Non-equilibrium stochastic processes
Part II B

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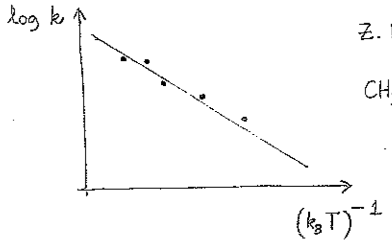
1. Kramers escape

Arrhenius law: temperature dependence of rate constant of a chemical reaction

$$k \sim A e^{-\frac{E_a}{k_B T}}$$

E_a activation energy
k_B Boltzmann constant
T temperature
A pre-exponential factor (could depend on T)
k reaction rate

Svante Arrhenius (1859 – 1927)



Z. Phys. chem. 4 (1889) 226

$CH_3J + C_2H_5ONa \rightarrow CH_3OC_2H_5 + NaJ$

Fig. 1

Hänggi, J. Stat. Phys. 42 (1986) 105

Transition state theory $\underline{x}_0 \rightarrow \underline{x}_R$

Assumptions: ① reduced description in terms of few 'reaction coordinates' $\underline{x}$ (friction due to remaining degrees of freedom)

② Local equilibrium $\underline{x}_0$ (friction and thermal fluctuations give rise to steady state)

③ Reaction $\hat{=}$ escape, no recrossings

④ Saddle $\underline{x}^*$ with one unstable direction

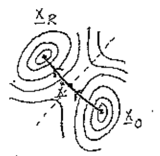


Fig. 2 contours of 'potential surface' $V(\underline{x})$

$$k \sim \frac{|\lambda_1(\underline{x}^*)|}{2\pi\gamma}\sqrt{\frac{\lambda_1(\underline{x}_0)\cdots\cdots\lambda_N(\underline{x}_0)}{|\lambda_1(\underline{x}^*)|\,\lambda_2(\underline{x}^*)\cdots\lambda_N(\underline{x}^*)}}\; e^{-\frac{E_a}{k_B T}}$$

$0<\lambda_1(\underline{x}_0)<\cdots<\lambda_N(\underline{x}_0)$ eigenvalues of Hessian $\underset{\sim}{H}(\underline{x}_0)$ with elements $H_{ij} = \frac{\partial V_i}{\partial x_j}(\underline{x}_0)$.

$\lambda_1(\underline{x}^*) < 0 < \lambda_2(\underline{x}^*) < \cdots < \lambda_N(\underline{x}^*)$ eigenvalues of $\underset{\sim}{H}(\underline{x}^*)$.

Kramers (1894 – 1952) formulated model explaining the mechanism underlying Arrhenius law: thermal fluctuations.

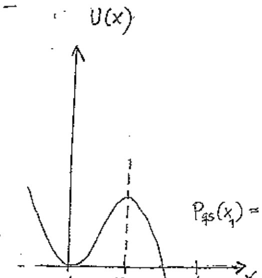


Fig. 3

Escape of 'particle' from metastable potential $U(x)$, position x is interpreted as a reaction coordinate describing the development of the reaction.

$$\dot{x} = \frac{p}{m}\,, \quad \dot{p} = -\gamma p - U'(x) + f(t)$$

Effect of thermal fluctuations: random force $f(t)$

$$\langle f(t) \rangle = 0 \qquad \langle\cdot\rangle \text{ ensemble average}$$

$$\langle f(0) f(t) \rangle = 2m\gamma k_B T\,\delta(t)\,.$$

with $\gamma = \frac{6\pi\eta a}{m}$

η (dynamic) viscosity
a particle size
m particle mass

Fluctuation-dissipation theorem.
Maxwell-Boltzmann distribution.

Maxwell-Boltzmann distribution

Stochastic process for the momentum of a Brownian particle (Ornstein & Uhlenbeck Phys. Rev. 36 (1930) 823)

$$\dot{p} = -\gamma p + f(t)$$

Write down corresponding Fokker-Planck equation

$$\frac{\partial}{\partial t} P(p,t) = \frac{\partial}{\partial p}\left[-a_1(p) + \frac{1}{2}\frac{\partial}{\partial p} a_2(p)\right] P(p,t)$$

$$a_1(p) = \frac{\langle \delta p \rangle_p}{\delta t}, \quad a_2(p) = \frac{\langle \delta p^2 \rangle_p}{\delta t}$$

$$\delta p = -\gamma p \delta t + \int_0^{\delta t} dt' f(t').$$

$$a_1(p) = -\gamma p.$$

$$a_2(p) = \frac{\langle \delta p^2 \rangle_p}{\delta t}$$

$$\langle \delta p^2 \rangle = \int_0^{\delta t} dt_1 \int_0^{\delta t} dt_2 \, \langle f(t_1) f(t_2) \rangle$$

$$= 2 m k_B T \, \delta t$$

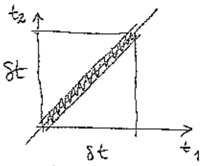


Fig. 4

$$a_2(p) = \frac{\langle \delta p^2 \rangle_p}{\delta t} = 2 m \gamma k_B T$$

Steady-state solution of Fokker-Planck equation

$$\frac{\partial}{\partial p}\left[\gamma p + m\gamma k_B T \frac{\partial}{\partial p}\right] P_s(p) = 0$$

$$P_s(p) \propto e^{-\frac{p^2}{2mk_BT}} \qquad \frac{p^2}{2mk_BT} = \frac{\frac{1}{2}mv^2}{k_BT}$$

Maxwell-Boltzmann distribution.

Back to Kramers' model.

To simplify consider overdamped limit (large damping ↝ set inertial term $\dot{p}$ to zero)

$$\dot{p} = 0$$

$$\dot{x} = \frac{-U'(x)}{m\gamma} + \frac{f(t)}{m\gamma}$$

Fokker-Planck equation

$$\frac{\partial P(x,t)}{\partial t} = \frac{\partial}{\partial x}\left[\frac{U'(x)}{m\gamma} + \frac{\partial}{\partial x} D\right] P(x,t)$$

with 'diffusion constant'

$$D = \frac{k_B T}{m\gamma}.$$

Still difficult to solve. Further approximation: 'quasi-steady state'

$$\frac{\partial P(x,t)}{\partial t} \approx 0. \qquad \left(\text{large barrier height}\right)$$

Write Fokker-Planck equation in the form of a continuity equation

$$\frac{\partial P}{\partial t} + \frac{\partial J}{\partial x} = 0$$

with probability current

$$J(x,t) = \left[-\frac{U'(x)}{m\gamma} - \frac{\partial}{\partial x} D\right] P(x,t)$$

Steady-state assumption corresponds to

$$J(x,t) = \text{constant} \equiv J,$$

that is

$$\left[-\frac{U'(x)}{m\gamma} - \frac{\partial}{\partial x} D\right] P_{qs}(x) = J.$$

Solve for $P_{qs}(x)$ by finding a so-called 'integrating factor' $\alpha(x)$ satisfying

$$\alpha(x)\left[-\frac{U'(x)}{m\gamma} - \frac{\partial}{\partial x} D\right] P_{qs}(x) = -\frac{\partial}{\partial x}\left[\alpha(x) D P_{qs}(x)\right]$$

Two steps: ① find $\alpha(x)$, ② once found determine $P_{qs}(x)$ from

$$-\frac{\partial}{\partial x}\left[\alpha(x) D P_{qs}(x)\right] = \alpha(x) J$$

$$P_{qs}(x) = -\frac{J}{\alpha(x) D} \int_{x_1}^{x} dx' \alpha(x')$$

$$= \frac{J}{\alpha(x) D} \int_{x}^{x_1} dx' \alpha(x')$$

Find integrating factor

$$-\frac{\alpha(x)\,U'(x)}{m\gamma} = -D\,\frac{\partial \alpha}{\partial x}$$

$$\log \alpha(x) = \frac{1}{m\gamma D}\int_{x_{min}}^{x} dx'\,U'(x') + \text{constant}$$

$$= \frac{U(x)}{k_B T} + \text{constant}$$

assume $U(x_{min}) = 0$.

$$\alpha(x) = C\, e^{\frac{U(x)}{k_B T}}$$

Put the two results together:

$$P_{qs}(x) = \frac{J}{D}\, e^{-\frac{U(x)}{k_B T}} \int_{x}^{x_1} dx\, e^{\frac{U(x)}{k_B T}}$$

Normalisation

$$\int_{-\infty}^{x_1} dx\, P_{qs}(x) = 1\,.$$

$$\frac{J}{D}\int_{-\infty}^{x_1} dx\, e^{-\frac{U(x)}{k_B T}} \int_{x}^{x_1} dx'\, e^{\frac{U(x')}{k_B T}} = 1$$

Escape rate ≙ reaction rate = J

$$J = D\left[\int_{-\infty}^{x_1} dx\, e^{-\frac{U(x)}{k_B T}} \int_{x}^{x_1} dx'\, e^{\frac{U(x')}{k_B T}}\right]^{-1}$$

Example

$$U(x) = -\frac{x^3}{3} - \frac{x^2}{2} + \frac{1}{6}\,.$$

$x_{min} = -1$, $U_{min} = 0$

$x_{max} = 0$, $U_{max} = \frac{1}{6}$

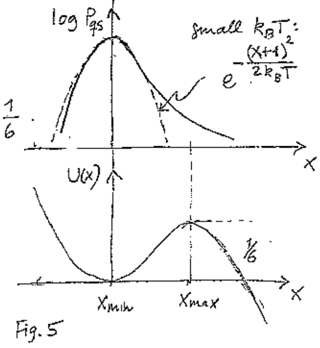


Fig. 5

Further simplification: evaluate both integrals in saddle-point approximation.

$$U(x') = U(x_{max}) - \frac{1}{2}\left|U''(x_{max})\right|\,\delta x'^2$$

$$U(x) \approx \frac{1}{2}\,U''(x_{min})\,\delta x^2 \qquad \Big|\, U(x_{min}) = 0$$

$$\int_{x}^{x_1} dx'\, e^{\frac{U(x')}{k_B T}} \approx e^{\frac{E_a}{k_B T}} \cdot \int_{-\infty}^{\infty} d\,\delta x'\, e^{-\frac{\frac{1}{2}|U''(x_{max})|\,\delta x'^2}{k_B T}}$$

$$\approx e^{\frac{E_a}{k_B T}} \sqrt{\frac{2\pi k_B T}{|U''(x_{max})|}}$$

$$\int_{-\infty}^{x_1} dx\, e^{-\frac{U(x)}{k_B T}} \approx \sqrt{\frac{2\pi k_B T}{U''(x_{min})}}$$

Find

$$J = \frac{D}{\sqrt{\frac{2\pi k_B T}{U''(x_{min})}}\; e^{\frac{E_a}{k_B T}}\; \sqrt{\frac{2\pi k_B T}{|U''(x_{max})|}}}$$

$$J = \frac{\varkappa\,\omega_0}{2\pi}\, e^{-\frac{E_a}{k_B T}}$$

$\omega_a = \sqrt{\frac{|U''(x_{max})|}{m}}$, $\omega_0 = \sqrt{\frac{U''(x_{min})}{m}}$, $\varkappa = \frac{\omega_a}{\gamma}$

This is the same as Eq. (17) in Kramer's paper. Arrhenius law.

