10. Random walks & diffusion in chaotic systems

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1. Brownian motion

Scottish botanist R. Brown (1773–1858) observed random motion of small particles suspended in water [1].

A. Einstein explained that their incessant motion is due to temperature characterising the concerted effect of the water molecules on the particles.
A. Einstein showed [2]

p. 559 of [2]

$$\langle X_t^2 \rangle = 2Dt \tag{1}$$

"diffusion constant"

mean square displacement
in x-direction in time t

$$D = \frac{k_B T}{6\pi \eta a} \tag{2}$$

temperature

particle radius

p.555 of [2].

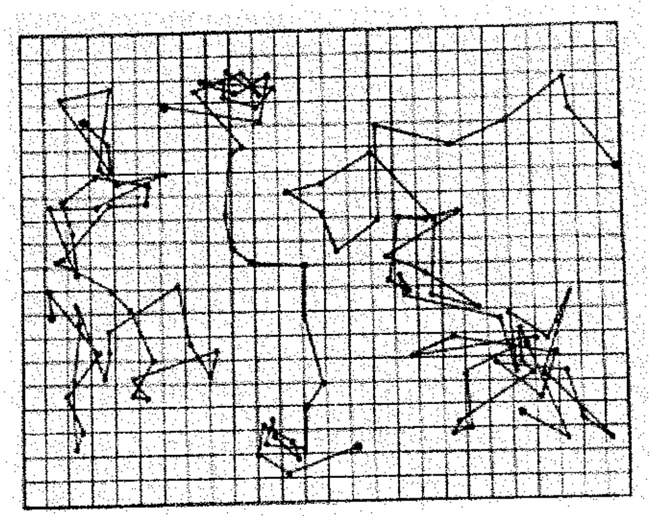
dynamic viscosity

Stokes–Einstein formula

$$[k_B T] = kg \frac{m^2}{s^2}$$

$$[\eta] = \frac{kg}{ms}$$

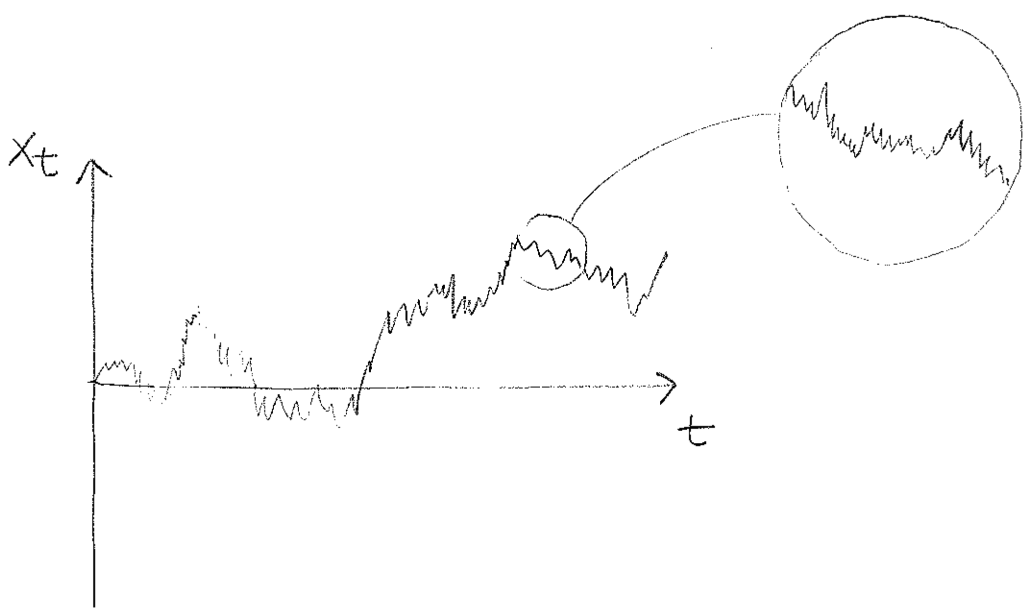
Experimental verification of these quantitative predictions by J Perrin (1870 – 1942) [3]



successive positions of particles every 30s, grid size 3.2 μm.

→ J. Perrin [3] and Wikipedia

A. Einstein



2. Random walks

Discrete time $t_j = j\,\delta t$.

Microscopic jumps δx_j.

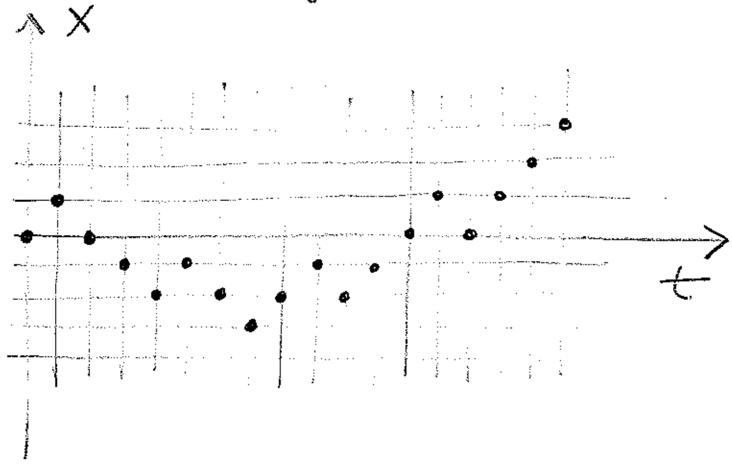
Start at origin.

$$\delta x_j = \begin{cases} \delta x & \text{with prob. } \frac{1}{2} \\ -\delta x & \text{with prob. } \frac{1}{2} \end{cases}$$

$$\langle \delta x_j \rangle = 0$$

$$\langle \delta x_i\, \delta x_j \rangle = \begin{cases} \delta x^2 & \text{if } i=j \\ 0 & \text{if } i \neq j \end{cases}$$

ensemble average



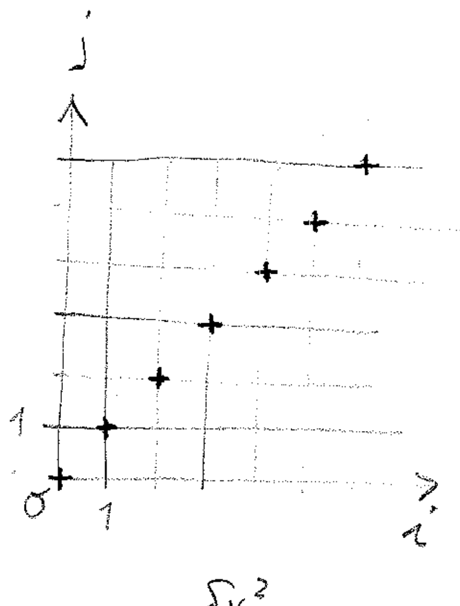
Position x_N after N steps

$$x_N = \sum_{j=1}^{N} \delta x_j$$

Find

$$\langle x_N \rangle = \sum_{j=1}^{N} \langle \delta x_j \rangle = 0$$

$$\begin{aligned} \langle x_N^2 \rangle &= \sum_{i,j=1}^{N} \langle \delta x_i\, \delta x_j \rangle \\ &= N\, \delta x^2 \\ &= 2\, \frac{\delta x^2}{2\delta t}\, t_N \\ &= 2 D\, t_N \end{aligned}$$



with diffusion constant $D = \dfrac{\delta x^2}{2\delta t}$.

