FLUCTUATIONS IN SMALL SYSTEMS.

Scope:

* Relaxation laws, Laplace transform, small-ε ow distributions
* Diffusion: Fick's laws, PDEs, Fourier transform, Gaussian solution, boundary value problems, continuity equation, master equation
* Random walks, continuum limit, "central limit theorem"
* External force fields: Fokker-Planck equation
* Random forces: From Newton's to Langevin's equation of motion
* First passage time problems, search processes
* Anomalous diffusion: continuous time random walks, fractional Brownian motion, generalised Langevin eq, fractals, percolation
* Ergodicity, ageing
* Fluctuation-dissipation relations, Einstein relations

Literature:

* N van Kampen, Stochastic processes in physics & chemistry
* H Risken, The Fokker-Planck equation
* C Gardiner, Stochastic methods
* BD Hughes, Random walks & random environments vol I
* J Klafter & IM Sokolov, First steps in random walks
* S Chandrasekhar, Rev Mod Phys 15, 1 (1943)
* R Metzler & J Klafter, Phys Rep 339, 1 (2000)

I. Relaxation processes.

Relaxation is the return of a perturbed system into equilibrium, typically characterised by the relaxation time τ.
The characteristic time scale τ allows us to define a dimensionless number quantifying whether during the experimental time T of observation the system reaches equilibrium, or not:

Deborah number $$\underline{\underline{ℸ \equiv \frac{\tau}{T}}}$$ defined by Markus Reiner. ℸ is the Hebrew letter daleth.

Simplest relaxation model: exponential (Debye) relaxation:

$$\underline{\underline{\frac{d\phi(t)}{dt} = -\frac{1}{\tau}\phi(t)}} \quad \text{with initial condition } \phi(0) = \phi_0$$

This is the relaxation equation.

Solution:

(1) Separation of variables:

$$\frac{d\phi}{\phi} = -\frac{1}{\tau}\,dt \rightsquigarrow [\ln\phi]_{\phi_0}^{\phi} = -\frac{1}{\tau}[t]_0^t$$

$$\rightsquigarrow \ln\phi - \ln\phi_0 = \ln\frac{\phi}{\phi_0} = -\frac{t}{\tau} \quad \rightsquigarrow \frac{\phi}{\phi_0} = e^{-t/\tau}$$

$$\Rightarrow \underline{\underline{\phi(t) = \phi_0\, e^{-t/\tau}}}$$

(2) Exponential ansatz:

$$\phi(t) = \phi_0 e^{-ct} \rightsquigarrow \dot\phi = -c\phi_0 e^{-ct} = -c\phi \Rightarrow c = \frac{1}{\tau}$$

(3) Laplace transformation:

$$\phi(u) \equiv \mathcal{L}\{\phi(t);\, t\to u\} = \int_0^\infty \phi(t)\, e^{-ut}\,dt$$

Differentiation theorem of Laplace transforms:

$$\int_0^\infty \dot{\phi}\, e^{-ut}\, dt \overset{?I.}{=} \left[\phi\, e^{-ut}\right]_{t=0}^{\infty} - \int_0^\infty (-u)\,\phi\, e^{-ut}\, dt$$

$$= -\phi(t=0) + u\phi(u)$$

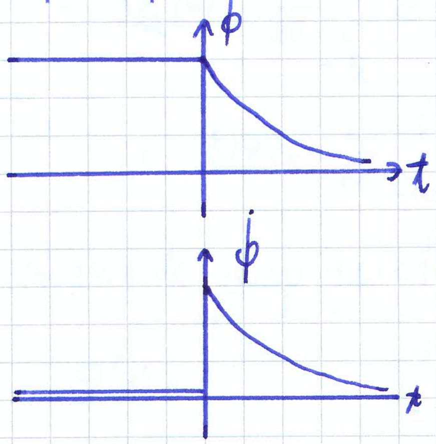
$$= u\phi(u) - \phi_0$$

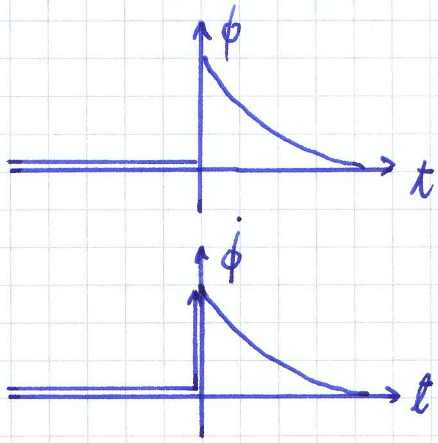
$$\Rightarrow \quad u\phi(u) - \phi_0 = -\frac{1}{\tau}\,\phi(u) \quad \rightsquigarrow \quad \phi(u) = \frac{\phi_0}{u + \tau^{-1}}$$