$\frac{\omega_0}{2\pi}$	frequency of oscillation in the bottom of the potential well
E_a	barrier height
$\varkappa$	degree of instability of 'transition state'

Assumptions

- quasi-steady state
- large damping
- low k_BT

Underdamped limit

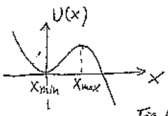


Fig. 6

$$\dot{x} = \frac{p}{m}, \quad \dot{p} = -\gamma p - U'(x) + f(t)$$

Fokker-Planck equation for x and p

$$\frac{\partial \underline{P}}{\partial t} = \left[-\frac{p}{m}\frac{\partial}{\partial x} + mU'(x)\frac{\partial}{\partial p} + \gamma \frac{\partial}{\partial p} p + \gamma m^2 k_B T \frac{\partial^2}{\partial p^2} \right] \underline{P}$$

where $\underline{P} = \underline{P}(x, p, t)$.

Aim: compute escape rate in the limit $\gamma \to 0$.
Consider first $\gamma = 0$

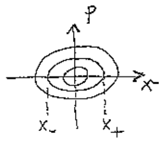
$$\dot{x} = \frac{p}{m}, \quad \dot{p} = -U'(x)$$

$$H = \frac{p^2}{2m} + U(x) \qquad \dot{x} = \frac{\partial H}{\partial p}, \quad \dot{p} = -\frac{\partial H}{\partial x}$$

$$= \text{constant} \equiv E$$

Harmonic oscillator

$$U(x) = \frac{m\omega_0^2 x^2}{2}$$



Turning points $(p=0)$

$$x_\mp = \mp \sqrt{\frac{2E}{m\omega_0^2}}$$

Action

$$I = \frac{1}{2\pi} \oint p\,dx = \frac{1}{2\pi}\, 2 \int_{x_-}^{x_+} dx \sqrt{2m(E - U(x))} = \frac{E}{\omega_0}$$

Anharmonic potential

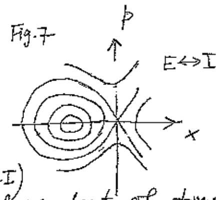


Fig. 7

$$\omega(I) = \frac{\partial E}{\partial I}$$

Energy E (equivalently action I) is 'conserved' that is independent of time.
Motion inside well is periodic with frequency ω.

In the limit of small values of γ approximate $\overline{\underline{P}}(x, p, t) \approx P(I, t)$.
averaged over one period

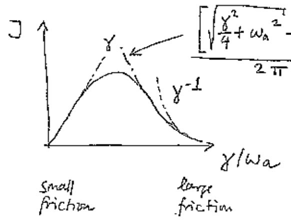
Find after change of variables $p \to I$

$$\frac{\partial}{\partial t} \underline{P} \approx \frac{\partial}{\partial I} \left[\gamma I + \gamma k_B T \frac{I}{\omega(I)} \frac{\partial}{\partial I} \right] \underline{P}$$

Escape rate can be computed in the same way as before ($\underline{P} = 0$ at $E = E_a$)

$$J = \frac{\gamma k_B T}{\int_0^{E_a} dE \, \frac{e^{-\frac{E}{k_B T}}}{\omega(E)} \int_E^{E_a} dE' \, \frac{e^{\frac{E'}{k_B T}}}{I(E')}}$$

$$\approx \frac{\gamma I(E_a)}{k_B T} \omega_0 e^{-\frac{E_a}{k_B T}} \qquad k_B T \gg \gamma I(E_a)$$



$$\frac{\left[\sqrt{\frac{\gamma^2}{4} + \omega_a^2} - \frac{\gamma}{2}\right] \omega_0}{2\pi\omega_a} e^{-\frac{E_a}{k_B T}}$$

$$\sqrt{\frac{\gamma^2}{4} - \omega_a^2} - \frac{\gamma}{2} \sim \frac{\omega_a^2}{\gamma}$$

Fig. 8

generalisations

1. multi-dimensional case
2. force not given by potential gradient.
   $J \sim A e^{-S/k_B T}$ S 'action'
   A prefactor much more difficult to compute
3. improved approximation schemes: inverse friction expansion
   continued-fraction approximation
   → Risken The Fokker Planck equation, Springer 1989

First-passage time problems

2. Correlated random walks

One-dimensional model describing random walkers in spatially smooth random displacement field.

Motivation: understand spatial clustering of inertial particles suspended in incompressible turbulent flow $\underline{u}(\underline{r},t)$; equation of motion $\ddot{\underline{r}} = \gamma(\underline{u}(\underline{r},t) - \dot{\underline{r}})$, Stokes damping γ. Individual particles diffuse but inertial effects give rise to clustering in smooth flows

initial condition steady state

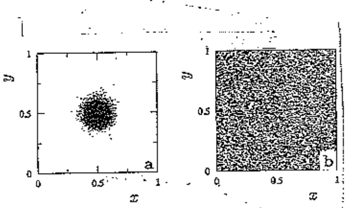


Fig. 9: particles diffusing independently

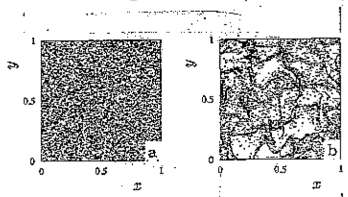


Fig. 10: particles diffusing in correlated incompressible flow

One-dimensional random walk

$$x(t_{n+1}) = x(t_n) + f(t_n)$$

Take $t_n = n\,\delta t$ and $f_n = f(t_n)$. The f_n are independent gaussian random variables with

$$\langle f_n \rangle = 0$$
$$\langle f_n f_m \rangle = \sigma^2 \delta_{nm}$$

Law of diffusion

$$\langle [x(t) - x(0)]^2 \rangle = 2Dt$$

with diffusion constant $D = \frac{\sigma^2}{2\delta t}$

Correlated random walks

N particles in spatially smooth displacement field $f(x, t_n)$: ($t_n = n\,\delta t$ as before)

$$x_i(t_{n+1}) = x_i(t_n) + f(x_i(t_n), t_n) \qquad (*)$$

$i = 1, \dots, N$ and $n = 0, 1, 2, \dots$.

$$\langle f(x, t_n) \rangle = 0$$
$$\langle f(0, t_n) f(x, t_m) \rangle = \sigma^2 \delta_{nm} e^{-\frac{(x-x')^2}{2\eta^2}}$$

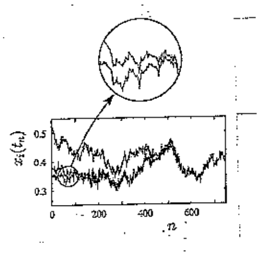


Fig. 11 Path coalescence in correlated random walks

Determine fate of initially close trajectories. Does their separation $\delta x(t_n)$ converge or diverge? Expect

$$\delta x(t_n) \sim \delta x(t_0)\, e^{\lambda t_n}$$

Compute λ

$$\lambda = \lim_{n\to\infty} \frac{1}{t_n} \left\langle \log \left| \frac{\delta x(t_n)}{\delta x(t_0)} \right| \right\rangle$$

as before average over independent realisations of f.

Is λ positive or negative?

$$= \lim_{n\to\infty} \frac{1}{t_n} \left\langle \log \prod_{j=1}^{n} \left| \frac{\delta x(t_j)}{\delta x(t_{j-1})} \right| \right\rangle$$

$$= \lim_{n\to\infty} \frac{1}{t_n} \sum_{j=1}^{n} \left\langle \log \left| \frac{\delta x(t_j)}{\delta x(t_{j-1})} \right| \right\rangle$$

But from Eq. (*) on p. 17

$$\delta x(t_j) \approx \delta x(t_{j-1}) + \frac{\partial f}{\partial x} \cdot \delta x(t_{j-1})$$

$$\frac{\delta x(t_j)}{\delta x(t_{j-1})} = 1 + \frac{\partial f}{\partial x}(x(t_{j-1}), t_{j-1})$$

gaussian random variable $A = \frac{\partial f}{\partial x}$

$$P(A) = \frac{1}{\sqrt{2\pi\sigma^2/\eta^2}}\, e^{-\frac{A^2}{2\sigma^2/\eta^2}}$$

Find

$$\lambda = \frac{1}{\delta t} \left\langle \log \left| 1 + \frac{\partial f}{\partial x} \right| \right\rangle$$

Simplify further by expanding the logarithm (assume that $\langle (\frac{\partial f}{\partial x})^2 \rangle = \frac{\sigma^2}{\eta^2} \ll 1$).

$$\lambda \approx -\frac{1}{2\delta t} \frac{\sigma^2}{\eta^2}.$$

This result ($\lambda < 0$) explains path coalescence.

Do better by expanding to higher orders. Ignore modulus in argument of log

$$\log(1+z) = \sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{k} z^k$$

Find series expansion $\qquad s = \sigma/\gamma$

$$\lambda \sim -\frac{1}{\delta t}\left[\sum_{l=1}^{\infty} \frac{1}{2l}\,\frac{(2l)!}{2^l\, l!}\, s^{2l}\right]$$

Coefficients c_l grow factorially:

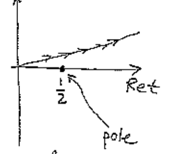
$$c_l \sim s_0^{-l}\,(l-1)! \qquad \text{with } s_0 = \tfrac{1}{2}$$

The series is thus asymptotically divergent.
Try to resum with Padé-Borel resummation.
Define Borel sum

$$B(s^2) = \sum_{l=1}^{\infty} \frac{c_l}{l!}\, s^{2l}$$

This series has a finite radius of convergence $s^2 < \frac{1}{2}$. Now try

$$\lambda \sim \mathrm{Re} \int_{\mathcal{C}} dt\; B(s^2 t)\, e^{-t}$$



This does not work because Borel sum has finite radius of convergence.