The law of diffusion

$$\langle x_t^2 \rangle = 2Dt$$

explains why early attempts to characterise the velocity of Brownian particles failed:

$$\frac{\Delta x}{\Delta t} \sim \frac{\sqrt{\langle x_t^2 \rangle}}{t} \longrightarrow \infty \quad \text{as } t \to 0$$

The central limit theorem implies that x_N is gaussian distributed (with mean zero and variance $2Dt_N$)

$$P(x_N, t_N) = \frac{1}{\sqrt{4\pi D t_N}} e^{-\frac{x_N^2}{4Dt_N}} . \qquad (3)$$

distribution of position x_N after time t_N
$P(x,t)\,dx$ = prob. of finding particle in $[x, x+dx]$ at time t

The law of diffusion is a consequence of the central limit theorem.

Diffusion ubiquitous.

3. Central limit theorem

Let $x_1, \ldots, x_N$ be a set of independently distributed random variables with identical distributions $P(x)$ with zero mean and finite variance σ^2.

Then the sum

$$S_N = \sum_{j=1}^{N} x_j$$

approaches a Gaussian

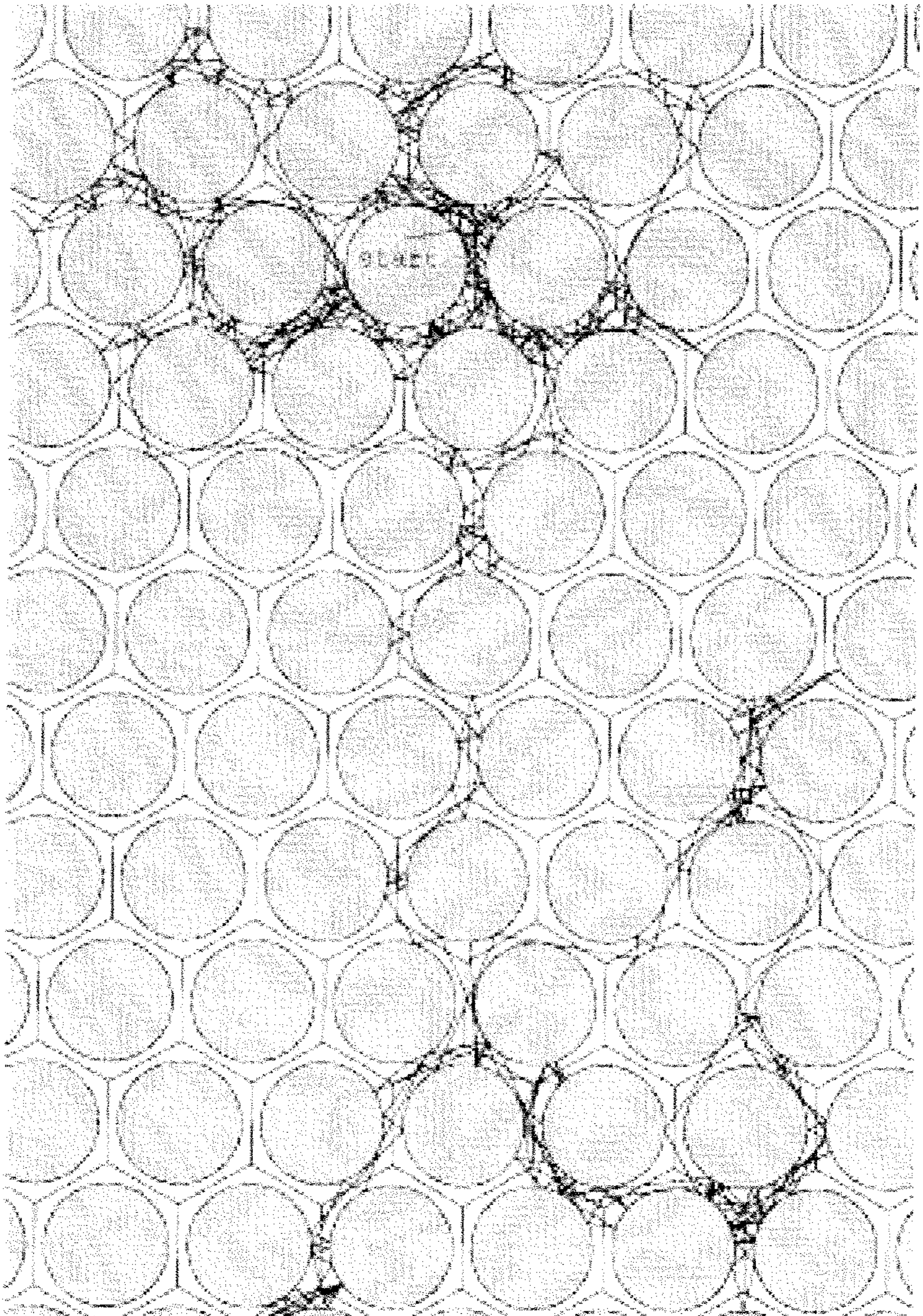
$$P(S_N) \longrightarrow \frac{1}{\sqrt{2\pi N \sigma^2}}\, e^{-\frac{S_N^2}{2N\sigma^2}}$$

as $N \to \infty$.

Since P becomes increasingly narrow as $N \to \infty$, it is often convenient to study the scaled sum

$$Z_N = \frac{1}{\sqrt{N}} \sum_{j=1}^{N} x_j$$

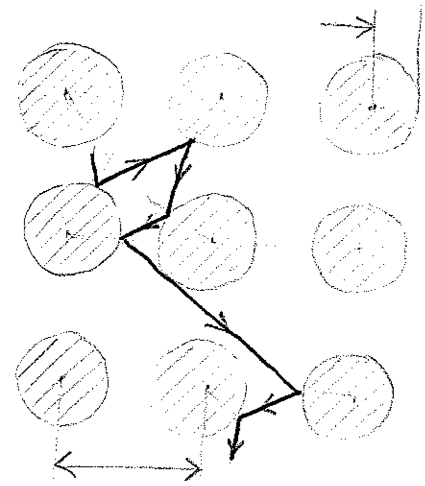
The corresponding Gaussian distribution approaches a finite variance (see p. 3).



Th. Schreiber

4. Anomalous diffusion

Lorentz gas with infinite horizon



$$\langle x_t^2 \rangle \sim t \log t$$

In general, law of anomalous diffusion

$$\langle x_t^2 \rangle \sim t^{2H} \qquad H \neq \tfrac{1}{2} \qquad (4)$$

Hurst exponent

In the random-walk model (see p. 3), the assumptions

$$\langle \delta x_i \, \delta x_j \rangle = 0 \text{ for } i \neq j \qquad \text{independence ("Markov property")} \qquad (5)$$

$$\langle \delta x_i^2 \rangle < \infty \qquad \text{finite variance} \qquad (6)$$

imply $H = \frac{1}{2}$. Anomalous diffusion in this model requires that either (5) or (6) are not satisfied.

If $\langle \delta x_i^2 \rangle = \infty$ (or $\langle \delta x_i \rangle = \infty$), need to regularise ensemble average of x_N^2 (or x_N).