Tables of Laplace transforms or symbolic maths program:

$$\phi(t) = \phi_0\, e^{-t/\tau}.$$

Question of causality: What about the system preparation, i.e. the prehistory of the process at times $t<0$? We consider two situations:





$$\phi(t) = \begin{cases} \phi_0 & t<0 \\ \phi_0 e^{-t/\tau} & t \geq 0 \end{cases} \qquad\qquad \phi(t) = \begin{cases} 0 & t<0 \\ \phi_0 e^{-t/\tau} & t \geq 0 \end{cases}$$

$$\dot{\phi}(t) = \begin{cases} 0 & t<0 \\ -\phi_0 \tau^{-1} e^{-t/\tau} & t \geq 0 \end{cases} \qquad\qquad \dot{\phi}(t) = \begin{cases} 0 & t<0 \\ \phi_0 \delta(t) - \phi_0 \tau^{-1} e^{-t/\tau} & t \geq 0 \end{cases}$$

System relaxes out of steady state. System relaxes after sudden impact

Can we distinguish these two cases mathematically? Cases are fully described by:

$$\phi(t) = \phi_0\, e^{-t/\tau} \qquad\qquad \phi(t) = \phi_0\, e^{-t/\tau}\,\Theta(t)$$

What is the correct differential equation for $\phi(t) = \phi_0 e^{-t/\tau}\,\Theta(t)$?

<u>Excursion: Distributions</u>

Consider the δ distribution ("function"):

$$\delta(x) = \begin{cases} \infty & x = 0 \\ 0 & x \neq 0 \end{cases} \quad \text{with the property} \quad \int_{-\infty}^{\infty} \delta(x)\,dx = 1$$

Limiting representations (w/o proof):

- $\delta_\varepsilon(x) = \frac{1}{\sqrt{\pi\varepsilon}}\, e^{-x^2/\varepsilon}$ $\qquad \delta(x) = \lim_{\varepsilon\to 0} \delta_\varepsilon(x)$
- $\delta_\varepsilon(x) = \frac{\varepsilon}{\pi}\, \frac{1}{x^2+\varepsilon^2}$
- $\delta_k(x) = \frac{k}{2}\, e^{-k|x|}$ $\qquad \delta(x) = \lim_{k\to\infty} \delta_k(x)$
- $\delta_k(x) = \frac{1}{\pi}\,\frac{\sin kx}{x}$
- $\delta_k(x) = \frac{1}{2\pi}\int_{-k}^{k} e^{ik'x}\,dk' = \frac{1}{2\pi i x}\left(e^{ikx} - e^{-ikx}\right) = \frac{1}{\pi}\,\frac{\sin kx}{x}$

i.e. $\delta(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{ik'x}\,dk'$

Heaviside jump function:

$$\Theta(x) = \begin{cases} 0 & x < 0 \\ 1 & x \geq 0 \end{cases}$$

Schwarz defined distributions in terms of test functions, $\phi(x)$:
$\phi(x)$ and $\phi^{(n)}(x)$ vanish at the integration limits, and then we consider the scalar product

$$\langle T(x), \phi(x)\rangle \equiv \int T(x)\,\phi(x)\,dx$$

$\rightsquigarrow$ Definition of δ function:

$$\langle \delta(x), \phi(x)\rangle = \int \delta(x)\,\phi(x)\,dx = \phi(0)$$

Derivative of Θ function:

$$\langle \Theta'(x), \phi(x) \rangle = \int_{-\infty}^{\infty} \frac{d\Theta}{dx} \phi(x)\, dx = \Big[\Theta(x)\phi(x)\Big]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \Theta(x)\phi'(x)\, dx$$

$$= -\int_0^{\infty} \frac{d\phi}{dx} dx = -\int_0^{\infty} d\phi = -\Big[\phi(x)\Big]_0^{\infty} = \phi(0) = \langle \delta(x), \phi(x) \rangle$$

$$\Rightarrow \underline{\underline{\Theta'(x) = \delta(x).}}$$

Properties of δ function:

- $\delta(-x) = \delta(x)$
- $\delta(ax) = \frac{1}{|a|}\delta(x), \quad a \neq 0$
- $f(x)\delta(x) = f(0)\delta(x)$

<u>Back to the question:</u> differential equation for $\phi(t) = \phi_0 e^{-t/\tau}\Theta(t)$

$$\dot{\phi}(t) = -\phi_0 \frac{1}{\tau} e^{-t/\tau}\Theta(t) + \phi_0 e^{-t/\tau}\delta(t)$$

$$= -\frac{1}{\tau}\phi(t) + \phi_0\delta(t)$$

$\Rightarrow \dfrac{d\phi}{dt} = -\dfrac{1}{\tau}\phi + \phi_0\delta(t)$ in this formulation the initial value is directly included in the differential equation!

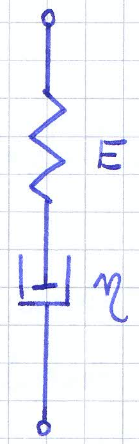
Application of relaxation equation: viscoelastic bodies

A body responds to an external stress $\sigma(t)$ by an extension $\varepsilon(t)$

Solid body: Hookean response $\sigma(t) = E\,\varepsilon(t)$ :: E elastic modulus

Liquid body: Newton's law $\sigma(t) = \eta\,\dot{\varepsilon}(t)$ :: η viscosity

Many materials combine both behaviours, they are visco-elastic. In condensed matter theory they are often described by simple mechanical models. We consider the Kelvin & Maxwell models:



Maxwell model:

The stresses are identical: $\sigma = \sigma_E = \sigma_\eta$

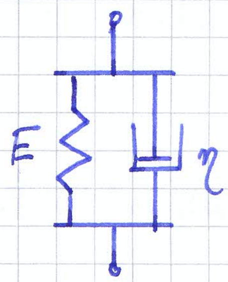
The total strain is the sum of the individual strains:

$\varepsilon = \varepsilon_E + \varepsilon_\eta$

$$\rightsquigarrow \quad \dot{\varepsilon}(t) = \frac{1}{E}\dot{\sigma}(t) + \frac{1}{\eta}\sigma(t)$$

Consider a stress relaxation experiment, in which a stress change is applied and then ε kept constant: $\dot{\varepsilon} = 0$

$$\rightsquigarrow \quad \frac{1}{E}\dot{\sigma} + \frac{1}{\eta}\sigma = 0 \quad \rightsquigarrow \quad \dot{\sigma} = -\frac{E}{\eta}\sigma \quad \Rightarrow \quad \underline{\underline{\sigma(t) = \sigma_0 \exp\left(-\frac{E}{\eta}t\right).}}$$



Kelvin model:

The strains are identical: $\varepsilon = \varepsilon_E = \varepsilon_\eta$

The stresses are additive: $\sigma = \sigma_E + \sigma_\eta$

$$\sigma(t) = E\,\varepsilon(t) + \eta\,\dot{\varepsilon}(t)$$

Load with σ_0 at $t=0$:

$$(E\varepsilon - \sigma) + \eta\dot{\varepsilon} = 0 \rightsquigarrow dt + \eta\frac{d\varepsilon}{E\varepsilon - \sigma} = 0 \rightsquigarrow \frac{E}{\eta}dt = \frac{d\varepsilon}{\sigma/E - \varepsilon}$$

$$\rightsquigarrow \frac{E}{\eta}\int_0^t dt = \frac{E}{\eta}t = \int_0^\varepsilon \frac{d\varepsilon}{\sigma/E - \varepsilon} = \left[\ln\left(\frac{\sigma}{E} - \varepsilon\right)\right]_\varepsilon^0 = \ln\frac{\sigma/E}{\sigma/E - \varepsilon}$$

$$\rightsquigarrow -\frac{E}{\eta}t = \ln\frac{\sigma/E - \varepsilon}{\sigma/E} \rightsquigarrow e^{-\frac{E}{\eta}t} = \frac{\sigma/E - \varepsilon}{\sigma/E}$$

$$\Rightarrow \quad \underline{\underline{\varepsilon(t) = \frac{\sigma}{E}\left(1 - e^{-Et/\eta}\right) \longrightarrow \frac{\sigma}{E}.}}$$

II. DIFFUSION.

Diffusion describes the spread of particles from regions of higher concentration to regions of lower concentration through random motion.
Originally, diffusion of particles was thought of in terms of concentrations while later the probabilistic picture of individual particles' independent motion emerged.