Try Padé approximants of $B(z)$

$$B_{[2,2]}(z) = \frac{\frac{z}{2} - \frac{51 z^2}{104}}{1 - \frac{45 z}{26} + \frac{145 z^2}{312}} \qquad (a_0 = 0)$$

$$B_{[3,3]}(z) = \frac{a_0 + a_1 z + a_2 z^2 + a_3 z^3}{1 + b_1 z + b_2 z^2 + b_3 z^3}$$

$$B_{[m,n]} = \frac{\sum_{k=0}^{m} a_k z^k}{1 + \sum_{k=1}^{n} b_k z^k}$$

Determine coefficients such that

$$B(z) - B_{[m,n]}(z) \sim c_{m+n+1}\, z^{m+n+1} + \text{higher orders}$$

Obtain fast convergence

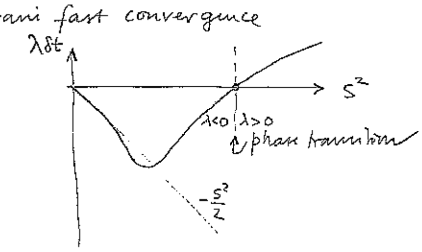


Fig. 12

3. One-dimensional model for inertial particles

Stokes equation

$$\ddot{x} = \gamma\,(u(x,t) - \dot{x})$$

random flow

$$\dot{x} = \frac{p}{m}, \quad \dot{p} = -\gamma p + f(x,t) \qquad f = m\gamma u$$

$$\langle f(x,t)\rangle = 0$$

$$\langle f(0,0)\, f(x,t)\rangle = C(|x|,|t|)$$

for example $\sigma^2 e^{-\frac{x^2}{2\eta^2} - \frac{t^2}{2\tau^2}}$

Aim: determine whether path coalescence occurs by computing Lyapunov exponent

$$\lambda \sim \frac{1}{t}\left\langle \log\left|\frac{\delta x(t)}{\delta x(0)}\right|\right\rangle .$$

Expect $\lambda > 0$ for small damping (random motion).
For large damping: $\dot{x} \approx \frac{f(x,t)}{m\gamma}$
By comparison with (*) on p. 17 expect that $\lambda < 0$.

As before linearise equation of motion

$$\delta\dot{x} = \frac{\delta p}{m} \qquad \delta\dot{p} = -\gamma\,\delta p + A\,\delta x$$

where $A = \frac{\partial f}{\partial x}$ is random variable.
Problem: ① fluctuations of A depend on (x_t, p_t). ② multiplicative noise.

Solve ② by introducing new variables

$$\begin{matrix} \delta x \\ \delta p \end{matrix} \;\longrightarrow\; \begin{matrix} \delta x \\ z = \frac{\delta p}{\delta x} \end{matrix}$$

Find:

$$\delta\dot{x} = \frac{z}{m}\,\delta x$$

$$\dot{z} = -\gamma z - \frac{z^2}{m} + A \qquad (*)$$

Now assume that force fluctuates rapidly. Expect that fluctuations of A do not depend on whether they are evaluated at (x_0, p_0) or along path (x_t, p_t) $\longrightarrow$ ergodicity. Solves problem ① (but at a price).

Then

$$\dot z = -\gamma z - \frac{z^2}{m} + A \qquad (*)$$

advantages:
- noise additive
- z is stationary process
- one-dimensional process
- caustics (see below)

independent of x_t, p_t, and δx_t. Moreover

$$\lambda = \lim_{t\to\infty} \frac{1}{t} \left\langle \log\left|\frac{\delta x_t}{\delta x_0}\right|\right\rangle$$

can be evaluated as follows: from

$$\frac{d}{dt}\log\frac{\delta x_t}{\delta x_0} = \frac{z_t}{m}$$

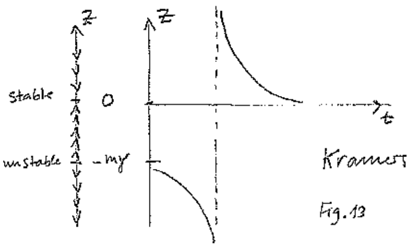
it follows

$$\frac{1}{t} \log \frac{\delta x_t}{\delta x_0} = \frac{1}{t}\int_0^t dt' \,\frac{z(t')}{m}.$$

Thus

$$\lambda = \frac{\langle z\rangle}{m}.$$

Find steady-state solution of (*) to compute λ. Consider (*) first in the absence of noise ($A=0$):



Kramers escape process!

Fig. 13

Introduce dimensionless variables

$$t' = \gamma t \qquad z' = \sqrt{\frac{\gamma}{\mathcal{D}}}\, z \qquad \mathcal{D} = -\frac{1}{2}\frac{\partial^2}{\partial x^2}\int_{-\infty}^{\infty} dt\, C(x,t)$$

Drop primes and write down Fokker-Planck equation

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial z}\left[z+\varepsilon z^2 + \frac{\partial}{\partial z}\right]P \qquad (*)$$

with

$$\varepsilon^2 = \frac{\mathcal{D}}{m\gamma^3} \qquad \text{and} \qquad \frac{\lambda}{\gamma} = \varepsilon\langle z\rangle \qquad (**)$$

The steady-state solution is obtained in the same way as in chapter 1 (by finding an integrating factor)

$$P_{qs}(z) = J e^{-\phi(z)}\int_{-\infty}^{z} dz'\, e^{\phi(z)}$$

with

$$\phi(z) = \frac{\varepsilon z^3}{3}+\frac{z^2}{2}$$

$$J^{-1} = -\int_{-\infty}^{\infty} dz\, e^{-\phi(z)}\int_{-\infty}^{z} dz'\, e^{\phi(z)}.$$

Lyapunov exponent

$$\frac{\lambda}{\gamma} = \varepsilon \left.\frac{\Psi'(\alpha)}{\Psi(\alpha)}\right|_{\alpha=0}, \qquad \Psi(\alpha) = \int_{-\infty}^{\infty} dz\, e^{\alpha z-\phi(z)}\int_{-\infty}^{z} dz'\, e^{\phi(z')}$$

This can be written as

$$\frac{\lambda}{\gamma} = -\frac{1}{2}\,\mathrm{Re}\left[\frac{1}{\sqrt{z}}\frac{Ai'(z)}{Ai(z)}+1\right] \qquad z = \frac{(i\varepsilon)^{-4/3}}{4}$$

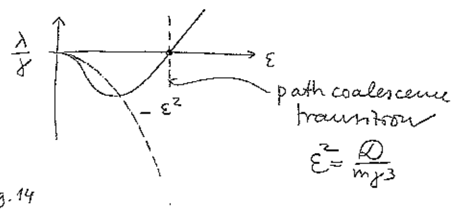


Fig. 14

3.1. WKB approximation (large-deviation theory)

Approximation scheme for finding (quasi-) steady state solution of Fokker-Planck equation.
Example: equation (*) from p. 25.

Change variables $z \to \frac{z}{\varepsilon}$ and drop index 'qs'

$$\frac{\partial}{\partial z}\left(z+z^2+\varepsilon^2\frac{\partial}{\partial z}\right)P(z) = 0 \qquad (*)$$

WKB approach: try ansatz

$$P(z) = \mathcal{A}\, e^{-\frac{1}{\varepsilon^2}\left(S_0(z)+\varepsilon^2 S_2(z)+\dots\right)}$$

Insert and expand in powers of ε^2. Obtain that the following condition must hold to lowest order in ε.

$$[S_0'(z)]^2 + v(z)\, S_0'(z) = 0 \qquad (*)$$

With $v(z) = -z-z^2$. This is the drift velocity in the stochastic differential equation (*) on p. 24, it reads in dimensionless variables

$$\dot z = v(z) + A$$

drift — noise (diff. constant ε^2 – dim. less variables)

Introduce $p = S_0'(z)$ and write this as

$$H(z,p) = 0 \quad \text{with} \quad H(z,p) = p^2 + V(z)p$$

This is interpreted as the Hamilton function of a Hamiltonian system.

$$\dot{z} = \frac{\partial H}{\partial p} \qquad (*)$$
$$\dot{p} = -\frac{\partial H}{\partial z}$$

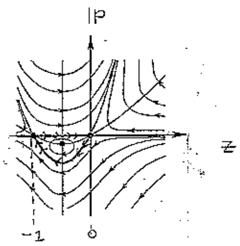
Then

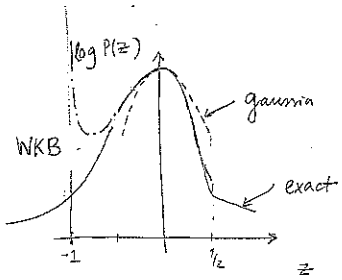
$$S_0(z) = \int^{z} p\, dz'$$

(Hamilton-Jacobi theory; $S_0(z)$ is called Maupertuis's action)

In order to find $P(z)$ near (quasi-) stable fixed point $z=0$ must integrate $(*)$ from $z=0$.
Must satisfy $H=0$ at every instance.

$$H = p^2 + V(z) = 0$$
$$\Rightarrow p = -V(z)$$
$$S_0(z) = \int_0^{z} dz\,(z+z^2)$$
$$= \frac{z^2}{2} + \frac{z^3}{3}$$
$$P(z) \sim e^{-\frac{1}{\varepsilon^2}\left(\frac{z^2}{2}+\frac{z^3}{3}\right)}$$





In order to compute the prefactor must consider next order in ε. Obtain

$$S_2(z) = \begin{cases} \log|z+z^2| + \text{constant} \\ \text{constant} \quad \text{when } S_0(z) = \text{constant} \end{cases}$$

This gives two possible solutions

$$P(z) \sim \begin{cases} |z+z^2|^{-1}\, e^{-\frac{1}{6\varepsilon^2}} & (*) \\ e^{-\frac{1}{\varepsilon^2}\left[\frac{z^2}{2}+\frac{z^3}{3}\right]} & (**) \end{cases}$$

Solution $(**)$ applies near $z=0$, solution $(*)$ in tails. Need to match so that overall $P(z)$ is smooth.

But: singularity at $z=-1$ (c.f. turning point in quantum oscillator)

3.2. Perturbation theory

Approximation scheme for finding (quasi-) steady state solution of FP equation

Example: equation $(*)$ from p.25:

$$\frac{\partial}{\partial z}\left[z + \varepsilon z^2 + \frac{\partial}{\partial z}\right] P(z) = 0 \qquad (*)$$

Aim: find an algebraic method to compute $P(z)$ in powers of ε. Note that for $\varepsilon = 0$

$$P_0(z) \propto e^{-z^2/2}$$

is unique normalisable solution.
Looks like ground state of quantum harmonic oscillator in position (z-) representation. Try to map problem to quantum problem and use raising and lowering operators.