Show that when $H \neq \frac{1}{2}$, (5) and (6) cannot hold simultaneously: assume for example

$$\langle \delta x_i^2 \rangle < \infty$$

and compute

$$\langle \delta x_1 \delta x_2 \rangle = \frac{1}{2} \left\langle (\delta x_1 + \delta x_2)^2 - \delta x_1^2 - \delta x_2^2 \right\rangle$$

$$\sim \frac{1}{2} \left[(2\, \delta t)^{2H} - 2\, \delta t^{2H} \right]$$

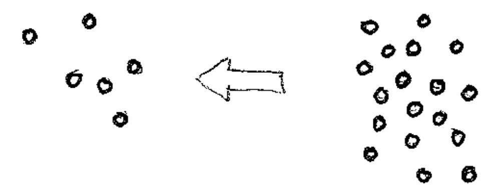
$$\neq 0 \quad \text{if } H \neq 1/2$$

Fractional Brownian motion: dispense with Markov property.

Lévy flights (Lévy walks): divergent $\langle \delta x_i^2 \rangle$ or $\langle \delta x_i \rangle$.

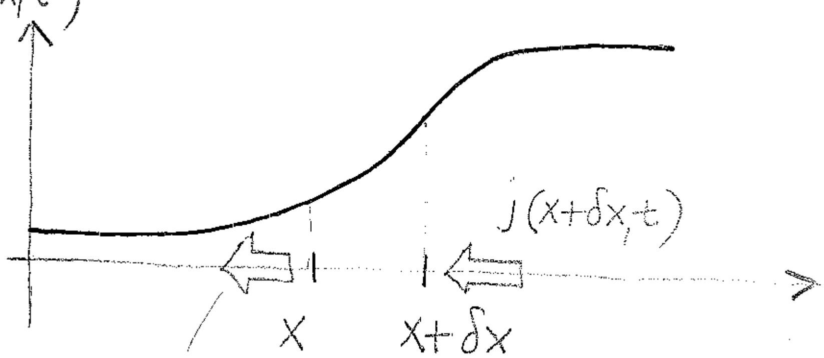
5. Fick's law and the diffusion equation

Empirical law relating particle flux j to concentration gradient $\frac{\partial n}{\partial x}$



Fick's law [4]

$$j(x,t) = -C\,\frac{\partial n}{\partial x} \tag{7}$$



Compute change of number of particles in the interval $[x, x+\delta x]$

$$\underbrace{\frac{\partial}{\partial t}\int_{x}^{x+\delta x} dx'\, n(x',t)}_{\#\text{ of particles}} = j(x,t) - j(x+\delta x,t)$$

(note $j<0$ because it is left-going)

In the limit of $\delta x \to 0$ obtain

$$\frac{\partial n}{\partial t} = - \frac{\partial j}{\partial x} . \qquad (8)$$

(continuity equation) Together with Fick's law (7) find

$$\frac{\partial n}{\partial t} = c \frac{\partial^2 n}{\partial x^2} . \qquad (9)$$

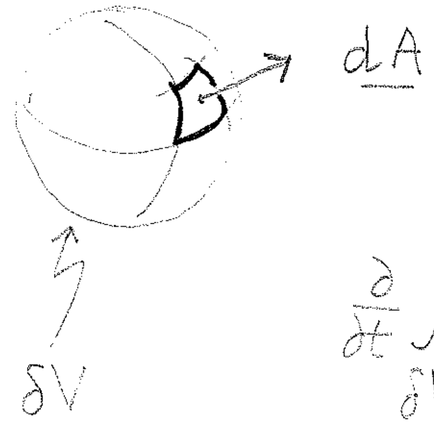
Assume all particles initially concentrated at origin $\left(n(x,0) = \delta(x) \right)$. Corresponding solution of (9)

$$n(x,t) = \frac{1}{\sqrt{4\pi c t}} e^{-\frac{x^2}{4ct}} .$$

Same as eq. (3) on page 4; $n(x,t) = P(x,t)$ when suitably normalised. Constant in Fick's law (7) is diffusion constant.

Eq. (9) is called diffusion equation, see p. 558 of [2].

Corresponding result in $d=3$ dimensions



$$\frac{\partial}{\partial t}\int_{\delta V} d^3r\, n(\underline{r},t) = -\int_{\delta A} d\underline{A}\cdot\underline{j}(\underline{r},t)$$

$$= -\int_{\partial V} d^3r\ \underline{\nabla}\cdot\underline{j}(\underline{r},t)$$

Obtain continuity equation

$$\frac{\partial n(\underline{r},t)}{\partial t} + \underline{\nabla}\,\underline{j}(\underline{r},t) = 0 . \qquad (10)$$

Together with Fick's law $\underline{j} = -D\underline{\nabla}n$ find

$$\frac{\partial}{\partial t} n(\underline{r},t) = D\,\Delta\, n(\underline{r},t) \qquad (11)$$

Solution for $n(\underline{r},0) = \delta^{(3)}(\underline{r})$:

$$n(\underline{r},t) = (4\pi Dt)^{-3/2}\, e^{-\frac{r^2}{4Dt}}$$

This implies

$$\langle x_t^2\rangle = 2Dt$$

Conditional transition probability density (t>0)

$$P(x,t) = \int dx' \; P(x,x';t) \; P(x',0)$$

$P(x,t)\,dx$ is prob. of finding particle in $[x, x+dx]$ at time t

$P(x,x';t)$ is conditional transition probability density from $x' \rightarrow x$

Now $P(x,t)$ obeys diffusion equation and $P(x,x';t)$ is $P(x,t)$ for the initial condition $P(x,0) = \delta(x-x')$. Therefore

$$\left(\frac{\partial}{\partial t} - D\frac{\partial^2}{\partial x^2}\right) P(x,x';t) = 0 \qquad (12)$$

for $t>0$.

This equation is valid for $t>0$ only.
Write instead

$$\left(\frac{\partial}{\partial t} - D\frac{\partial^2}{\partial x^2}\right) P(x,x';t) = -\delta(t)\,\delta(x-x') \qquad (13)$$

Solution in infinite domain

$$P(x,x';t) = \frac{\theta(t)}{\sqrt{4\pi D t}}\, e^{-\frac{(x-x')^2}{4Dt}} \qquad (14)$$

depends only on difference $x-x'$.

6. Solutions of diffusion equation in finite domains

Electrons in disordered metal

Fluorescent markers in random medium (skin)

Compute $P(x,t)$ by eigenfunction expansion of $P(x,x';t)$.

$$\left(\frac{\partial}{\partial t} - D\frac{\partial^2}{\partial x^2}\right) P(x,x';t) = \delta(t)\,\delta(x-x')$$

$$P(x,x';t) = \theta(t)\sum_\alpha \varphi_\alpha(x)\,\varphi^*_\alpha(x')\,\exp(-DK_\alpha^2 t) \qquad (15)$$

Eigenfunctions $\varphi_\alpha(x)$ satisfy

$$\left(\frac{\partial^2}{\partial x^2} + K_\alpha^2\right)\varphi_\alpha(x) = 0 \qquad (16)$$

appropriate boundary conditions

1. no current across boundary $\hat{=}$ normal component of gradient vanishes $\hat{=}$ Neumann boundary conditions
2. periodic boundary conditions
3. ...