In around 50 BCE Titus Lucretius Carus describes the "battling" motion of dust particles in air.

1757 Dutch physician Jan Ingenhousz accounts experiments on the jittery motion of coal dust particles on an alcohol surface.

In 1827 Scottish botanist Robert Brown describes the zigzag motion of small particles enclosed in pollen grains found in amber.

Brown and Ingenhousz used control experiments to exclude active motion of "animalcules".

In 1855 Adolf Fick derived the diffusion equation

$$\frac{\partial P(x,t)}{\partial t} = D \frac{\partial^2 P(x,t)}{\partial x^2}$$

Here, D is the diffusion coefficient of physical dimension $[D] = \frac{cm^2}{sec}$.
P is the probability density function (PDF).

Solution:

(1) Laplace transform:

$$u P(x,u) - P(x,0) = D \frac{\partial^2 P(x,u)}{\partial x^2} \quad \text{with } P(x,0) \stackrel{!}{=} \delta(x)$$

$$u P(x,u) - \delta(x) = D \frac{\partial^2 P(x,u)}{\partial x^2}$$ reduction to ODE of 2^{nd} order.

Standard methods.

(2) Fourier-Laplace method:

Fourier transform: $g(k) \equiv \mathcal{F}\{g(x); x \to k\} = \int_{-\infty}^{\infty} g(x) e^{ikx} dx$

$$g(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} g(k) e^{ikx} dk$$

Differentiation theorem: $\int_{-\infty}^{\infty} \frac{dg(x)}{dx} e^{ikx} dx = \left[g(x) e^{ikx} \right]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} ik\, g(x) e^{ikx} dx$

$$= -ik\, g(k)$$

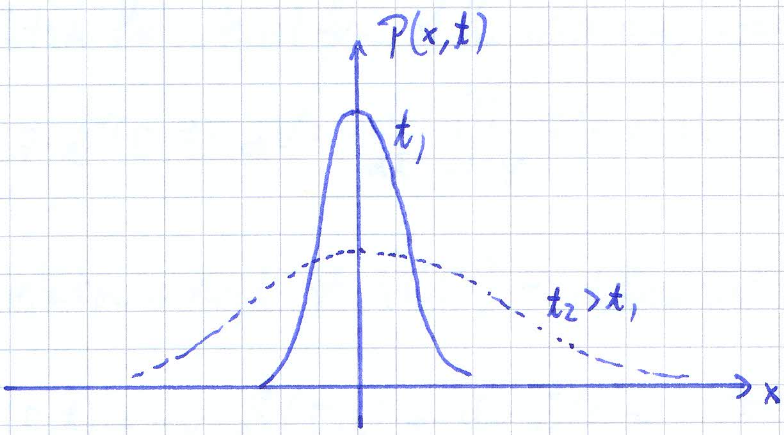
$$\int_{-\infty}^{\infty} \frac{d^2 g(x)}{dx^2} e^{ikx} dx = -k^2 g(k)$$

$\Rightarrow u P(k,u) - 1 = -Dk^2 P(k,u)$ algebraic equation!

$\Rightarrow P(k,u) = \frac{1}{u + Dk^2}$

Laplace inversion: $P(k,t) = e^{-Dk^2 t}$ Gaussian

Fourier inversion: $\underline{\underline{P(x,t) = \frac{1}{\sqrt{4\pi D t}} e^{-x^2/4Dt}}}$



Das 2. Moment:

$\underline{\underline{\langle x^2(t) \rangle}} = \int_{-\infty}^{\infty} x^2 P(x,t)\, dx \overset{\text{Tabelle}}{=\!=} \underline{\underline{2Dt}}$

Trick to calculate: start with diffusion equation

$$x^2 \frac{\partial P}{\partial t} = \frac{\partial}{\partial t} x^2 P = D x^2 \frac{\partial^2 P}{\partial x^2} \quad \Big| \int_{-\infty}^{\infty} dx \,.$$

$$\frac{d}{dt} \langle x^2 \rangle = D \left\{ \left[x^2 P' \right]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} 2x \frac{\partial P}{\partial x} dx \right\} = D \left\{ -\left[2xP \right]_{-\infty}^{\infty} + \int_{-\infty}^{\infty} 2P \, dx \right\} = 2D$$