First step: Dirac notation
Write $(*)$ as

$$\hat{F}|P\rangle = 0 \quad \text{with} \quad P(z) \equiv \langle z|P\rangle$$
$$\frac{\partial}{\partial z}\left[z+\varepsilon z^2+\frac{\partial}{\partial z}\right]P(z) \equiv \langle z|\hat{F}|P\rangle$$

$$\langle f|\hat{F}|g\rangle = \int_{-\infty}^{\infty} dz\, \langle f|z\rangle\langle z|\hat{F}|g\rangle$$
$$= \int_{-\infty}^{\infty} dz\, f(z)\, \vec{\partial}_z\left[z+\varepsilon z^2+\vec{\partial}_z\right] g(z)$$

This is not equal to

$$\langle g|\hat{F}|f\rangle = \int_{-\infty}^{\infty} dz\, g(z)\, \vec{\partial}_z\left[z+\varepsilon z^2+\vec{\partial}_z\right] f(z)$$

In other words: the operator $\hat{F}$ is not Hermitian (not equal to its adjoint). Perturbation expansion of non-Hermitian operators is difficult. Try to at least make $\hat{F}_0$ Hermitian

$$\hat{F} = \hat{F}_0 + \varepsilon \hat{F}_1, \qquad \langle z|\hat{F}_0|P\rangle = \partial_z(z+\partial_z)P(z)$$
$$\langle z|\hat{F}_1|P\rangle = \partial_z z^2 P(z)$$

This is accomplished by $|P\rangle \to |Q\rangle = e^{z^2/4}|P\rangle$

$$\hat{H} = e^{z^2/4}\,\hat{F}\,e^{-z^2/4} \qquad \langle z|Q\rangle = e^{z^2/4}\langle z|P\rangle$$

($\hat{H}_0$ and $\hat{H}_1$ are defined accordingly).

Show that $\hat{H}_0$ is Hermitian.

$$\langle z|\hat{H}_0|g\rangle = e^{z^2/4}\,\partial_z(z+\partial_z)\,e^{-z^2/4} g(z)$$
$$= e^{z^2/4}\Big[e^{-z^2/4}g - \frac{z^2}{2}e^{-z^2/4}g + z e^{-z^2/4}g' + \underbrace{\partial_z\left(-\frac{z}{2}e^{-z^2/4}g + e^{-z^2/4}g'\right)}_{= -\frac{1}{2}e^{-z^2/4}g + \frac{z^2}{4}e^{-z^2/4}g - \frac{z}{2}e^{-z^2/4}g' - \frac{z}{2}e^{-z^2/4}g' + e^{-z^2/4}g''}\Big]$$

$$= \left[\tfrac{1}{2} - \tfrac{z^2}{4} + \partial_z^2\right] g(z)$$

The operator $\hat{H}_0 = \partial_z^2 - \frac{z^2}{4} + \frac{1}{2}$ is Hermitian. Looks like harmonic oscillator!

Analogous computation gives

$$\hat{H}_1 = \left(-\partial_z + \tfrac{z}{2}\right) z^2 .$$

Not Hermitian, but can't do better.

<u>general rule</u>

$\boxed{\text{Non-Hermitian FP operator } \hat{F}. \text{ Find steady-state solution } P_0(z). \text{ Then } \hat{H} = P_0(z)^{-\frac{1}{2}} \hat{F}\, P_0(z)^{\frac{1}{2}} \text{ is Hermitian.}}$

<u>Remark</u>: connection to lattice problem: asymmetric hopping in external field. Corresponding diffusion-advection operator is non-Hermitian. How is the above rule applied in lattice problem?

This was the first step.

Second step: Rewrite $\hat{H}_0$ and $\hat{H}_1$ in terms of lowering and raising operators $\hat{a}$ and $\hat{a}^+$

$$\hat{a} = \partial_z + \tfrac{z}{2} \qquad \hat{a}^+ = -\partial_z + \tfrac{z}{2}$$

(Hermitian conjugate of $\hat{a}$)

Find

$$\hat{H}_0 = -\hat{a}^+\hat{a} \qquad \text{and} \qquad \hat{H}_1 = -\hat{a}^+(\hat{a}+\hat{a}^+)^2$$

Third step: diagonalise $\hat{H}_0$. To this end note that

$$[\hat{a},\hat{a}^+]_- = \hat{a}\hat{a}^+ - \hat{a}^+\hat{a} = 1,$$

$$\hat{a}|0\rangle = 0 \qquad \left(\langle z|\hat{a}|0\rangle = \left(\partial_z + \tfrac{z}{2}\right) e^{-z^2/4} = 0\right),$$

$$[\hat{H}_0,\hat{a}^+]_- = -\hat{a}^+ \quad \text{and} \quad [\hat{H}_0,\hat{a}]_- = \hat{a}.$$

Now

$$\begin{aligned} \hat{H}_0\, \hat{a}^+|0\rangle &= \left(\hat{a}^+\hat{H}_0 - [\hat{H}_0,\hat{a}^+]_-\right)|0\rangle \\ &= -\hat{a}^+|0\rangle \\ \hat{H}_0\, \hat{a}^{+2}|0\rangle &= \left(\hat{a}^+\hat{H}_0 - [\hat{H}_0,\hat{a}^+]_-\right)\hat{a}^+|0\rangle \\ &= -2\,\hat{a}^{+2}|0\rangle \\ &\ \ \vdots \end{aligned}$$

Eigenstates

$$|n\rangle = \underbrace{\frac{1}{\sqrt{n!}}}_{\text{normalisation}}(\hat{a}^+)^n|0\rangle \quad \text{with eigenvalues } -n$$

$n = 0, 1, 2, \ldots$

Summary

$$\hat{H}_0|n\rangle = -n|n\rangle$$

$$\hat{a}^+|n\rangle = \sqrt{n+1}\,|n+1\rangle \quad \text{and} \quad \hat{a}|n\rangle = \sqrt{n}\,|n-1\rangle$$

Aim find $|Q\rangle$ satisfying $(\hat{H}_0 + \varepsilon\hat{H}_1)|Q\rangle = 0$ by perturbation theory.

Once that is achieved (next page) compute λ. This is done as follows. Start from (**) on p.25:

$$\begin{aligned} \frac{\lambda}{\gamma} &= \varepsilon\langle z\rangle = \varepsilon\int_{-\infty}^{\infty} dz\, z\, P(z) \\ &= \varepsilon\int_{-\infty}^{\infty} dz\, e^{-z^2/4}\, z\, \underbrace{e^{z^2/4}P(z)}_{Q(z)} \\ &= \varepsilon\, \frac{\langle 0|z|Q\rangle}{\langle 0|Q\rangle} \end{aligned}$$

inserted normalisation factor so that $|0\rangle, |Q\rangle$ need not be normalised (not necessary).

Fourth step perturbation expansion. Write

$$|Q\rangle = |0\rangle + \varepsilon|Q_1\rangle + \varepsilon^2|Q_2\rangle + \ldots$$

Insert into $(\hat{H}_0 + \varepsilon\hat{H}_1)|Q\rangle = 0$. Find

$$\hat{H}_0|Q_{k+1}\rangle + \hat{H}_1|Q_k\rangle = 0.$$

$$|Q_{k+1}\rangle = -\hat{H}_0^{-1}\hat{H}_1|Q_k\rangle \qquad (*)$$

no problem since $\langle 0|\hat{H}_1 = 0$

To determine $|Q_k\rangle$ recursively expand in basis $|n\rangle$

$$|Q_k\rangle = \sum_{n=0}^{\infty} a_{kn}|n\rangle$$

Find recursion for a_{kn} from (*):

$$a_{k+1\,n} = \sum_{m=0}^{\infty} F_{nm}\, a_{km}$$

Kronecker δ

$$F_{nm} = -(2m+1)\sqrt{m+1}\,\delta_{n\,m+1} - \frac{\sqrt{(m+1)(m+2)(m+3)}}{m+3}\,\delta_{n\,m+3} - \sqrt{m}\,\delta_{n\,m-1}$$

This gives

ℓ	c_ℓ
1	1
2	5
3	60
4	1105
5	27120
6	828250
7	30220800

Table 1

$$\frac{\lambda}{\gamma} = -\sum_{\ell=1}^{\infty} c_\ell\, \varepsilon^{2\ell}$$

$$c_{\ell+1} = (6\ell-2)c_\ell + \sum_{j=1}^{\ell} c_j c_{\ell+1-j}, \qquad c_1 = 1$$

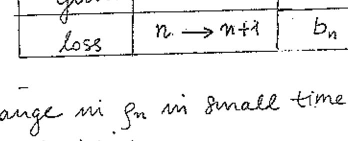
Asymptotic series, $c_\ell \sim S_0^{-1}(\ell-1)!$ with $S_0=\frac{1}{6}$.

Padé-Borel resummation converges quickly to exact result (drawn on p. 26).

3.3. Caustics

4. Population dynamics

One-step processes



gain-loss equation for the probability $\rho_n(t)$ of observing system in state n at time t. Consider effect of births

gain	$n-1 \to n$	b_{n-1}
loss	$n \to n+1$	b_n

Change in ρ_n in small time intervall δt due to births

$$(b_{n-1}\rho_{n-1} - b_n\rho_n)\,\delta t$$

and due to deaths

$$(d_{n+1}\rho_{n+1} - d_n\rho_n)\,\delta t$$

Together

$$\frac{d\rho_n}{dt} = b_{n-1}\rho_{n-1} + d_{n+1}\rho_{n+1} - (b_n+d_n)\rho_n$$

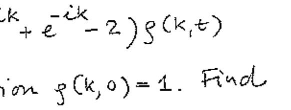
(master equation)

Examples ① Poisson process

$$d_n = 0 \qquad b_n = q$$

$$\frac{d\rho_n}{dt} = q(\rho_{n-1}-\rho_n) \quad \leadsto \quad \rho_n(t) = \frac{(qt)^n}{n!}e^{-qt}$$

② Random walk



$$\frac{d\rho_n}{dt} = \rho_{n+1} + \rho_{n-1} - 2\rho_n, \quad \rho_n(0) = \delta_{n0}$$

Solution by Fourier ansatz $\rho(k,t) = \sum_{n=-\infty}^{\infty} \rho_n(t)e^{ikn}$

$$\frac{d}{dt}\rho(k,t) = (e^{ik} + e^{-ik} - 2)\rho(k,t)$$

with initial condition $\rho(k,0) = 1$. Find

$$\rho(k,t) = e^{2(\cos k - 1)t}$$

Using $e^{z\cos k} = \sum_{n=-\infty}^{\infty} e^{ikn} I_n(z)$ ($I_n(z)$ n-th modified Bessel function)

$$\rho_n(t) = e^{-2t} I_n(2t)$$

Compare to solution of diffusion equation.

