}\right)^{\frac{1}{3}} b.$$

Paired and unpaired nucleation

- As $\varepsilon \to 0$, $\rho_0 \to \left(\frac{b\Gamma}{2D}\right)^{\frac{1}{2}}$. Nucleation rate $\propto \rho_0^2$ for paired nucleation.

- As $\varepsilon \to \infty$, $\rho_0 \to \left(\frac{\Gamma}{4D}\right)^{\frac{1}{3}}$. Nucleation rate $\propto \rho_0^3$ for unpaired nucleation.

- Zoltan Rácz, Phys. Rev. Lett. **55** 1707 (1985)

DENSITIES: HIERARCHY

Let $f_n(x_1, \ldots x_n; t)\mathrm{d}x_1 \ldots \mathrm{d}x_n$ be the probability that there is

one particle in $(x_1, x_1 + \mathrm{d}x_1)$, one in $(x_2, x_2 + \mathrm{d}x_2)$, $\ldots$

and one in $(x_n, x_n + \mathrm{d}x_n)$ at time t.

$f_1(x_1, t)$ is the density of particles at position x_1 and time t. If the nucleation rate is independent of x, the reaction kernel $k(x_1, x_2)$ is a function of $|x_2 - x_1|$ only, and $f_1(x, 0)$ is independent of x,

then $f_1(x, t) = \rho(t)$, independent of x. (The mean density or concentration of particles.)

Let $g(y) = \frac{1}{\rho(t)^2} f_2(x, x + y, t)$ and $K(y) = k(x, x + y)$.

Exact rate equation (in terms of the correlation function)

An exact expression is obtained for $\rho(t)$, but can we find a simple ODE rate equation,

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho = \qquad ?$$

We need the correlation function $g(y,t)$. We know that $g(0,t) = 0$ and

$$\dot{\rho} = 2\Gamma - 4D\rho^2 g'(0^+, t).$$

Harder:

1. $g(y,t)$,

2. Distribution of particle lifetimes.

RATE EQUATION FOR UNPAIRED NUCLEATION?

If $\dot{\rho} = Q - k_s \rho^2$ then

1. Steady-state density $\dot{\rho} = 0$ so $\rho_{\mathrm{s}} \propto Q^{1/2}$.
2. Without nucleation, $Q = 0$ so $\rho(t) \propto t^{-1}$.

Both statements are incorrect.

- Ovchinnikov and Zeldovich (1978), de Gennes (1982), Toussaint and Wilczek (1983), Nagai and Kawasaki (1983), Kang and Redner (1984), Lushnikov (1986).
  Scaling argument: Without nucleation, $\rho(t) \propto (Dt)^{-1/2}$.
- D. C. Torney and H. M. McConnell (1983). Exact solution:
  If $Q = 0$ and the initial distribution of particles is random then,
  as $t \to \infty$, $\rho(t) \to (8\pi Dt)^{-1/2}$.

So $\dot{\rho} = Q - k_c \rho^3$? Not good enough either.

Exact reaction kernel

$$\dot{\rho}(t) = -2\rho^2(t)\int_0^\infty g(y,t)K(y)\mathrm{d}y + Q.$$

Let $s(y,\Delta t)$ be the probability that two particles, with initial separation y, collide before Δt. Then

$$K(y) = \lim_{\Delta t \to 0} \frac{1}{\Delta t} s(y,\Delta t).$$

The differential equation for $\rho(t)$ is well-defined if

$$\lim_{\Delta t \to 0}\left(\Delta t^{-1}\int_0^\infty g(y,t)s(y,\Delta t)\mathrm{d}y\right) = \text{constant}.$$

CONSEQUENCE: $g(0,t)=0$

If both particles diffuse with diffusivity D then $s(y,\Delta t) = \mathrm{erfc}\left(\frac{y}{(8D\Delta t)^{\frac{1}{2}}}\right)$.

$$
\begin{aligned}
&\int_0^\infty g(y,t)s(y,\Delta t)\mathrm{d}y \\
&\qquad = \int_0^\infty s(y,\Delta t)\left(g(0,t) + yg'(0^+,t) + \frac{1}{2}y^2 g''(0^+,t) + \cdots\right)\mathrm{d}y \\
&\qquad = \left(\frac{1}{\sqrt{\pi}}(8D\Delta t)^{\frac{1}{2}} g(0,t) + \frac{1}{4}(8D\Delta t)g'(0^+,t) + \cdots\right).
\end{aligned}
$$

Thus $g(0,t)=0$ and $\dot{\rho} = Q - 4D\rho^2 g'(0^+,t)$.

- Salman Habib, Katja Lindenberg, GL and Carmen Molina-París. J. Chem. Phys. **115** 73-89 (2001)