$\Rightarrow \langle x^2 \rangle = 2Dt.$

<u>Fick's derivation of the diffusion equation:</u>

(1) <u>Continuity equation:</u> Given a probability density $P(\underline{r}, t)$ with

$\iiint_{-\infty}^{\infty} P(\underline{r}, t) dV = 1$, and the probability flux $\underline{S}(\underline{r}, t)$:

$$\oint\!\!\oint_{\delta V} \underline{S}(\underline{r}, t) \, d\underline{A} = -\frac{d}{dt} \iiint_V P(\underline{r}, t) \, dV = -\frac{d}{dt} \mathcal{S}(t)$$

where $\mathcal{S}(t)$ is the survival probability.

With the divergence theorem (Gauss' theorem):

$$\oint\!\!\oint_{\delta V} \underline{S}(\underline{r}, t) \, d\underline{A} = \iiint_V \nabla \cdot \underline{S}(\underline{r}, t) \, dV$$

we obtain the integral form of the continuity equation:

$$\iiint_V \nabla \cdot \underline{S}(\underline{r}, t) \, dV = -\frac{d}{dt} \iiint_V P(\underline{r}, t) \, dV = -\iiint_V \frac{\partial P(\underline{r}, t)}{\partial t} dV$$

This relation is valid $\forall \, (V, \delta V) \Rightarrow$ differential form:

$$\frac{\partial}{\partial t} P(\underline{r}, t) = -\nabla \cdot \underline{S}(\underline{r}, t) = -\operatorname{div} \underline{S}(\underline{r}, t). \quad \text{continuity equation}$$

(2) <u>Fick's first law:</u>

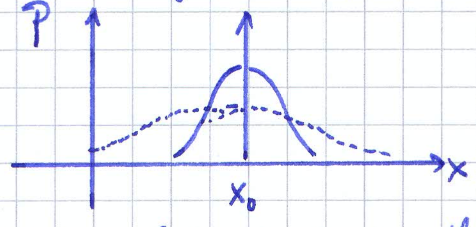
$$\underline{S} = -D \nabla P(\underline{r}, t)$$ the flux is proportional to the gradient of the probability density function P.

$$\Rightarrow \frac{\partial}{\partial t} P(\underline{r},t) = -\nabla \cdot \underline{S}(\underline{r},t) = D\nabla^2 P(\underline{r},t) \quad \text{Fick's second law}$$

In the following, for simplicity we will deal with the one-dimensional case.

Boundary value problems:

(1) Reflecting boundary at $x=0$ & initial condition $P_0(x) = \delta(x-x_0)$, $x \geq 0$



$$\left.\frac{\partial P(x,t)}{\partial x}\right|_{x=0} = 0$$

Solution: (a) Standard method: Laplace transform & solution of ODE in x.

(b) Method of images: The portion of the probability "leaking" out to $x<0$ of the Gaussian $(4\pi D t)^{-1/2} \exp(-[x-x_0]^2/(4Dt))$ is compensated by the influx of probability from a mirror source at $-x_0$. The resulting Green's function solves the boundary value problem:

$$Q(x,t) = G(x-x_0,t) + G(x+x_0,t) \quad \text{where } G(x,t) = \frac{1}{\sqrt{4\pi D t}} e^{-x^2/4Dt}$$

Moreover Q is normalised. Thus the image Q is the sought-after solution.

Diffusion on average moves the particle away from the origin:

$$\langle x \rangle = \int_0^\infty Q(x,t)\,dx = 2\sqrt{\frac{Dt}{\pi}}\, e^{-x_0^2/4Dt} + x_0 \operatorname{erf}\left(\frac{x_0}{\sqrt{4Dt}}\right) \sim \sqrt{\frac{4Dt}{\pi}}.$$

(2) Absorbing boundary conditions at $x=0$:

$$P(0,t) = 0$$

Image solution $Q(x,t) = G(x-x_0,t) - G(x+x_0,t)$.

Survival probability: $\mathcal{S}(t) = \int_0^\infty Q(x,t)\,dx = \operatorname{erf}\left(\frac{x_0}{\sqrt{4Dt}}\right) \sim \frac{x_0}{\sqrt{\pi D t}}$.