③ Steady state of one-step processes $n=0,1,\dots,N$
Convenient way of writing master equation in terms of operators $\mathbb{E}^{\pm}$

$$\mathbb{E}^{\pm} g_n = g_{n\pm 1}$$

In terms of $\mathbb{E}^{\pm}$ the master equation can be written as

$$\frac{d\rho_n}{dt} = (\mathbb{E}^{-}-1)\, b_n \rho_n + (\mathbb{E}^{+}-1)\, d_n \rho_n$$

Steady state

$$0 = (\mathbb{E}^{-}-1)\, b_n \rho_n^{(s)} + (\mathbb{E}^{+}-1)\, d_n \rho_n^{(s)}$$

Using $(\mathbb{E}^{+}-1)\,\mathbb{E}^{-} = -(\mathbb{E}^{-}-1)$

$$0 = (\mathbb{E}^{+}-1)\underbrace{\left[d_n \rho_n^{(s)} - \mathbb{E}^{-} b_n \rho_n^{(s)} \right]}_{\text{must be independent of } n}$$

$$d_n \rho_n^{(s)} - \mathbb{E}^{-} b_n \rho_n^{(s)} = -J$$

probability current

For $n=0$ boundary condition $d_0 = 0$ and $b_{-1}=0$ $\leadsto$ $J=0$. Obtain recursion

$$\rho_n^{(s)} = \frac{b_{n-1}}{d_n}\, \rho_{n-1}^{(s)}$$

So

$$\rho_n^{(s)} = \frac{b_{n-1}\, b_{n-2} \cdots b_0}{d_n\, d_{n-1} \cdots d_1}\, \rho_0^{(s)}$$

Normalisation

$$\sum_{n=0}^{\infty} \rho_n^{(s)} = 1$$

gives

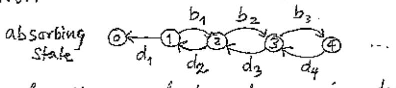
$$\rho_0^{(s)} + \sum_{n=1}^{\infty}\left(\prod_{j=1}^{n} \frac{b_{j-1}}{b_j} \right) \rho_0^{(s)} = 1$$

$$\rho_0^{(s)} = \frac{1}{1+\sum_{n=1}^{\infty}\left(\prod_{j=1}^{n} \frac{b_{n-1}}{d_n}\right)} \quad \text{provided sum converges}$$

If $b_0 = 0$ then $n=0$ is an absorbing state and

$$\rho_n^{(s)} = \delta_{n,0}\,.$$

④ Non-linear birth-death process



Stochastic population dynamics due to random sequence of births and deaths. Population size n

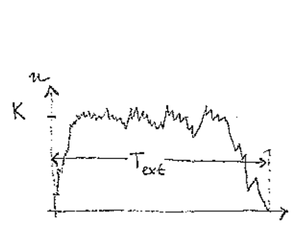
Birth rate $b_n = rn$
Death rate $d_n = \mu n + \frac{r-\mu}{K} n^2$

where r is per capita birth rate, μ per capita death rate, and K is the 'carrying capacity':

$$b_K - d_K = 0 \quad (\text{'equilibrium' condition})$$

Trivial steady state since $b_0 = 0$ (absorbing state). But long-lived quasi-steady state when K is large.

eventual extinction is certain



Fundamental dichotomy of population dynamics.

Compute probability of extinction starting from n individuals.

$$P_n^{ext} = \frac{b_n}{b_n+d_n} P_{n+1}^{ext} + \frac{d_n}{b_n+d_n} P_{n-1}^{ext}\,, \qquad P_0^{ext} = 1$$

$$(b_n+d_n) P_n^{ext} = b_n P_{n+1}^{ext} + d_n P_{n-1}^{ext}$$

$$b_n \left(P_{n+1}^{ext} - P_n^{ext}\right) = d_n \left(P_n^{ext} - P_{n-1}^{ext}\right)$$

Let $\Delta_n = P_{n+1}^{ext} - P_n^{ext}$:

$$\Delta_n = \frac{d_n}{b_n}\Delta_{n-1} \leadsto \Delta_n = \Delta_0 \prod_{j=1}^{n} \frac{d_j}{b_j} \qquad (*)$$

$$P_{n+1}^{ext} = P_1^{ext} + \sum_{i=1}^{n} \Delta_i = P_1^{ext} + (P_1^{ext}-1)\sum_{i=1}^{n}\prod_{j=1}^{i}\frac{d_j}{b_j} \qquad (**$$

Now $R_i = \prod_{j=1}^{i} \frac{d_j}{b_j}$ is an increasing function of i for $i > K$ (since $d_i > b_i$ in this range).
This implies that

$$\sum_{i=1}^{\infty} R_i = \infty\,.$$

We must have $0 \le P_n^{ext} \le 1$ for all values of n.
Relation (**) implies $P_1^{ext} = 1$, and thus $P_n^{ext} = 1$.

Time to extinction starting from n individuals:

$$T_n = \text{Prob}(n\to n+1)\,T_{n+1} + \text{Prob}(n\to n-1)\,T_{n-1}$$
$$+ \text{average time to take a step from state } n$$

$$= \frac{b_n}{b_n+d_n}T_{n+1} + \frac{d_n}{b_n+d_n}T_{n-1} + \frac{1}{b_n+d_n} \qquad T_0 = 0$$

Rewrite as

$$(b_n+d_n)T_n = b_n T_{n+1} + d_n T_{n-1} + 1$$

$$b_n(T_n - T_{n+1}) = d_n(T_{n-1} - T_n) + 1$$

Write $\Delta_n = T_n - T_{n+1}$

$$\Delta_n = \frac{d_n}{b_n}\Delta_{n-1} + \frac{1}{b_n}$$

Inhomogeneous recursion. Homogenous recursion (*) on p. 43 has solution R_n. Seek integrating factor α_n

$$\Delta_n = \alpha_n R_n$$

Must have

$$\alpha_n R_n = \frac{d_n}{b_n}\alpha_{n-1}R_{n-1} + \frac{1}{b_n}$$

$$\alpha_n = \alpha_{n-1} + \frac{1}{b_n R_n}$$

$$\alpha_n = \sum_{j=1}^{n}\frac{1}{b_j R_j}.$$

$$\Delta_n = R_n\sum_{j=1}^{n}\frac{1}{b_j R_j}$$

$$T_n = T_1 - \sum_{i=1}^{n} R_{i-1}\sum_{j=1}^{i-1}\frac{1}{b_j R_j} \qquad \text{set } b_0 = 1$$

Using $T_1 = \sum_{i=1}^{n} R_{i-1}\sum_{j=1}^{\infty}\frac{1}{b_j R_j}$ find

$$T_n = \sum_{i=1}^{n} R_{i-1}\sum_{j=i}^{\infty}\frac{1}{b_j R_j}$$

Alternative procedure (→ van Kampen).

Large-deviation theory for time to extinction

$$\frac{d\rho_n}{dt} = (\mathbb{E}^{-}-1)\,b_n\rho_n + (\mathbb{E}^{+}-1)\,d_n\rho_n$$

$$b_n = rn$$
$$d_n = \mu n + \frac{r-\mu}{K}n^2$$

Consider large but finite values of K. In this limit

$$x = \frac{n}{K}$$

is approximately continuous. Define $b(x)$ and $d(x)$ by

$$b_n = K\,b(x) \;\leadsto\; b(x) = rx$$
$$d_n = K\,d(x) \;\leadsto\; d(x) = \mu x + (r-\mu)x^2$$

Expect that $\rho(x,t)$ is a smooth function of x in the limit of large K. Expand

$$\mathbb{E}^{\pm} g(x) = g\left(x \pm \tfrac{1}{K}\right)$$
$$= \sum_{\ell=0}^{\infty}\frac{(\pm\frac{1}{K})^{\ell}}{\ell!}\frac{d^{\ell}g}{dx^{\ell}}$$
$$= e^{\pm\frac{1}{K}\frac{\partial}{\partial x}}g(x)$$

This gives

$$\frac{\partial}{\partial t}\rho(x,t) = \left(e^{-\frac{1}{K}\frac{\partial}{\partial x}}-1\right)K\,b(x)\,\rho(x,t)$$
$$+ \left(e^{\frac{1}{K}\frac{\partial}{\partial x}}-1\right)K\,d(x)\,\rho(x,t)$$

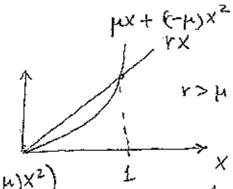
Now expand in K^{-1}. To lowest order

$$\approx \frac{\partial}{\partial x}\big(d(x)-b(x)\big)\rho(x,t)$$

This is a transport or conservation equation

$$\frac{\partial\rho}{\partial t} + \frac{\partial}{\partial x}v(x)\rho = 0 \quad \text{with } v(x) = b(x)-d(x)$$

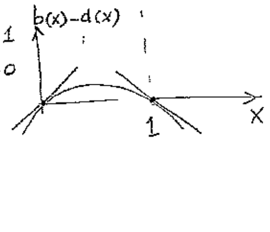
It corresponds to



$$\frac{dx}{dt} = v(x)$$
$$= rx - \left(\mu x + (r-\mu)x^2\right)$$
$$= (r-\mu)\,x\,(1-x)$$

deterministic limit
logistic equation!

For $r>\mu$:
Stable steady state $x^* = 1$
unstable steady state $x^* = 0$



In the presence of fluctuations (finite values of K) expect long-lived quasi-steady state

$$\frac{d\rho_0}{dt} \approx 0$$

just as in Kramers problem.

$$0 \approx \left(e^{-\frac{1}{K}\frac{\partial}{\partial x}} - 1\right) K b(x) \rho_0(x) \qquad (*)$$
$$+ \left(e^{\frac{1}{K}\frac{\partial}{\partial x}} - 1\right) K d(x) \rho_0(x)$$

Ansatz (compare p. 27)

$$\rho_0(x) = e^{-K S_0(x) - S_1(x) - \frac{1}{K} S_2(x) - \dots}$$

Insert into $(*)$. Use $\left(S' \equiv \frac{dS}{dx}\right)$

$$e^{\pm \frac{1}{K}\frac{\partial}{\partial x}} \, e^{-K S_0(x) - S_1(x) - \dots}$$
$$= e^{-K\left(S_0 \pm \frac{S_0'}{K} \dots\right) - \left(S_1 \pm \frac{S_1'}{K}\right)}$$
$$= \rho_0(x)\, e^{\mp S_0'} \left(1 + \text{corrections in } \tfrac{1}{K}\right)$$

Find

$$0 = \rho_0(x)\left[K b(x)\left(e^{S_0'} - 1\right) + K d(x)\left(e^{-S_0'} - 1\right)\right]$$

This corresponds to $(p = S_0')$

$$H(x,p) = 0 \quad \text{with} \quad H(x,p) = b(x)\left(e^{p} - 1\right) + d(x)\left(e^{-p} - 1\right)$$

Analogous to condition on p. 28.

Note: obtain form of H on p. 28 by further approximation. Expand in p. Get

$$H(x,p) \approx \frac{b(x) + d(x)}{2} p^2 + V(x)\, p + \dots$$

The "diffusion constant" $\frac{b(x) + d(x)}{2} \equiv \mathcal{D}(x)$ depends upon x. It vanishes at $x = 0$ (absorbing state).