Eigenfunctions form complete ortho-normal system

$$\int_0^L dx\, \varphi_\alpha(x)\, \varphi_\beta^*(x) = \delta_{\alpha\beta}$$

$$\sum_\alpha \varphi_\alpha(x)\, \varphi_\alpha^*(x') = \delta(x-x') \qquad (17)$$

<u>Example</u>: periodic boundary conditions

$\varphi_\alpha(x) = \varphi_\alpha(x+L)$

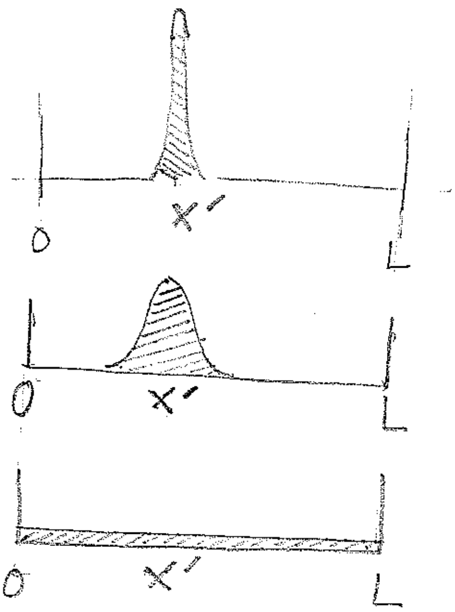
$$\varphi_\alpha(x) = \frac{1}{\sqrt{L}}\, e^{i k_\alpha x}$$

$$k_\alpha = \frac{2\pi\alpha}{L} \qquad \alpha = -\infty, \dots, \infty$$

$$P(x,x';t) = \theta(t)\, \frac{1}{L} \sum_{\alpha=-\infty}^{\infty} e^{i k_\alpha (x-x') - D k_\alpha^2 t}$$

initial condition

$P(x,0) = \delta(x-x')$



As $t \to \infty$ $\left(t \gg \frac{L^2}{D}\right)$

$$P(x,x';t) \to \frac{1}{L}$$

and thus

$$P(x,t) \longrightarrow \frac{1}{L}$$

(independently of initial condition).

This corresponds to equidistribution. Diffusion smoothes out singularities in density.

For $t \ll \frac{L^2}{D}$ expect that $P(x,x';t)$ and $P(x,t)$ are gaussian (see p. 12, boundary conditions not important when $t \ll \frac{L^2}{D}$). Show this by <u>Poisson summation</u>

If two functions $f(\alpha)$ and $F(\mu)$ are related by

$$F(\mu) = \int_{-\infty}^{\infty} d\alpha\, f(\alpha)\, e^{-2\pi i \alpha \mu}$$

then

$$\sum_{\alpha=-\infty}^{\infty} f(\alpha) = \sum_{\mu=-\infty}^{\infty} F(\mu)$$

(Poisson summation formula).

Here

$$f(\alpha) = \frac{1}{L} e^{\frac{2\pi i \alpha (x-x')}{L} - D\left(\frac{2\pi\alpha}{L}\right)^2 t}.$$

Find

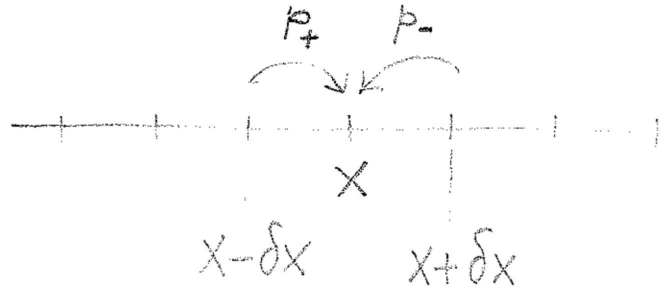
$$F(\mu) = \frac{1}{\sqrt{4\pi D t}}\, e^{-\frac{(x-x'-\mu L)^2}{4Dt}}$$

Thus if $0<t < \frac{L^2}{D}$, $P(x,x';t) \approx \frac{1}{\sqrt{4\pi D t}}\, e^{-\frac{(x-x')^2}{4Dt}}$

7. Fokker-Planck equation

$p_\pm = \delta t \, w_\pm$ (transition probability; transition rate)

Random walk with drift



$p_+ + p_- = 1$
$p_+ - p_- = \varepsilon$

Determine probability $P(x,t)$ to find particle at x at time t.
Discrete time steps δt. Start from

$$P(x,t+\delta t) = p_+ \, P(x-\delta x,t) + p_- \, P(x+\delta x,t) \qquad (18)$$

Now expand in δx

$$P(x \mp \delta x, t) = P(x,t) \mp \delta x \frac{\partial P}{\partial x} + \frac{\delta x^2}{2} \frac{\partial^2 P}{\partial x^2} + \dots$$

Insert into (18) to obtain

$$P(x,t+\delta t) = P(x,t) + \delta x \frac{\partial P}{\partial x}(-p_+ + p_-) + \frac{\delta x^2}{2}\frac{\partial^2 P}{\partial x^2}(p_+ + p_-) + \dots$$

$$\frac{P(x,t+\delta t) - P(x,t)}{\delta t} = -\frac{\delta x}{\delta t}\varepsilon \frac{\partial P}{\partial x} + \frac{\delta x^2}{2\delta t}\frac{\partial^2 P}{\partial x^2} + \dots$$

Now let $\varepsilon, \delta t, \delta x$ tend to zero so that

$$\frac{\delta x^2}{2\delta t} \longrightarrow D,$$

$$\frac{\delta x\, \varepsilon}{\delta t} \longrightarrow v.$$

Find

$$\frac{\partial P(x,t)}{\partial t} = \frac{\partial}{\partial x}\Big(\underbrace{-v}_{\substack{\text{drift term}\\ (\text{"advection"})}} + \underbrace{\frac{\partial}{\partial x} D}_{\text{diffusion term}}\Big)\, P(x,t) \qquad (19)$$

When $p_+ = p_- = \frac{1}{2}$ obtain diffusion equation. Eq. (19) is a generalised diffusion equation (Fokker-Planck equation, discussed in text books such as [5]).

transition probability
per unit time

More generally consider stochastic process given by microscopic <u>transition</u> <u>rates</u> $w(x, \delta x)$. Assume

$w(x,\delta x) \approx 0$ unless δx is small,

$w(x,\delta x) \approx w(x', \delta x)$ when $|x-x'|$ small.

