

Lectures on diffusion in complex and random media

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Chapter 1

Introduction

1.1 Subject of the lectures

These lectures concern diffusion processes in heterogeneous environments. The diffusion processes we will examine have two driving mechanisms (i) a drift due to external forces such as electric fields, gravity *etc.* as well as a random noise term whose amplitude can vary in space. A typical example is the diffusion of a colloid in a medium whose local properties vary in space (and possibly in time), for example the heterogeneous medium found inside biological cells. In general, the behavior of these processes is difficult to characterize, however in many cases (in fact almost all cases), when seen at sufficiently large length and time scales the process behaves as a simple random walk with bias, it can be characterized by its mean displacement and mean squared displacement which are in turn described by effective drifts and diffusion constants. These effective transport properties effectively characterize the dispersion properties of the system and are the basic parameters needed to compute reaction rates, survival probabilities, mean exit times *etc.*

1.2 A few remarks about notation

We will examine stochastic equations which contain random noise, for instance due to random molecular collisions in the case of Brownian motion. The history of noise in the system is a random functional, the mean displacement of a particle, whose position is denoted by $\mathbf{X}(t)$, at time t is denoted by

$$\mathbb{E}(\mathbf{X}(t)), \tag{1.1}$$

here \mathbb{E} denotes the average over all possible realizations of the noise. In physics the average value of a random variable X usually denoted as $\langle X \rangle$. In these lectures the environment can also be random and so there are both averages over the random noise (\mathbb{E}) and averages over the environmental disorder (for instance time independent random potentials) which

we will denote by $\langle \cdot \rangle$. Finally we will denote by $\langle f \rangle_s$ the spatial average of a function $f(\mathbf{x})$ defined over a volume V as

$$\langle f \rangle_s = \frac{1}{V} \int_V d\mathbf{x} f(\mathbf{x}). \quad (1.2)$$

Unless otherwise stated I will use the Einstein summation convention where repeated spatial indices are summed over, for instance the scalar product between two vectors (which are written in boldface) \mathbf{a} and \mathbf{b} , whose components are denoted by a_i and b_i respectively, is written as

$$\mathbf{a} \cdot \mathbf{b} = a_i b_i \quad (1.3)$$

Chapter 2

Crash course on stochastic calculus

Here we will look at a class of stochastic processes, known as Langevin processes in physics, from an informal probabilistic point of view. The slight effort required, with respect to physical approaches, is worth it as many aspects such as the derivation of the Fokker-Planck equation and first passage times are immediate in this formalism. A basic knowledge of this approach will also be useful in Wall Street or London if you decide that you are more interested in making money than doing physics. The stochastic calculus is the foundation of financial mathematics and the basis of the famous Black-Scholes formula for pricing options.

2.1 Discrete time continuous space stochastic processes

Consider a discrete time stochastic process in one dimension (defined at a discrete set of times $t = n\Delta t$ where $n \in \mathbb{Z}$) obeying the difference equation

$$X_{(n+1)\Delta t} - X_{n\Delta t} = \Delta X_t = u(X_t)\Delta t + a(X_t)\Delta B_t \quad (2.1)$$

Here $u(x)$ is a local drift field which is deterministic and depends on the particle's position X_t - it can be due to convection in a fluid for example or the buoyancy force for a fluid particle in the Stokes regime of hydrodynamics (viscous flows). The second term is a noise term due to random fluctuations which are often thermal in nature depending on $k_B T$, for a colloid in a fluid the noise term generates an effective molecular diffusivity which disperses the particle even in the absence of any overall hydrodynamic flow. The stochastic increment ΔB_t is Gaussian with zero mean so

$$\mathbb{E}(\Delta B_t) = 0, \quad (2.2)$$

and we choose the variance to be

$$\mathbb{E}([\Delta B_t]^2) = \Delta t. \quad (2.3)$$

This means that its probability density function $p(x)$ is given by

$$p(x)dx = \text{Prob}(\Delta B_t \in [x, x + dx]) = \frac{1}{\sqrt{2\pi\Delta t}} \exp\left(-\frac{x^2}{2\Delta t}\right)dx. \quad (2.4)$$