Now solve for $S_0(x)$ as on p. 28; Hamilton's equations

$$\frac{dx}{dt} = \frac{\partial H}{\partial p} \qquad H(x,p) = 0$$
$$\frac{dp}{dt} = -\frac{\partial H}{\partial x}$$

Boundary conditions

$$\begin{cases} x(t) \longrightarrow x^* = 1 \\ p(t) \longrightarrow 0 \end{cases} \quad \text{as } t \to -\infty$$
$$x(t) \longrightarrow x \quad \text{as } t \to \infty$$

And from $p = S_0'$ one finds

$$S_0(x) = \int_{-\infty}^{\infty} dt \, \frac{dx}{dt} \, p$$

Hamilton's equations take the form

$$\frac{dx}{dt} = b(x) e^{p} - d(x) e^{-p}$$
$$\frac{dp}{dt} = -b'(x)\left(e^{p} - 1\right) - d'(x)\left(e^{-p} - 1\right)$$
$$= -r\left(e^{p} - 1\right) - \left[\mu - 2(r-\mu)x\right]\left(e^{-p} - 1\right)$$

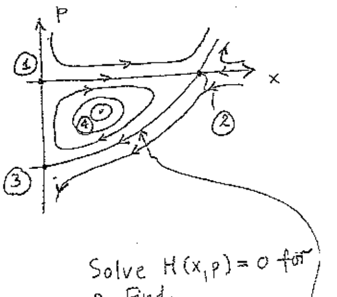
Steady states $\binom{x^*}{p^*}$:

① $\binom{0}{0}$ saddle

② $\binom{1}{0}$ saddle

③ $\binom{0}{\log\frac{\mu}{r}}$ saddle

④ elliptic point $(H \neq 0)$



Solve $H(x,p) = 0$ for p. Find

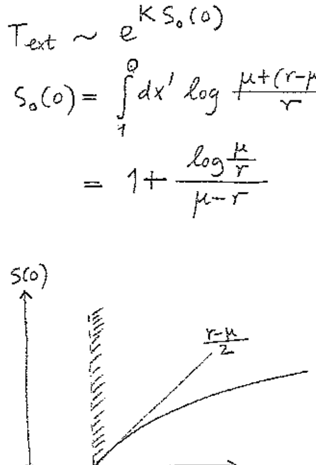
$$p = \log \frac{\mu + (r-\mu)x}{r}$$

$$S_0(x) = \int_1^x dx' \, p(x') = \int_1^x dx' \log \frac{\mu + (r-\mu)x}{r}$$

where $p(x')$ was determined from $H(x,p) = 0$.

Time of extinction (for $r > \mu$)

$$T_{ext} \sim e^{K S_0(0)}$$
$$S_0(0) = \int_1^0 dx' \log \frac{\mu + (r-\mu)x}{r}$$
$$= 1 + \frac{\log \frac{\mu}{r}}{\mu - r}$$



Time-dependent WKB

Example: Poisson process.

$$\frac{d\rho_n}{dt} = q(\mathbb{E}^- - 1)\rho_n \qquad (*)$$

No steady state. Attempt to describe time evolution from initial condition $\rho_n(0) = \delta_{n,0}$.

Assume that n is large and write $\rho_n(t) = e^{-R(n,t)}$ with smooth $R(n,t)$.

Write $\mathbb{E}^- = \exp(-\frac{\partial}{\partial n})$ and insert into (*).
Find

$$H(n,p) + \frac{\partial R}{\partial t} = 0 \quad \text{with} \quad H(n,p) = q(e^p - 1) \quad \text{and} \quad p = \frac{\partial R}{\partial x}$$

Solution for R:

$$R(n_f, t_f) = \int_0^{t_f} dt\, \left(p\dot{n} - H(n,p)\right)$$

along solution of

$$\dot{n} = \frac{\partial H}{\partial p} \qquad \text{initial condition: } n(0) = 0$$
$$\dot{p} = -\frac{\partial H}{\partial n} \qquad \text{final condition: } n(t_f) = n_f$$

Since H does not explicitly depend upon n, the solution of Hamilton's equations is simply

$$\dot{p} = 0 \qquad n(t) = qte^p$$

Must determine p (and thus the energy H) so that $n(t_f) = n_f$:

$$p = \log\frac{n_f}{qt_f}$$

Different from steady-state WKB (p.49) where $H = 0$. The path taken by n is simply

$$n(t) = qte^p = n_f\frac{t}{t_f}$$

Thus $\dot{n} = \frac{n_f}{t_f}$ and

$$R(n_f, t_f) = n_f \log\frac{n_f}{qt_f} - t_f q\left(\frac{n_f}{qt_f} - 1\right)$$
$$= n_f \log n_f - n_f - n_f \log qt_f + qt_f$$

$$\rho_n \sim e^{-R} = e^{-n\log n + n}(qt)^n e^{-qt}$$

Stirling's formula $\log n! \sim n\log n - n$ gives Poisson formula.

Fokker-Planck expansion of Master equation.
Introduce $x = \frac{1}{N}$:

$$\tilde{p}(x,t)\,dx = \rho(n,t)\,dn$$
$$\rightsquigarrow \tilde{p}(x,t) = \rho(xN,t)N$$

Expand

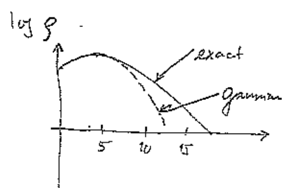
$$(\mathbb{E}^- - 1) \sim -\frac{1}{N}\frac{\partial}{\partial x} + \frac{1}{2N^2}\frac{\partial^2}{\partial x^2} + \dots$$

Find

$$\frac{\partial \tilde{p}}{\partial t} = \frac{\partial}{\partial x}\left(\frac{q}{N} - \frac{q^2}{2N}\frac{\partial}{\partial x}\right)\tilde{p}, \qquad \tilde{p}(x,0) = \delta(x)$$

$$\rightsquigarrow \tilde{p}(x,t) = \frac{N}{\sqrt{2\pi qt}}\, e^{-\frac{(Nx - tq)^2}{2tq}}$$

$$\rightsquigarrow \rho(n,t) = \frac{1}{\sqrt{2\pi qt}}\, e^{-\frac{(n - qt)^2}{2tq}}$$



$t=5,\ q=1$

5, Reaction kinetics

5.1. Branching-annihilation reaction

$$A \xrightarrow{\lambda} A + A \quad \text{and} \quad A + A \xrightarrow{\mu} \emptyset$$

Mean-field theory: neglect fluctuations
Kinetic equation for concentration

$$\frac{dc}{dt} = \lambda c - \mu c^2 \qquad c = \langle n \rangle$$

(law of mass action). But fluctuations.

Master equation (reaction well-mixed)

$$\frac{d\rho_n}{dt} = \lambda\left[(n-1)\rho_{n-1} - n\rho_n\right] + \mu\left[\frac{(n+2)(n+1)}{2}\rho_{n+2} - \frac{n(n-1)}{2}\rho_n\right]$$
$$= \lambda(\mathbb{E}^- - 1)n\rho_n + \frac{\mu}{2}\left((\mathbb{E}^+)^2 - 1\right)n(n-1)\rho_n$$

Moment equations. Derive equations for the rate of change of $\langle n \rangle$, $\langle n^2 \rangle$, and so forth.

$$\frac{d\langle n\rangle}{dt} = \sum_{n=0}^{\infty} n \frac{dP_n}{dt}$$

$$= \lambda \sum_{n=0}^{\infty} \left((n-1)n\rho_{n-1} - n^2\rho_n \right)$$

$$+ \frac{\mu}{2} \sum_{n=0}^{\infty} \left((n+2)(n+1)n\,\rho_{n+2} - n^2(n-1)\rho_n \right)$$

$$m(m-1)(m-2) - m^2(m-1) = -2m^2+2m$$

$$= \lambda \sum_{m=0}^{\infty} m\rho_m$$

$$- \mu \sum_{m=0}^{\infty} (m^2+m)\rho_m$$

Obtain

$$\frac{d\langle n\rangle}{dt} = -\mu\langle n^2\rangle + (\lambda+\mu)\langle n\rangle .$$

Different from mean-field equation (*) on p. 55.
Neglect fluctuations: $\langle n^2\rangle \approx \langle n\rangle^2$ and assume that $\mu \ll \lambda$ (for instance $\mu \sim \frac{\lambda}{N}$ for N large).

$$\frac{d\langle n\rangle}{dt} \approx \lambda\langle n\rangle - \mu\langle n\rangle^2$$

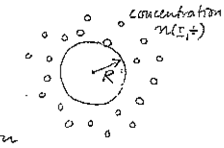
In a similar way

$$\frac{d\langle n^2\rangle}{dt} = -2\mu\langle n^3\rangle + (4\mu+2\lambda)\langle n^2\rangle + (\lambda-2\mu)\langle n\rangle$$

Show: approximately Gaussian fluctuations

Taken from: Krapivsky, Redner, Eli Ben-Naim "A kinetic view of Statistical Physics" CUP

5.2. Reaction rate: diffusive adsorption



Rate of chemical reactions limited by the rate at which reactants come into contact.
Simple example: adsorption of diffusing particles onto surface of a sphere of radius R. Reaction rate

$$k = -\int_{\substack{\text{Surface}\\ \text{of sphere}}} d\underline{s}\,\underline{j}$$

where $\underline{j}$ is the current density of the diffusing molecules:

$$\underline{j}(\underline{r},t) = -D\,\underline{\nabla}\, n(\underline{r},t) . \qquad \text{Fick's law}$$

D is diffusion constant and $n(\underline{r},t)$ concentration of molecules. Symmetry: $n(\underline{r},t) = n(r,t)$.
Diffusion equation in spherical coordinates

$$\frac{\partial n}{\partial t} = D\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} n \qquad = \frac{1}{r}\frac{\partial^2}{\partial r^2} rn$$

$$= D\left[\frac{\partial^2 n}{\partial r^2} + \frac{2}{r}\frac{\partial n}{\partial r}\right]$$

Note: define $\rho(r,t) = n(r,t)\,4\pi r^2$, the probability to find a particle at r.

$$\frac{\partial\rho}{\partial t} = D\frac{\partial}{\partial r}\left[-\frac{2\rho}{r} + \frac{\partial\rho}{\partial r}\right]$$

In two spatial dimensions $\frac{\partial\rho}{\partial t} = D\frac{\partial}{\partial r}\left[-\frac{\rho}{r} + \frac{\partial\rho}{\partial r}\right]$.

Assume steady state (molecules replenished from afar).

$$D\left[-\frac{2\rho_0}{r} + \frac{\partial\rho_0}{\partial r}\right] = -J$$

$$\rho_0(r) = \frac{J}{D}r + Ar^2$$

boundary condition as $r\to\infty$: uniform concentration $A = 4\pi n_0$

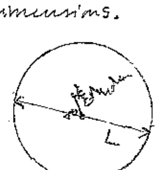
Boundary condition: $\rho_0(R) = 0$. Thus

$$J = -4\pi D n_0 R$$

$$k = 4\pi D n_0 R$$

Reaction rate increases as R increases (larger surface area).