Define moments $(\delta t \to 0)$

$$a_\nu(x) = \frac{\langle \delta x^\nu \rangle_x}{\delta t} = \int dx\, x^\nu\, w(x, \Delta x)$$

<u>Fokker-Planck equation</u>

$$\frac{\partial}{\partial t} P(x,t) = \frac{\partial}{\partial x}\left[-a_1(x) + \frac{1}{2}\frac{\partial}{\partial x} a_2(x)\right] P(x,t) \tag{20}$$

Diffusion: $a_1 = 0$, $a_2 = 2D$
Drift: $a_1 = v$

The Fokker-Planck equation has the form of a continuity equation (see p. 10)

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

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

"<u>probability current</u>"

Steady state $\hat{=}$ constant probability current J

if $J=0$ at boundary then $J \equiv 0$

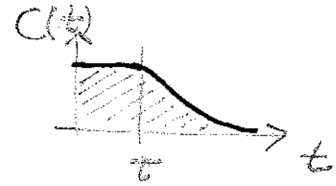
8. Ornstein – Uhlenbeck process

Stochastic process for momentum of Brownian particle [6]

$$\dot{p} = \underbrace{-\gamma p}_{\text{viscous damping}} + \underbrace{f}_{\text{stochastic force}} \tag{21}$$

Assume

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



$$\langle f(t) f(t') \rangle = \sigma^2 C(t-t')$$

correlations decay on time scale τ

Derive Fokker-Planck equation. Compute a_1 by integrating (21) over a small time interval δt

$$\delta p = -\gamma p \, \delta t + \underbrace{\int_t^{t+\delta t} dt' f(t')}_{\equiv \, \delta W}$$

random impulse

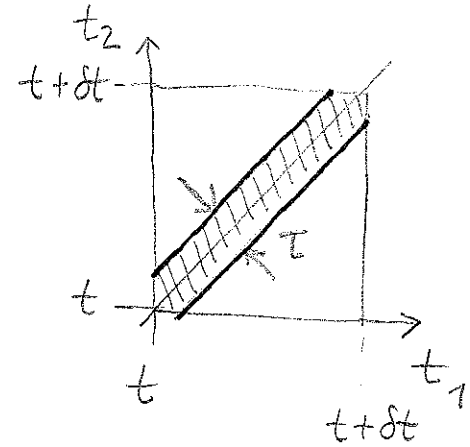
Since $\langle f \rangle = 0$ have $\langle \delta W \rangle = 0$ and thus

$$a_1(p) = \frac{\langle \delta p \rangle_p}{\langle \delta t \rangle} = -\gamma p .$$

Now compute a_2. Calculate $D_0 \equiv \dfrac{\langle \delta p^2 \rangle_p}{2\delta t}$:

$$\frac{\langle \delta p^2 \rangle_p}{2\delta t} = \frac{\langle \delta w^2 \rangle}{2\delta t} = \frac{1}{2\delta t} \int_t^{t+\delta t} dt_1 \int_t^{t+\delta t} dt_2 \, \langle f(t_1) f(t_2) \rangle$$

$$\approx \frac{1}{2} \int_{-\infty}^{\infty} dt \, C(t)$$



if $f(t)$ fluctuates so rapidly that $\tau \ll \delta t$. Find

$$D_0 = \frac{1}{2} \int_{-\infty}^{\infty} dt \, C(t)$$

index to distinguish from spatial diffusion constant

Find the following Fokker-Planck equation

$$\frac{\partial}{\partial t} P(p,t) = \frac{\partial}{\partial p} \left(\gamma p + \frac{\partial}{\partial p} D_0 \right) P(p,t) \qquad (22)$$

(Ornstein-Uhlenbeck equation [6]).
Note $[D_0] = kg^2 \frac{m^2}{s^3}$.

Note that (22) is equivalent to an equation of <u>Langevin form</u> [5] (see previous page)

$$\delta p = -\gamma p \, \delta t + \delta w \leftarrow \text{Stochastic displacement} \qquad (23)$$

$$\langle \delta w \rangle = 0$$
$$\langle \delta w^2 \rangle = 2 D_0 \, \delta t$$

(22) or equivalently (23) are adequate descriptions of the stochastic dynamics (21)

if the force fluctuates sufficiently rapidly (and jumps δp sufficiently small).

Steady-state solution $P_\infty(p)$ satisfies

$$\left(\gamma p + \frac{\partial}{\partial p} D_0\right) P_\infty(p) = 0 \qquad (24)$$

and is thus of gaussian form

$$P_\infty(p) \propto e^{-\frac{\gamma p^2}{2D_0}} \qquad (25)$$

Expect Maxwell-Boltzmann distribution for Brownian velocities $v = p/m$ in thermal equilibrium

$$\frac{\frac{1}{2}mv^2}{k_B T} = \frac{\gamma m^2 v^2}{2D_0}$$

This implies

viscous dissipation

$$D_0 = \gamma m k_B T \qquad (26)$$

D_0 characterises fluctuation of force

(fluctuation-dissipation theorem).

Transition probability for Ornstein-Uhlenbeck process. In dimensionless variables

$$z = \sqrt{\frac{\gamma}{D_0}}\, p$$

$$s = \gamma t$$

have [6]

initial coordinate

$$P(z, z'; s) = \frac{1}{\sqrt{2\pi\left(1-e^{-2s}\right)}}\, e^{-\frac{\left(z - z' e^{-s}\right)^2}{2\left(1-e^{-2s}\right)}} \tag{27}$$

Compute correlation function $\langle p(t)p(0)\rangle$ in equilibrium

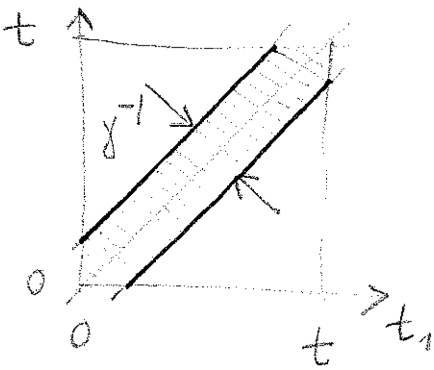
$$\begin{aligned}\langle p(t)\, p(0)\rangle &= \int dp_1\, dp_2\; p_1 p_2\; P(p_1, p_2; t)\; P_\infty(p_2) \\ &= \frac{D_0}{\gamma}\, e^{-\gamma t}\end{aligned} \tag{28}$$

On time scales $\gg \gamma^{-1}$ the velocities of the particles appear uncorrelated and they are expected to diffuse.
Check this by writing

$$x_t = \frac{1}{m}\int_0^t dt'\; p(t')$$

$$\langle x_t^2 \rangle = \frac{1}{m^2} \int_0^t dt_1 \int_0^t dt_2 \, \langle p(t_1)\, p(t_2) \rangle$$

$$\sim \frac{D_0}{m^2 \gamma^2}\, t$$



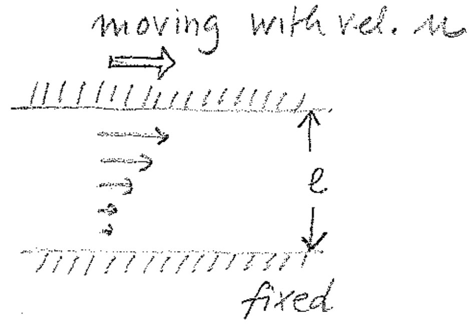
So the spatial diffusion constant is

$$D \sim \frac{D_0}{m^2\gamma^2} \sim \frac{k_B T}{m\gamma}$$

fluctuation-dissipation relation (28)

Stokes' formula for damping constant $\gamma = \frac{6\pi\eta a}{m}$ gives Stokes-Einstein result from p. 1

$$D = \frac{k_B T}{6\pi\eta a}. \qquad (29)$$



Stokes formula

Definition of viscosity:

$$\text{Shear stress} = \underset{\text{(dynamic)}}{\text{viscosity}} \times \text{strain rate}$$

$$\sigma = \frac{F}{A} \qquad \eta \qquad \frac{1}{l}\frac{dl}{dt} \sim \frac{u}{l}$$

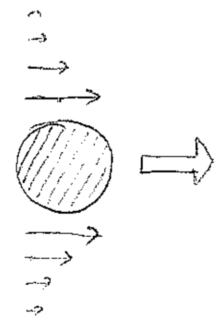
$$\sigma = \eta \, \frac{1}{l} \frac{dl}{dt}$$

$$[\eta] = \frac{kg}{ms}$$

Kinematic viscosity $\nu = \frac{\eta}{\rho}$ ← density

$$[\nu] = \frac{m^2}{s}$$

Consider sphere in viscous fluid



$$\frac{F}{A} \sim \eta \frac{u}{a} \leftarrow \text{radius}$$

$$F \sim \eta \frac{u}{a} a^2$$

Writing $F = m\gamma u$ find $\gamma \sim \frac{\eta a}{m}$.