If the noise has no memory then the fundamental stochastic increments are statistically independent so

$$\mathbb{E}(\Delta B_t \Delta B_{t'}) = \mathbb{E}(\Delta B_t) \mathbb{E}(\Delta B_{t'}) = 0 \quad (2.5)$$

for two different times t and t' . Noise which is uncorrelated in time is referred to as white noise, noise with a non-zero correlation time is referred to as colored. The hypothesis of white noise requires a separation of times scales, for instance, in colloids the molecular time scales responsible for the noise are indeed much shorter than the times scales for colloidal motion. In the simplest case where $u = 0$ and a is constant we can write down the particle position at time $t = n\Delta t$ as

$$X_t = x_0 + a \sum_{i=1}^n \Delta B_{i\Delta t}, \quad (2.6)$$

where x_0 is the starting position at time 0. The easiest way of calculating the distribution of X_t , $p(x, t)$ is via its Fourier transform (known as the characteristic function)

$$\begin{aligned} \tilde{p}(k, t) &= \int dx p(x, t) \exp(-ikx) = \mathbb{E}(\exp(-ikX_t)) \\ &= \exp(ikx_0) \prod_{i=1}^n \mathbb{E}(\exp[-ika\Delta B_{i\Delta t}]) = \exp(ikx_0) \exp\left(-\frac{a^2}{2}k^2n\Delta t\right). \end{aligned} \quad (2.7)$$

Now noting that $n\Delta t = t$ and inverting the Fourier transform we find⁽¹⁾

$$p(x, t) = \frac{1}{2\pi} \int dk \exp(ikx) \mathbb{E}(\exp[-ikX_t]) = \frac{1}{\sqrt{2\pi a^2 t}} \exp\left(-\frac{1}{2a^2 t}(x - x_0)^2\right) \quad (2.8)$$

The continuous diffusion equation in one dimension is

$$\frac{\partial p(x, t)}{\partial t} = D \frac{\partial^2}{\partial x^2} p(x, t). \quad (2.9)$$

The term, D has dimensions L^2/T and is called the diffusion constant. If the particle is started at x_0 at time $t = 0$ the initial condition is $p(x, 0) = \delta(x - x_0)$. The easiest way to solve the diffusion equation is by taking a Fourier transform, so calculate the characteristic function, to obtain

$$\frac{\partial \tilde{p}(k, t)}{\partial t} = -Dk^2 \tilde{p}(k, t), \quad (2.10)$$

⁽¹⁾Exercise - show the formula that follows

which has the general solution

$$\tilde{p}(k, t) = \tilde{p}(k, 0) \exp(-Dk^2t) = \exp(-ikx_0) \exp(-Dk^2t). \quad (2.11)$$

This is the same characteristic function as for our discrete model if we identify $D = a^2/2$. In the continuum limit $\Delta t \rightarrow 0$ we have constructed a stochastic process whose statistics are described by the diffusion equation. The average displacement of the stochastic process $\mathbb{E}(X_t - x_0) = 0$, while the mean squared displacement is given by $\mathbb{E}((X_t - x_0)^2) = a^2t = 2Dt$ ⁽²⁾.

2.2 The Ito Stochastic Calculus

Here we want to take the continuum limit of the stochastic equation (2.1). We see that by construction the noise term ΔB_t is $O(\sqrt{\Delta t})$ and so the term ΔB_t^2 is $O(\Delta t)$ and so we need to keep it in deriving differential equations. Consider for a moment

$$S = \sum_{i=1}^N \Delta B_{i\Delta t}^2. \quad (2.12)$$

We find that the mean of S is given by

$$\mathbb{E}(S) = \sum_{i=1}^N \mathbb{E}(\Delta B_{i\Delta t}^2) = N\Delta t = t. \quad (2.13)$$

However we have from Wick's theorem⁽³⁾:

$$\begin{aligned} \mathbb{E}(S^2) &= \sum_{ij=1}^N \mathbb{E}(\Delta B_{i\Delta t}^2 \Delta B_{j\Delta t}^2) \\ &= \sum_{ij=1}^N \mathbb{E}(\Delta B_{i\Delta t}^2) \mathbb{E}(\Delta B_{j\Delta t}^2) + 2\mathbb{E}(\Delta B_{i\Delta t} \Delta B_{j\Delta t})^2 \\ &= \sum_{ij=1}^N \Delta t^2 + 2\delta_{ij}\Delta t^2 = t^2 + 2\frac{t^2}{N} \end{aligned} \quad (2.14)$$