The situation is substantially different in one and two spatial dimensions.
Consider density of points visited in time t

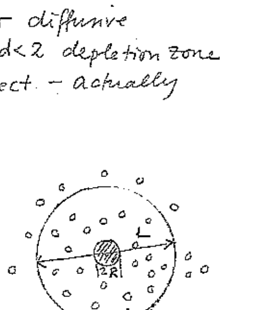


$\#$ points visited $\sim t$

$\#$ volume swept $\sim L^d \sim (Dt)^{d/2}$

$$\text{density of points visited} \sim t^{1-\frac{d}{2}} \to \begin{cases} 0 & d>2 \quad \text{transient} \\ \infty & d<2 \quad \text{recurrent} \end{cases}$$

What does this imply for diffusive absorption problem? For $d<2$ depletion zone forms around absorbing object - actually also for $d=2$.



Outside depletion zone (size $L\sim\sqrt{Dt}$) molecules are unlikely to be absorbed, $n(r,t)\approx n_0$ for $r>L$

Assume that $n(r,t)$ depends only weakly on time in depletion zone.

Solve steady-state equation but with time-dependent boundary condition

$$n(r=L) = n_0 .$$

Steady-state solution

$$n(r) = \begin{cases} A + B r & d=1 \\ A + B \log r & d=2 \end{cases}$$

Boundary condition at R: $n(R) = 0$.
For $d=1$:

$$A = -BR$$

$$A + B\sqrt{Dt} = n_0 \quad \Rightarrow \quad A\left(1 - \frac{\sqrt{Dt}}{R}\right) = n_0$$

$$n(r,t) = \frac{n_0}{1-\frac{\sqrt{Dt}}{R}}\left(1-\frac{r}{R}\right) \sim \frac{R}{\sqrt{Dt}}$$

For $d=2$:

$$A = -B \log R \quad \Rightarrow \quad B = -\frac{A}{\log R}$$

$$A + B \log\sqrt{Dt} = n_0 \quad \Rightarrow \quad A = \frac{n_0}{1 - \log\frac{\sqrt{Dt}}{R}}$$

$$n(r,t) \sim \frac{\log\frac{r}{R}}{\log\frac{\sqrt{Dt}}{R}}$$

(Second term in $A + B\log r$ dominates for large values of t)

Finally compute reaction rate

$$k = D\int d\underline{S}\, \nabla n = 4\pi D \left.\frac{\partial n}{\partial r}\right|_{r=R}$$

In $d=1$ dimensions this gives

$$k(t) \sim \frac{D n_0}{\sqrt{Dt}} \qquad \text{for large } t$$

and in $d=2$ dimensions

$$k(t) \sim \frac{4\pi D n_0}{\log\frac{\sqrt{Dt}}{R}} \qquad \text{for large } t$$

Summary

5.3. Diffusion limited annihilation reactions

In this section the kinetics of the reactions

$$A + A \to \emptyset$$

$$A + A + A \to \emptyset$$

is discussed. Main question: role of fluctuations? Note: the $A + A \to \emptyset$ annihilation reaction is exactly solvable in one spatial dimension. This is discussed in Section 8.3.

First $A + A \to \emptyset$. Particles of radius R and diffusion constant D.

Mean-field theory

$$\frac{dn}{dt} = -2k\, n^2$$

Dimensional analysis:

$$[n] = \frac{1}{L^d} \qquad [k] = \frac{L^d}{T}$$

$$\Rightarrow k \sim D R^{d-2}$$

$$\Rightarrow n(t) \sim \frac{1}{D R^{d-2} t} \qquad (*)$$

But the mean-field prediction fails in one spatial dimension, where the reaction rate cannot depend upon R. From $[k] = \frac{L}{T}$ it thus follows that

$$k \sim \sqrt{\frac{D}{t}}$$

is time-dependent and from $[n] = \frac{1}{L}$

$$n(t) \sim \frac{1}{\sqrt{Dt}}.$$

Alternative derivation see pp. 59-61.

Summary

$$k(t) \sim \begin{cases} \sqrt{\frac{D}{t}} & d=1 \\ \frac{D}{\log\frac{Dt}{R^2}} & d=2 \\ DR & d=3 \quad (\text{p. } 58) \end{cases}$$

$$n(t) \sim \begin{cases} \frac{1}{\sqrt{Dt}} & d=1 \\ \frac{\log\frac{Dt}{R^2}}{Dt} & d=2 \\ \frac{1}{DtR} & d=3 \end{cases}$$

The density decays more slowly than the mean-field prediction (*) on p.58 when $d \leq 2$.

This dimension is referred to as critical dimension d_c. Here $d_c = 2$.

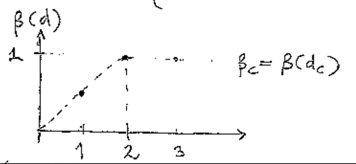
generic situation

For $d < d_c$ mean-field theory fails
$n(t)$ decays more slowly than mean-field result

For $d = d_c$ logarithmic corrections to mean-field result

For $d > d_c$ mean-field theory works

$$n(t) \sim \begin{cases} t^{-\beta(d)} & d < d_c \\ t^{-\beta_c} (\log t)^{\gamma} & d = d_c \\ t^{-\beta_c} & d > d_c \end{cases}$$

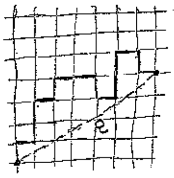


$\beta_c = \beta(d_c)$

Examples

① Self-avoiding random walk

$$R \sim \begin{cases} t & d=1 \\ t^{3/4} & d=2 \\ t^{\nu} & d=3 \quad \nu \approx 0.59 \\ t^{\frac{1}{2}} (\log t)^{\frac{1}{8}} & d=4 \\ t^{1/2} & d>4 \end{cases}$$



end-to-end distance R

The critical dimension is $d_c = 4$.
Flory's theory for self-avoiding random walk is an excellent approximation. It gives

$$\beta = \frac{3}{d+2} \text{ for } d \leq d_c$$

② Three-particle reaction $A+A+A \to \emptyset$.
Caveat: single species three-particle reaction is artificial, requires three molecules to meet.

Mean-field theory (compare p.58)

$$\frac{dn}{dt} \sim -kn^3$$

Define reaction to occur when three particles (radius R) overlap

$$[k] = \frac{L^{2d}}{T} \quad \rightsquigarrow \quad k \sim D R^{2d-2}$$

$$\rightsquigarrow \quad n(t) \sim \frac{1}{\sqrt{kt}} \sim \frac{1}{R^{d-1}} \frac{1}{\sqrt{Dt}}$$

This R-dependence becomes wrong at $d \leq 1$.
Conclude that critical dimension is $d_c = 1$.

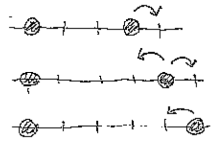
5.4. Single-species reactions in one dimension

Aim: exhibit role of fluctuations. Why does mean-field theory fail?

① Irreversible coalescence $A + A \to A$

Particles hop left or right with rate $\frac{1}{2}$. When a target site is already occupied then particles coalesce (case (c)).

Analyse dynamics in terms of the density of voids, ρ_n



gain in ρ_3
loss in ρ_3
gain in ρ_3

same on left side

Master equation

$$\frac{d\rho_n}{dt} = \rho_{n+1} + \rho_{n-1} - 2\rho_n \qquad \text{for } n \geq 1$$

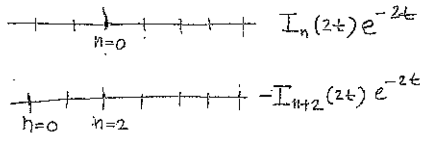
For $n=0$

$$\frac{d\rho_0}{dt} = \rho_1 - 2\rho_0$$

Write this in the form (*) on p. 63 by letting $\rho_{-1} \equiv 0$.

$$\frac{d\rho_n}{dt} = \rho_{n+1} + \rho_{n-1} - 2\rho_n$$

is just a random walk, see example ② on p. 39. Initial condition $\rho_n(0) = \delta_{n,0}$ (all sites occupied). Boundary condition $\rho_{-1}(t)=0$. The general solution on p. 39 $I_n(t)e^{-2t}$ does not satisfy this boundary condition.



$$\rho_n(t) = \left[I_n(2t) - I_{n+2}(2t)\right]e^{-2t}$$

$$= \frac{n+1}{t} I_{n+1}(2t)\, e^{-2t}$$

Now compute particle density from void density:

$$\text{particle density} = \sum_{k=0}^{\infty} \rho_k(t)$$

(a particle at the end of each void).

$$= \sum_{k=0}^{\infty} \frac{k+1}{t} I_{k+1}(2t)\, e^{-2t}$$

$$= \tfrac{1}{2}\left[I_0(2t) + I_1(2t)\right]e^{-2t} \sim \frac{1}{2}\frac{1}{\sqrt{\pi t}} \quad (*)$$

Role of fluctuations.

Mean-field theory (note factor $\frac{1}{2}$ compared with p.)

$$\frac{dn}{dt} = -k n^2 \qquad [n] = L^{-d}$$

$$[k] = \frac{L^d}{T} \Rightarrow k = D R^{d-2}$$

$$\Rightarrow n(t) \sim \frac{1}{R^{d-2} D t}$$

as opposed to (*). Density decays more slowly than mean-field prediction. Reason: fluctuation induced repulsion between particles. If particles were behaving independently then the probability of a short void of length x would behave as

$$P(x) \sim e^{-n(t)x}$$

But void sizes diffuse; $P(x)$ is much larger.

② Irreversible annihilation $A + A \to \emptyset$ in one dimension

Solved analogously to ①. For an initially full system find

$$n(t) = I_0(2t)\, e^{-2t} \sim \frac{1}{\sqrt{4\pi t}}$$

consistent with result on p. 59.

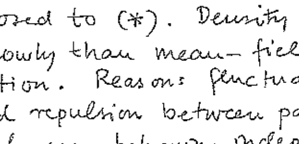
Fundamental principle: domain walls diffuse

6. Brownian motors and ratchets

6.1. Introduction

Aim: understand molecular motors (myosin, kinesin).

Related question: how do microorganisms propel themselves?



At Low Reynolds numbers $Re = \frac{v\,L}{\nu}$ fluid dynamics is governed by neglecting inertial terms in Navier Stokes equation

$$-\underset{\text{pressure}}{\nabla p} + \eta\, \nabla^2 \underset{\text{fluid velocity}}{\underline{v}} = 0 \qquad \eta = \rho_{fluid}\,\nu, \quad [\eta] = \frac{kg}{m\,s}$$

+ incompressibility

Time does not enter in this equation, therefore motion depends only on the sequence of configurations of the oar, not on how quickly (or slowly) any part is executed.

Conclusion: oar must have at least two degrees of freedom to avoid retracing its steps (symmetry breaking).

Role of noise ?

time required to move a by swimming $\sim \frac{a}{V}$ ← propulsion velocity

time required to diffuse distance a $\sim \frac{a^2}{D}$ $\qquad D = \frac{k_B T}{6\pi\eta a}$

At room temperature and in water a bacterium requires more time to diffuse a distance a than it requires to swim the same distance.

But smaller objects diffuse faster, and diffusion is not directed. How can molecular motors in cells achieve directed transport ?