Exact result

$$\gamma = \frac{6\pi\eta a}{m}. \tag{30}$$

9. Generalised Ornstein-Uhlenbeck process

Natural extension: in general f depends upon x as well as t:

$$\dot{x} = p/m \qquad \langle f(x,t)\rangle = 0 \qquad (31)$$

$$\dot{p} = -\gamma p + f(x,t) \qquad \langle f(x,t) f(x',t')\rangle = C(x-x', t-t')$$

Derive Fokker-Planck equation when particles move fast so that fluctuations of f are mainly due to changes in x.

Proceed as on pp. 19, 20

$$\delta W = \int_t^{t+\delta t} dt' \underbrace{f(x_{t'}, t')}_{\approx f\left(x_0 + \frac{p(t'-t)}{m}, t'\right)}$$

Expand and average:

$$\langle \delta W\rangle = \delta t \frac{d}{dp} D(p) \qquad D(p) = \frac{1}{2}\int_{-\infty}^{\infty} dt\, C\left(\frac{pt}{m}, t\right)$$

$$\langle \delta W^2\rangle = 2D(p)\,\delta t \qquad \sim \begin{cases} D_0 & p \ll p_0 \\ \frac{D_1 p_0}{|p|} & p \gg p_0 \end{cases}$$

Find Fokker-Planck equation

$$\frac{\partial P(p,t)}{\partial t} = \frac{\partial}{\partial p}\left[\gamma p + D(p)\frac{\partial}{\partial p}\right] P(p,t) \qquad p_0 = m\xi/\tau \qquad (32)$$

For $D(p) = \frac{D_1 p_0}{|p|}$ this equation can be solved exactly (mapping to "quantum" problem). Find anomalous diffusion at short times and non-Maxwellian velocity distribution in steady state.

10. Kramers' explanation of Arrhenius law

Diffusion model of chemical reactions [8].
Consider one-dimensional caricature.
Reaction coordinate X (representing reaction progress e.g. bond length, bond angle, ..) subject to random fluctuations (interaction with environment e.g. solvent).

Reaction proceeds via transition state modelled by potential barrier $U(x)$

$$\frac{\partial P(x,t)}{\partial t} = \frac{\partial}{\partial x}\left[\frac{U'(x)}{m\gamma} + \frac{\partial}{\partial x} D\right] P(x,t) \qquad (33)$$

with $D = \frac{k_B T}{m\gamma}$ (see p. 22) Eq. (33) is a simplified version of the problem considered in [8], valid in the high-friction limit:

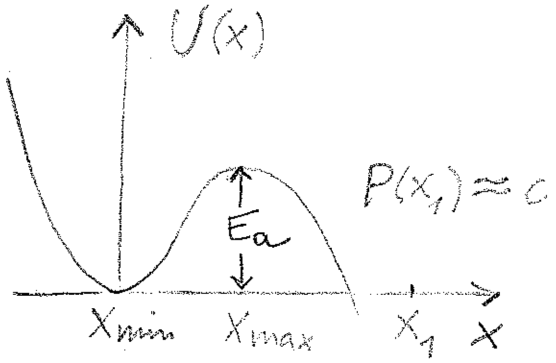
$$\dot{x} = \frac{p}{m} \quad \dot{p} = -\gamma p - U'(x) + f(t)$$

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

High-friction limit

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

Reaction rate $\hat{=}$ escape rate from $U(x)$.



limit of large activation energy E_a where escape rate is small

Consider (quasi-) steady state where $\partial P/\partial t \approx 0$.
Expect constant probability current

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

The steady-state solution for P (and thus J) is obtained by finding an <u>integrating factor</u> $\alpha(x)$ satisfying

$$\alpha \underbrace{\left[-\left(\frac{U'(x)}{m\gamma} + D \frac{\partial}{\partial x} \right) P \right]}_{J} = -\frac{\partial}{\partial x} \alpha D P \,, \qquad (34)$$

because then the required solution is simply given by

$$-\frac{\partial}{\partial x} \alpha D P = \alpha J$$

$$\curvearrowright \; P(x) = -\frac{J}{D\alpha} \int_{x_1}^{x} dx' \alpha(x') = \frac{J}{D\alpha} \int_{x}^{x_1} dx' \, \alpha(x') \,.$$

The integrating factor $\alpha(x)$ is determined by writing out (34)

$$\frac{\alpha U'}{m\gamma} = D\alpha'.$$

This differential equation has the Solution

$$\alpha(x) = C\, e^{\frac{1}{k_BT}\int_{x_{min}}^{x} dx'\, U'(x')}$$

$$= C\, e^{\frac{U(x)}{k_BT}} \qquad U(x_{min}) = 0$$

Obtain

$$P(x) = \frac{J}{D}\, e^{-\frac{U(x)}{k_BT}} \int_{x}^{x_1} dx\, e^{\frac{U(x)}{k_BT}}$$

From normalisation

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

it follows that

$$\frac{J}{D} \int_{-\infty}^{x_1} dx\, e^{-\frac{U(x)}{k_BT}} \int_{x}^{x_1} dx'\, e^{\frac{U(x')}{k_BT}} = 1$$

and therefore

$$J = \frac{D}{\int_{-\infty}^{x_1} dx\, e^{-\frac{U(x)}{k_BT}} \int_{x}^{x_1} dx'\, e^{\frac{U(x')}{k_BT}}}$$

Evaluate both integrals in saddle-point approximation

$$U(x') \approx \overbrace{U(x_{max})}^{E_a} - \frac{1}{2}|U''(x_{max})|\,\delta x'^2,$$

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

Find

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

$$\varkappa = \frac{\sqrt{|U''(x_{max})|/m}}{\gamma} \qquad (35)$$

$$\omega_0 = \sqrt{U''(x_{min})/m}$$

Arrhenius law. Same as eq. (17) in [8].

11. Fisher-Wright model

Widely used stochastic model for reproduction in population genetics [9, 10].

