Escape and periodic potential problems

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Working now in the nondimensional variables for the escape problem, dropping the primes, we have the following nondimensionalized Fokker-Planck equation:

$$\frac{\partial \rho}{\partial t} = \frac{\partial}{\partial x}\left(\frac{d\hat{\varphi}}{dx}\rho\right) + \varepsilon \frac{\partial^2 \rho}{\partial x^2}$$

$$\varepsilon = \frac{k_B T}{A} = \frac{\text{thermal energy}}{\text{barrier height}}$$

A very interesting case for physical applications is the case $\varepsilon \ll 1$ because then the local minimum behaves as a metastable state, meaning the particle stays trapped for a long time and relies on thermal fluctuations to eventually push it over the barrier and escape. How long does this take?

A mathematically interesting aspect of this problem is that it turns out, even in more complex settings, that rare transitions tend to behaves in a predictable way, when they happen. This related to large deviation theory (mathematics) or instanton calculations (physics).

For the purposes of estimating the time scale of transition, we can use a relatively simple asymptotic procedure using the small parameter.

The procedure we will follow falls in the framework of so-called adiabatic approximaitons (one infers a separation of time scales and computes what's happening on the fast time scale by assuming the slow dynamics are frozen. This is the same idea as behind the multiple scales analysis, but a little more ad hoc. The particular incarnation of this adiabatic approximation in this problem is called the flux overpopulation method. Multiple scales method doesn't actually work here....only gives trivial results.

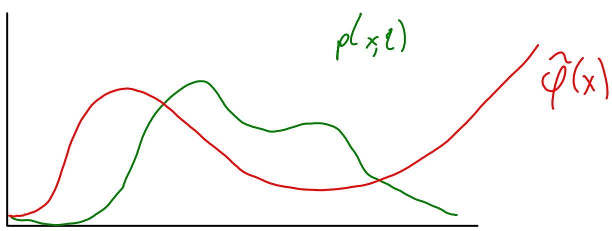
First we interpret the Fokker-Planck equation in terms of continuum mechanics:

$$\frac{\partial \rho(x,t)}{\partial t} = -\frac{\partial J(x,t)}{\partial x}$$

$$J(x,t) = \underbrace{\left(-\frac{d\hat{\varphi}}{dx}\right)\rho}_{\substack{\text{advective flux}\\ = \text{density} \times \text{velocity}}} \underbrace{-\, \varepsilon \frac{\partial \rho}{\partial x}}_{\text{diffusive flux}} = \text{probability flux}$$

$-\frac{d\hat{\varphi}}{dx}$ = nondimensionalized particle velocity of x

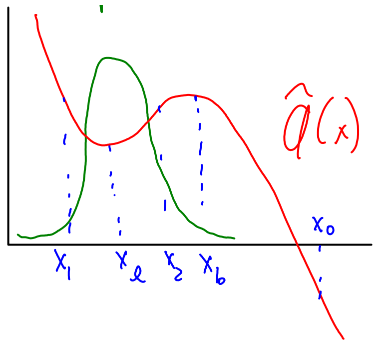
ρ = probability density



The intuition here is that the fast dynamics correspond to dynamics within the local minimum, whereas the slow dynamics is the process of escaping.

For this reason, we will take the probability density for the particle to be in a quasistationary state...not quite stationary because there is the possibility for the particle to escape over the barrier....but this takes a long time.

$$\rho^{(qs)}(x)$$



We calculate the quastistationary state by looking for a steady solution of the Fokker-Planck equation but we don't demand zero flux, which is usually the case for a truly stationary state. Instead, we allow for a small flux of probability density corresponding to the flow of particles from the metastable state over the barrier.

The quasi-stationary state therefore simply has constant flux $J^{(qs)} \neq 0$

$$J^{(qs)} = -\frac{d\hat{\varphi}}{dx} p^{(qs)} - \varepsilon \frac{dp^{(qs)}}{dx}$$

as yet unknown constant

Solve as first order ODE for $p^{(qs)}$

Integrating factor: $e^{\hat{\varphi}(x)/\varepsilon}$

$$J^{(qs)} e^{\hat{\varphi}(x)/\varepsilon} = -\varepsilon \frac{d}{dx}\left(e^{\hat{\varphi}(x)/\varepsilon} p^{(qs)}(x)\right)$$

$$\int_{x_\ell}^{x} \quad x$$

$$J^{(qs)} \int_{x_\ell}^{x} e^{\hat{\varphi}(x')/\varepsilon}\, dx' = -\varepsilon\left(e^{\hat{\varphi}(x)/\varepsilon} p^{(qs)}(x) - e^{\hat{\varphi}(x_\ell)/\varepsilon} p^{(qs)}(x_\ell)\right)$$