In the cell motion is constrained along actin cables, making it essentially one-dimensional, along a sequence of energy wells and troughs which restrict the diffusion. Aim of the following pages is to show :

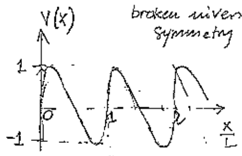
Require symmetry breaking and thermal dis equilibrium for directed transport.

6.2. No current in equilibrium

Brownian particle in asymmetric periodic potential

$$V(x) = V_0 \left(\sin kx + A \sin mkx \right)$$

with $k = \frac{2\pi}{L}$, $m = 0, 1, 2, \ldots$



broken inversion symmetry

$U_0 = 1,\ m = 2,\ A = 0.1$

Equation of motion

$$\dot{x} = P/m$$

$$\dot{p} = -\gamma p - U' + f(t) \qquad (*) \qquad \langle f(t) \rangle = 0$$

$$\langle f(0) f(t) \rangle = 2m\gamma k_B T\, \delta(t)$$

When viscous forces dominate: overdamped limit (p. 6) $\qquad \gamma = \frac{6\pi\eta a}{m}$

$$\dot{x} = -\frac{U'}{m\gamma} + \frac{f}{m\gamma}. \qquad \text{See p. 8}$$

Corresponding Fokker-Planck equation

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial x}\left[\frac{U'}{m\gamma} + \frac{\partial}{\partial x} D \right] P \qquad (**)$$

for probability density $P(x,t)$. Diffusion constant $D = \frac{k_B T}{m\gamma}$ (see p. 6).

Does this system exhibit directed transport ? In other words: is there a finite current $\langle \dot{x} \rangle$?

Write Fokker-Planck equation in terms of probability current $J(x,t)$

$$\frac{\partial P}{\partial t} + \frac{\partial J}{\partial x} = 0 \quad \text{with} \quad J(x,t) = -\left(\frac{U'}{m\gamma} + \frac{\partial}{\partial x} D \right) P(x,t)$$

$$\langle \dot{x} \rangle = \int_{-\infty}^{\infty} dx\, J(x,t)$$

Note: alternative expressions for $\langle \dot{x} \rangle$.
Assume that $J(\pm\infty, t) = 0$ at any finite time t.
Integration by parts gives

$$\langle \dot{x} \rangle = -\int_{-\infty}^{\infty} dx\, x\, \frac{\partial J}{\partial x}(x,t)$$

$$= \frac{d}{dt} \int_{-\infty}^{\infty} dx\, x\, P(x,t) = \frac{d\langle x \rangle_t}{dt}.$$

Alternatively

$$\langle \dot{x} \rangle = \int_{-\infty}^{\infty} dx\, J(x,t) = -\int_{-\infty}^{\infty} dx \left(\frac{U'}{m\gamma} + \frac{\partial}{\partial x} D \right) P(x,t)$$

$$= -\int_{-\infty}^{\infty} dx\, \frac{U'}{m\gamma} P(x,t) \qquad \text{assuming that } P(\pm\infty, t) = 0$$

Could have obtained this directly from (*) on p. ... using the fact that $\langle f(t) \rangle = 0$.

To solve the Fokker-Planck equation introduce 'reduced probability density'

$$\hat{P}(x,t) = \sum_{n=-\infty}^{\infty} P(x+nL, t)$$

and reduced probability current

$$\hat{J}(x,t) = \sum_{n=-\infty}^{\infty} J(x+nL, t)$$

Normalisation

$$1 = \int_{-\infty}^{\infty} dx\, P(x,t) = \sum_{n=-\infty}^{\infty} \int_{x_0+nL}^{x_0+(n+1)L} dx\, P(x,t)$$

$$= \sum_{n=-\infty}^{\infty} \int_{x_0}^{x_0+L} dx\, P(x+nL, t)$$

$$= \int_{x_0}^{x_0+L} dx\, \hat{P}(x,t).$$

Similarly

$$\langle \dot{x} \rangle = \int_{x_0}^{x_0+L} dx\, \hat{J}(x,t).$$

When $P(x,t)$ is a solution of the Fokker-Planck equation (**) on p. then also $P(x+nL,t)$ (since U is periodic with period L).
Therefore

$$\frac{\partial \hat{P}}{\partial t} + \frac{\partial \hat{J}}{\partial x} = 0. \quad \text{with } \hat{J} = -\left(\frac{U'}{m\gamma} + \frac{\partial}{\partial x} D\right)\hat{P}.$$

Compute $\langle \dot{x} \rangle$ in terms of reduced probability current and density.

$$0 = \int_{x_0}^{x_0+L} dx\, x \left(\frac{\partial \hat{P}}{\partial t} + \frac{\partial \hat{J}}{\partial x}\right)$$

$$= \frac{d}{dt}\int_{x_0}^{x_0+L} dx\, x\, \hat{P}(x,t) + \left[x \hat{J}(x,t)\right]_{x_0}^{x_0+L} - \int_{x_0}^{x_0+L} dx\, \hat{J}(x,t)$$

Using (*) on p. one finds

$$\langle \dot{x} \rangle = \int_{x_0}^{x_0+L} dx\, \hat{J}(x,t) = \frac{d}{dt}\int_{x_0}^{x_0+L} dx\, x\, \hat{P}(x,t) + L\hat{J}(x_0,t)$$

Comment Berry's phase
→

Assume that reduced dynamics is in steady state

$$\frac{\partial \hat{P}}{\partial t} = 0$$

Then $\hat{J}(x,t) = \hat{J}_s$ and

$$\langle \dot{x} \rangle = L \hat{J}_s$$

Show that $\hat{J}_s = 0$ in steady state.
Steady-state equation

$$\left(\frac{U'}{m\gamma} + \frac{\partial}{\partial x} D\right)\hat{P} = -\hat{J}_s$$

$$= D\left(\frac{U'}{k_B T} + \frac{\partial}{\partial x}\right)\hat{P}$$

$$= D e^{-\frac{U}{k_B T}} \frac{\partial}{\partial x}\left(e^{\frac{U}{k_B T}} \hat{P}\right) = -\hat{J}_s$$

It follows that

$$\frac{\partial}{\partial x}\left(e^{\frac{U}{k_B T}} \hat{P}\right) = -\frac{1}{D} e^{\frac{U}{k_B T}} \hat{J}_s$$

Integrate from x_0 to x_0+L

$$e^{\frac{U(x_0+L)}{k_B T}} \hat{P}_s(x_0+L) - e^{\frac{U(x_0)}{k_B T}} \hat{P}_s(x_0) = -\frac{\hat{J}_s}{D}\int_{x_0}^{x_0+L} dx\, e^{\frac{U(x)}{k_B T}}. \qquad (*)$$

Since $U(x_0) = U(x_0+L)$ and $\hat{P}_s(x_0) = \hat{P}_s(x_0+L)$, the only solution is $\hat{J}_s = 0$, in other words

$$\langle \dot{x} \rangle = 0$$

$$\hat{P}_s = Z^{-1} e^{-\frac{U(x)}{k_B T}} \quad \text{with } Z = \int_0^L dx\, e^{-\frac{U(x)}{k_B T}}$$

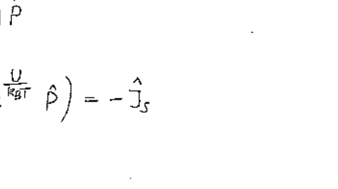
No current in thermal equilibrium.

6.3. Transport under constant load F

$$m\gamma \dot{x} = -U' + F + f(t)$$

Define $U_{eff} = U - Fx$

When $F=0$ have $\langle \dot{x} \rangle = 0$.



Expect

$\langle \dot{x} \rangle < 0$ when $F<0$ and $\langle \dot{x} \rangle > 0$ when $F>0$.

U_{eff} is not periodic, when $F \neq 0$: can have non-zero current in this case. Use (*) on p. :

$$e^{\frac{U_{eff}(x_0+L)}{k_B T}} \hat{P}_s(x_0) - e^{\frac{U_{eff}(x_0)}{k_B T}} \hat{P}_s(x_0) = -\frac{\hat{J}_s}{D}\int_{x_0}^{x_0+L} dx\, e^{\frac{U_{eff}(x)}{k_B T}},$$

Since U'_{eff} is periodic and thus also $\hat{P}_s$.

Now use that

$$U'_{eff}(x+L) - U'_{eff}(x) = 0$$

It follows that $U_{eff}(x+L) - U_{eff}(x) =$ const. $= U_{eff}(L) - U_{eff}(0)$

Thus

$$\hat{P}_s(x) = - \frac{e^{-\frac{U_{eff}(x)}{k_BT}}}{1-e^{\frac{U_{eff}(x+L)-U_{eff}(x)}{k_BT}}} \frac{\hat{J}_s}{D} \int_x^{x+L} dy\, e^{\frac{U_{eff}(y)}{k_BT}}$$

Normalisation gives current:

$$\hat{J}_s = \frac{1}{Z}\left[1 - e^{+\frac{U_{eff}(L)-U_{eff}(0)}{k_BT}}\right] = \frac{1-e^{-FL/k_BT}}{Z}$$

with

$$Z = \frac{1}{D}\int_0^L dx \int_x^{x+L} dy\, e^{\frac{-U_{eff}(x)+U_{eff}(y)}{k_BT}}$$

Note that time-independent probability density does not imply that the current vanishes.

Discuss sign of current:

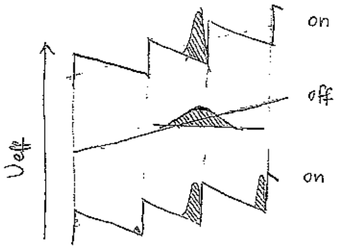
$$\langle \dot{x} \rangle = \frac{L}{Z}\left(1 - e^{-\frac{F \cdot L}{k_BT}}\right)$$

6.4. out-of-equilibrium directed transport

① Make U time-dependent. Assume that $U(x,t)$ is periodic in time with zero mean

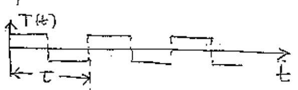
$$\int_0^\tau dt\, U(x,t) = 0$$

Show: despite the fact that U vanishes on average, the system can do work against F!



$\Longrightarrow$ transport

② Modulate temperature periodically in time.
For example



The Fokker-Planck equation

$$\frac{\partial \hat{P}}{\partial t} = \frac{\partial}{\partial x}\left[\frac{U'-F}{m\gamma} + \frac{k_B T(t)}{m\gamma}\frac{\partial}{\partial x}\right]\hat{P}$$

does not admit a time-independent solution since $T(t)$ oscillates. Expect that $\hat{P}$ oscillates in the long-time limit.

$$\langle \dot{x} \rangle = \frac{1}{\tau}\int_t^{t+\tau} dt \int_0^L dx\, \frac{F-U'(x)}{m\gamma}\hat{P}(x,t)$$

Resulting current as a function of F