Consider a single locus A in a population of N diploid individuals (Chromosomes occur in pairs).
Assume that there are two distinct alleles (genetic variants) at locus A, denoted by A_1 and A_2. The Fisher-Wright model is based on four assumptions concerning inheritance:

① Non-overlapping generations

② Mendelian inheritance: chromosome pairs in a diploid organism segregate to form gametes. Progeny inherits random gamete from mother and random gamete from father

mother		father		progeny
A_1/A_1	X	A_1/A_1	$\longrightarrow$	all A_1/A_1
A_1/A_1	X	A_1/A_2	$\longrightarrow$	A_1/A_1 and A_1/A_2 in equal proportions

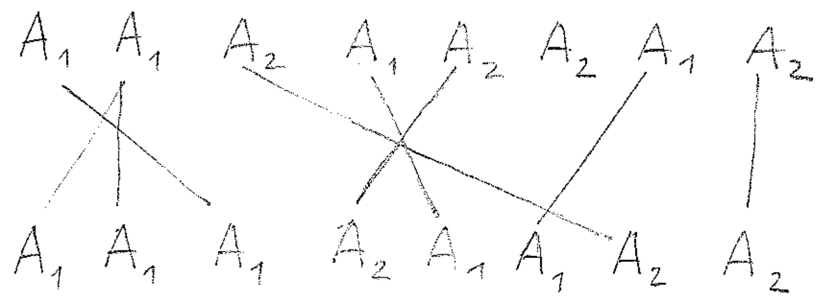
and so forth.

③ Random mating

④ Neutrality

In an infinite population, Mendelian inheritance and random mating give rise to Hardy-Weinberg equilibrium (genotype frequencies remain constant over time).

But in finite population: <u>genetic drift</u>.
Consider pool of $2N$ alleles in a given generation. Inheritance: random choice with replacement



Given that there are i alleles of type A_1 in a generation, the probability of observing j in the next generation is

$$p_{ij} = \binom{2N}{j} \left(\frac{i}{2N}\right)^{j} \left(1 - \frac{i}{2N}\right)^{2N-j} \qquad (36)$$

$$\frac{(2N)!}{(2N-j)!\,j!}$$

Large but finite population.

Within diffusion approximation represent possible gene frequencies $0, \frac{1}{2N}, \frac{2}{2N}, \dots, \frac{2N}{2N}$ by continuous variable $0 \leq x \leq 1$.

Measure time in units of $2N$ ($\delta t = \frac{1}{2N}$) and derive Fokker-Planck equation

$$a_1(x) = \frac{\langle \delta x \rangle_x}{\delta t} = 0$$

$$a_2(x) = \frac{\langle \delta x^2 \rangle_x}{\delta t} = 2N \sum_j \left(\frac{i-j}{2N}\right)^2 \binom{2N}{j} \left(\frac{i}{2N}\right)^j \left(1-\frac{i}{2N}\right)^{2N-j}$$

$$= \frac{i\,(2N-i)}{4N^2} = x\,(1-x)$$

Fokker-Planck equation

$$\frac{\partial P(x,t)}{\partial t} = \frac{\partial^2}{\partial x^2} \frac{x(1-x)}{2} P(x,t) \qquad (37)$$

Probability current

$$J(x,t) = -\frac{\partial}{\partial x}\, x(1-x)\, P(x,t)$$

Boundary condition: no probability leaves $[0,1]$

$$J(0,t) = 0$$

$$J(1,t) = 0$$

Steady-state solution $P_\infty(x)$ satisfies (constant J must vanish due to boundary conditions)

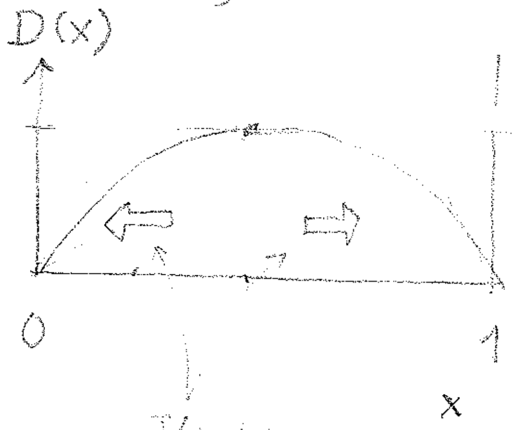
$$x(1-x)\,P_\infty(x) = \text{const.}$$

$$P_\infty(x) = \frac{C}{x(1-x)} + C_0\,\delta(x) + C_1\,\delta(1-x)$$

$P_\infty(x)$ must be normalised, so $C=0$, and $C_0 + C_1 = 1$

$$P_\infty(x) = C_0\,\delta(x) + (1-C_0)\,\delta(1-x) \qquad (38)$$

Eventually all alleles are of type A_1, or all of type A_2 (<u>fixation</u>). C_0 is initial frequency of A_1 alleles.



$P(x,t)$ approaches a constant (in x) for $0<x<1$ which vanishes as $t\to\infty$

$J(x,t)$ for x-independent P

12. Advection

Dynamics of tracer particles in a random (or turbulent) velocity field $\underline{u}(\underline{r},t)$

$$\dot{\underline{r}} = \underline{u}(\underline{r},t) \tag{39}$$

Corresponding stochastic advection equation for concentration $\varrho(\underline{r},t) = \sum_i \delta^{(3)}(\underline{r}-\underline{r}_i)$

$$\frac{\partial \varrho(\underline{r},t)}{\partial t} + \underline{\nabla}\, \underline{u}(\underline{r},t)\, \varrho(\underline{r},t) = 0 \tag{40}$$

Note: concentration depends upon realisation of the random function $\underline{u}(\underline{r},t)$.
(40) is continuity equation with current $\underline{u}\varrho$.

Perform ensemble average. Take one spatial dimension

$$\frac{\partial \varrho(x,t)}{\partial t} + \frac{\partial}{\partial x}\Big(u(x,t)\, \varrho(x,t) \Big) = 0 \tag{41}$$

where $u(x,t)$ is a random velocity field with properties

$$\langle u(x,t) \rangle = 0$$
$$\langle u(x,t)\, u(x',t') \rangle = C(x-x', t-t') \tag{42}$$

Consider finite domain $0 \leq x \leq L$ with periodic b.c.

Expect $\langle \rho(x,t)\rangle = $ const. Compute correlation function

$$K(x,x';t) = \langle \rho(x,t)\,\rho(x',t)\rangle. \qquad (43)$$

Derive Fokker-Planck equation for correlation function. Write equation analogous to (19) on p. 16

$$K(x,x';t+\delta t) = \delta t \int dy \int dy'\, W_{\delta t}(x,x',y,y')\, K(y,y';t)$$

Here $W_{\delta t}(x,x',y,y')$ is the rate for two particles initially at positions y and y' to jump to x and x' in time δt.