Trying to solve this equation for the quasistationary probability density gives:

$$p^{(qs)}(x) = e^{(\hat{\varphi}(x_\ell) - \hat{\varphi}(x))/\varepsilon}\, \underbrace{p^{(qs)}(x_\ell)}_{\text{unknown constant}} - \frac{1}{\varepsilon} \underbrace{J^{(qs)}}_{\text{unknown constant}} \int_{x_\ell}^{x} e^{(\hat{\varphi}(x') - \hat{\varphi}(x))/\varepsilon}\, dx'$$

This is to be expected as the quasistationary probability density solves a second order differential equation and we haven't imposed any boundary conditions or auxiliary conditions yet. We'll do that now to determine the remaining constants.

First we will assume (and then check for self-consistency) that $\frac{1}{\varepsilon} J^{(qs)} \ll 1$

We can also assume that the probability density is mostly concentrated in the interval $[x_1, x_2]$. This is again using the assumption that the thermal energy is much smaller than barrier height so that the probability density for the particle position is concentrated on a much smaller region than the fuller domain of the local minimum. This also assumes the potential has order 1 curvature-- if it were like a square well this would be bad.

Using these approximations, we apply the normalization condition

$$1 = \int_{-\infty}^{\infty} p^{(qs)}(x')\, dx' \approx \int_{x_1}^{x_2} p^{(qs)}(x')\, dx'$$

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$$\approx \int_{x_1}^{x_2} e^{(\hat{\varphi}(x_\ell)-\hat{\varphi}(x'))/\varepsilon}\,\underbrace{p^{(qs)}(x_\ell)}_{\text{constant}}\,dx'$$

$$\therefore\; p^{(qs)}(x_\ell) \approx \frac{1}{\int_{x_1}^{x_2} e^{(\hat{\varphi}(x_\ell)-\hat{\varphi}(x'))/\varepsilon}\,dx'}$$

To determine the other constant, we will exploit the fact that the potential falls rapidly on the other side of the barrier, so that at some point x_o over the barrier, we can approximate

$$e^{(\hat{\varphi}(x_o)-\hat{\varphi}(x_\ell))/\varepsilon} \approx 0$$

(See Risken Sec. 5.10 for escape-time examples that don't make this assumption, equivalent to no regurgitation of particles from over the barrier once they've crossed.

To determine a formula for the flux (the other remaining undetermined constant), we will use our solution for the quasistationary probability density and evaluate it at over-barrier location x_o.

$$\underbrace{p^{(qs)}(x_o)}_{\text{negligible}} = \underbrace{e^{(\hat{\varphi}(x_\ell)-\hat{\varphi}(x_o))/\varepsilon}}_{\text{"}}\, p^{(qs)}(x_\ell) - \frac{1}{\varepsilon} J^{(qs)} \int_{x_\ell}^{x_o} e^{(\hat{\varphi}(x')-\hat{\varphi}(x_o))/\varepsilon}\,dx'$$

so these balance

plug in above expression

$$J^{(qs)} = \frac{\varepsilon\, e^{(\hat{\varphi}(x_\ell)-\cancel{\hat{\varphi}(x_o)})/\varepsilon}\, p^{(qs)}(x_\ell)}{\int_{x_\ell}^{x_o} e^{(\hat{\varphi}(x')-\cancel{\hat{\varphi}(x_o)})/\varepsilon}\,dx'}$$

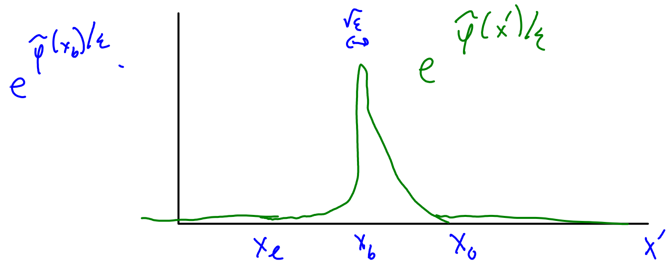
$$J^{(qs)} = \frac{\varepsilon\, e^{\cancel{\hat{\varphi}(x_\ell)}/\varepsilon}}{\int_{x_\ell}^{x_o} e^{\hat{\varphi}(x')/\varepsilon}\,dx' \int_{x_1}^{x_2} e^{(\cancel{\hat{\varphi}(x_\ell)}-\hat{\varphi}(x''))/\varepsilon}\,dx''}$$

$$J^{(qs)} = \frac{\varepsilon}{\int_{x_\ell}^{x_o} e^{\hat{\varphi}(x')/\varepsilon}\,dx' \int_{x_1}^{x_2} e^{-\hat{\varphi}(x'')/\varepsilon}\,dx''}$$

This is more or less an explicit expression for the flux of the probability density (which since it's constant, is also the flux over the barrier) in the quasistationary state corresponding to a system with thermal energy small compared to the energy barrier height. One should not take this rather complicated formula too seriously as it stands because it's all premised on approximations related to small ε

so may as well take a small ε approximation of these integrals -- no real loss. This can be done by Laplace's method, special case of method of steepest descents.

$$\int_{x_e}^{x_e} e^{\hat{\varphi}(x')/\varepsilon}\, dx'$$



The integrands are very tightly concentrated about their maxima, so can rigorously justify approximating them by Taylor expanding the term in the exponential and keeping only the leading order nontrivial terms.

$$\hat{\varphi}(x') = \hat{\varphi}(x_b) + \overset{0}{\cancel{\left(\frac{d}{dx}\hat{\varphi}\right)}}(x_b)\,(x'-x_b) + \frac{1}{2}\left(\frac{d^2}{dx^2}\hat{\varphi}\right)(x_b)\,(x'-x_b)^2$$

$$\int_{x_b}^{x_e} e^{\hat{\varphi}(x)/\varepsilon}\, dx' \approx \int_{x_b}^{x_e} e^{\left(\hat{\varphi}(x_b) + \frac{1}{2}\left(\frac{d^2\hat{\varphi}}{dx^2}\right)(x_b)(x'-x_b)^2\right)/\varepsilon}\, dx'$$

$$\sim e^{\hat{\varphi}(x_b)/\varepsilon} \int_{x_b}^{x_e} e^{\frac{1}{2}\overset{<0}{\left(\frac{d^2\hat{\varphi}}{dx^2}\right)}(x_b)\,(x'-x_b)^2}\, dx'$$

$$\approx e^{\hat{\varphi}(x_b)/\varepsilon} \underbrace{\int_{-\infty}^{\infty} e^{\frac{1}{2\varepsilon}\left(\frac{d^2\hat{\varphi}}{dx^2}\right)(x_b)\,(x'-x_b)^2}\, dx'}_{\text{Gaussian integral}}$$

$$= e^{\hat{\varphi}(x_b)/\varepsilon} \sqrt{\frac{\pi}{\frac{1}{2\varepsilon}\left|\frac{d^2\hat{\varphi}}{dx^2}(x_b)\right|}}$$

$$\int_{x_e}^{x_0} e^{\hat{\varphi}(x')/\varepsilon}\, dx' \approx e^{\hat{\varphi}(x_b)/\varepsilon} \sqrt{\frac{2\pi\varepsilon}{\left|\frac{d^2\hat{\varphi}}{dx^2}(x_b)\right|}}$$

$$\int_{x_1}^{x_2} e^{-\hat{\varphi}(x'')/\varepsilon}\, dx'' \sim e^{-\hat{\varphi}(x_e)/\varepsilon} \sqrt{\frac{2\pi\varepsilon}{\frac{d^2\hat{\varphi}}{dx^2}(x_e)}}$$

Substituting these into the expression for the flux:

$$J \sim e^{\left(\hat{\varphi}(x_e) - \hat{\varphi}(x_b)\right)/\varepsilon} \frac{\sqrt{\left|\frac{d^2\hat{\varphi}}{dx^2}(x_b)\right| \left|\frac{d^2\hat{\varphi}}{dx^2}(x_e)\right|}}{2\pi}$$

for $\varepsilon \ll 1$

The flux can be understood to be the rate at which particles leave the metastable state and cross the barrier. And just in analogy to radioactive decay, the expected time for a particle to cross the barrier is $1/J$

The exponential term is just $e^{-\Delta F_{bar}/k_B T}$ in nondimensional terms.

energy barrier height