Translational invariance

$$K(x,x';t) = k(x'-x,t) \qquad x'-x = \Delta x$$

$$W_{\delta t}(xx'yy') = \frac{p(x-y,\, x'-y',\, y-y')}{\delta t}$$

Have

$$k(\Delta x, t+\delta t) = \int dz \int dz'\, p(z,z',\Delta x-(z-z')) \times k(\Delta x-(z-z'), t)$$

Now expand in $z-z'$ around Δx

$$k(\Delta x, t+\delta t) = \sum_{j=0}^{\infty} \frac{1}{j!} \int dz \int dz' \, (z-z')^j \times \frac{\partial^j}{\partial \Delta x^j} (pk)$$

$$= \delta t \sum_{j=0}^{\infty} \frac{1}{j!} \frac{\partial^j}{\partial \Delta x^j} \left[a_j(\Delta x) \, k(\Delta x, t) \right]$$

with

$$a_j(\Delta x) = \frac{1}{\delta t} \int dz \int dz' \, (z-z')^j \, p(z, z'; \Delta x).$$

Find

$$a_0(\Delta x) = \frac{1}{\delta t}$$

$$a_1(\Delta x) = 0$$

$$a_2(\Delta x) = \frac{1}{\delta t} \left\langle \left(z(x') - z(x) \right)^2 \right\rangle$$

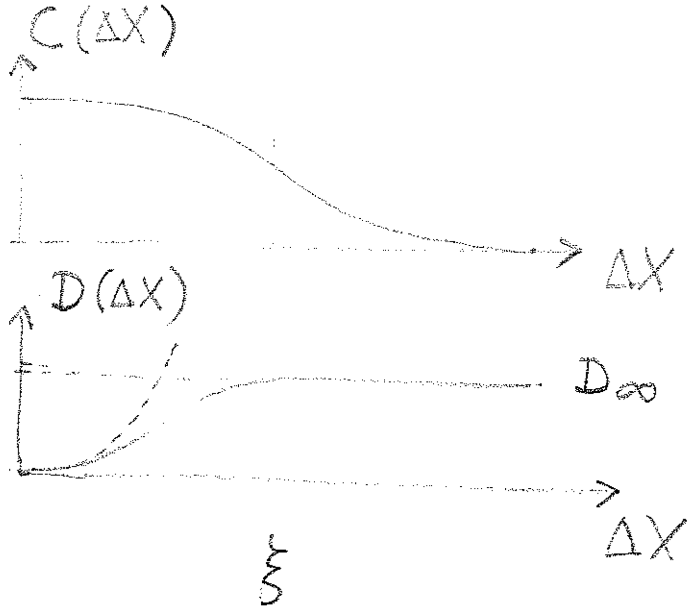
$$= 2 \left[c(0) - c(\Delta x) \right]$$

Fokker Planck equation [11, 12]

$$\frac{\partial k(\Delta X, t)}{\partial t} = \frac{\partial^2}{\partial \Delta X^2} D(\Delta X)\, k(\Delta X, t) \tag{45}$$

with diffusion constant

$$D(\Delta X) = C(0) - C(\Delta X) \tag{46}$$



$$D(\Delta X) \sim D_\infty, \quad \Delta X \gg \xi$$

$$D(\Delta X) \sim \varkappa \Delta X^2, \quad \Delta X \ll \xi$$

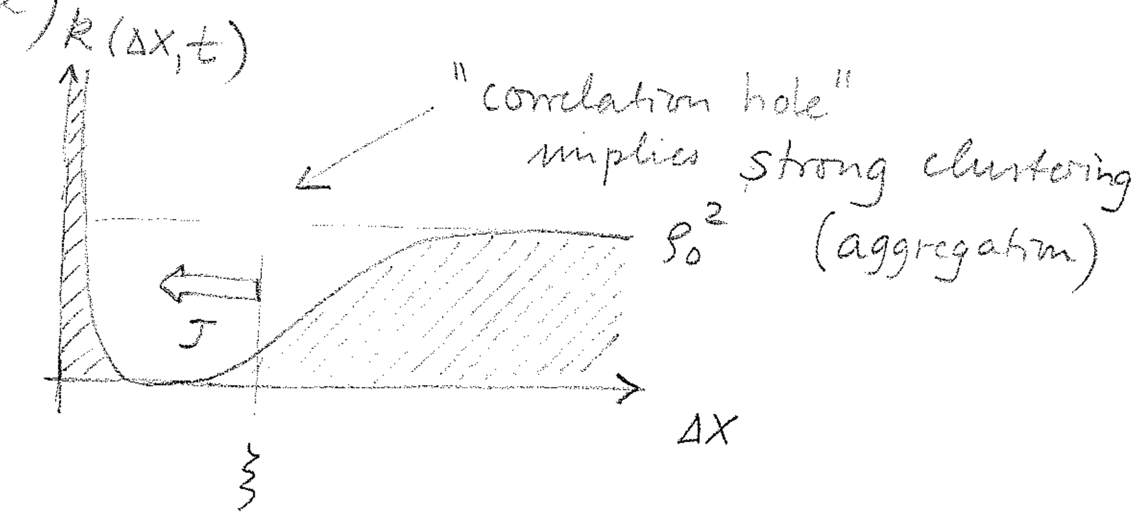
because $C(\Delta X)$ is smooth and even in ΔX.

Probability current

$$J(\Delta X, t) = -\frac{\partial}{\partial \Delta X} D(\Delta X)\, k(\Delta X, t) \qquad (47)$$

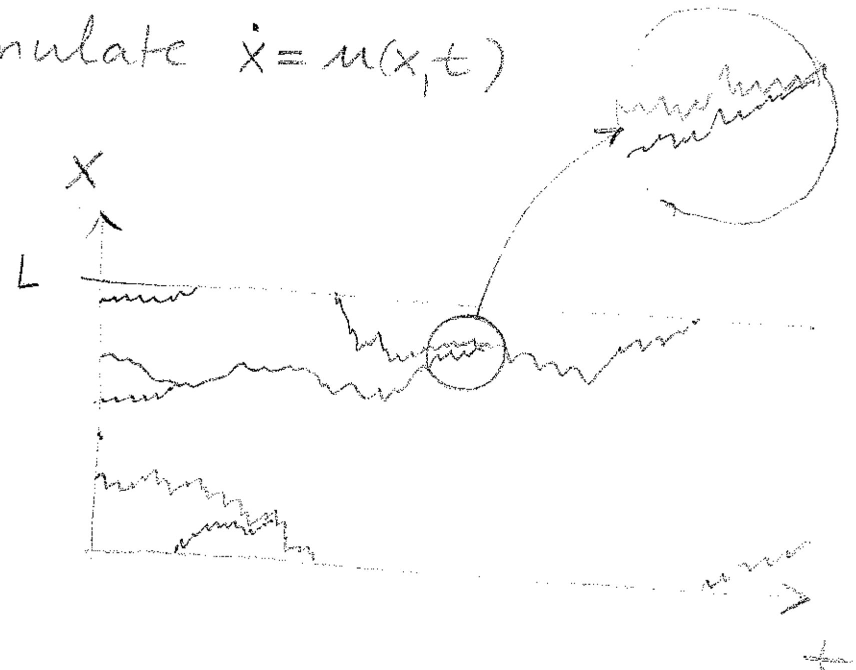
Consider initially uniform density ρ_0 so that $k = \rho_0^2$ is constant. Eq. (47) then implies that there is an initial probability current towards the origin $\Delta X = 0$.

Steady-state solution would be $\sim \frac{\text{const.}}{D(\Delta X)}$ since this diverges as ΔX^{-2}, this steady-state solution is not normalisable. Expect that $k(\Delta X, t)$ becomes very sharply peaked at the origin, developing a δ-function singularity (see discussion of Fisher-Wright model)



Path coalescence [12]

Simulate $\dot{x} = u(x,t)$



Each individual particle diffuses.