The variance of S is thus given by

$$\text{var}(S) = \mathbb{E}(S^2) - \mathbb{E}^2(S) = 2\frac{t^2}{N}, \quad (2.15)$$

⁽²⁾Exercise - derive this formula using the characteristic function

⁽³⁾Exercise: If you don't know, find out what Wick's theorem is, and prove the following formulas

so in the limit of large N this means $\text{var}(S) \rightarrow 0$ and so $S = E(S)$ (this is basically the central limit theorem). The continuum stochastic differential equation Eq. (2.1) now becomes

$$dX_t = u(X_t)dt + a(X_t)dB_t \quad (2.16)$$

where $\mathbb{E}([dB_t]^2) = dt$, further more we find from above that over any time interval t ,

$$\int_0^t dB_s^2 = \mathbb{E} \left(\int_0^t [dB_s]^2 \right) = t, \quad (2.17)$$

differentiating this with respect to t (completely non-rigorously) then gives

$$[dB_t]^2 = dt. \quad (2.18)$$

Using this we can see how an arbitrary function f of the process X_t evolves, i.e. find the SDE for $f(X_t)$

$$df(X_t) = \frac{\partial f(X_t)}{\partial x} dX_t + \frac{1}{2} \frac{\partial^2 f(X_t)}{\partial x^2} [dX_t]^2 + O(dt^{\frac{3}{2}}), \quad (2.19)$$

here we need to keep the second term in the Taylor expansion to makes sure we have all the terms $O(dt)$. We have that

$$dX_t^2 = a^2(X_t)[dB_t]^2 + O(dt^{\frac{3}{2}}) = a^2(X_t)dt, \quad (2.20)$$

where we have used Eq. (2.18). The SDE for f is then

$$df(X_t) = \frac{\partial f(X_t)}{\partial x} (u(X_t)dt + a(X_t)dB_t) + \frac{1}{2} \frac{\partial^2 f(X_t)}{\partial x^2} a^2(X_t)dt. \quad (2.21)$$

Because dB_t is chosen independently of the position X_t , taking the average of Eq. (2.21) yields

$$\mathbb{E} \left(\frac{df(X_t)}{dt} \right) = \mathbb{E} \left(\frac{\partial f(X_t)}{\partial x} u(X_t) + \frac{1}{2} \frac{\partial^2 f(X_t)}{\partial x^2} a^2(X_t) \right) \quad (2.22)$$

2.3 Examples of Stochastic Differential Equations

What a physicist calls Brownian motion is actually the process obeying the equation

$$mdV_t = -\gamma V_t dt + a dB_t, \quad (2.23)$$

here V_t is the velocity of a particle of mass m , the SDE is simply Newton's second law relating the momentum change on the right hand side to the force on the left hand side. The process V_t , the velocity of the Brownian particle, is called an Orstein-Uhlenbeck process. The forces acting are: a friction term, with friction coefficient γ plus a random noise due to molecular collisions with the solvent molecules (which are also responsible for the

friction). For a spherical colloidal particle in the limit of Stokes flow (low Reynolds number or viscous flow) the friction coefficient is given by the Stoke's formula $\gamma = 6\pi\eta R$, where R is the colloid radius and η the liquid's viscosity.

Taking the average value of this equation shows that the average value of the velocity $\mathbb{E}(V_t)$ is zero. Consider now the variable $S_t = V_t^2$, we see that S_t obeys

$$\begin{aligned} dS_t &= 2V_t dV_t + \frac{1}{2}2[dV_t]^2 = 2V_t\left(-\frac{\gamma}{m}V_t dt + \frac{a}{m}dB_t\right) + \frac{a^2}{m^2}dt \\ &= -2\frac{\gamma}{m}S_t dt + 2\frac{a}{m}\sqrt{S_t}dB_t + \frac{a^2}{m^2}dt. \end{aligned} \quad (2.24)$$

Taking the average of this equation then gives

$$\mathbb{E}(dS_t) = \left[-2\frac{\gamma}{m}\mathbb{E}(S_t) + \frac{a^2}{m^2}\right]dt. \quad (2.25)$$

In thermodynamic equilibrium averages (of quantities at a single time) become time independent, and this implies that

$$\mathbb{E}(S_t) = \frac{a^2}{2\gamma m}. \quad (2.26)$$

However equipartition of energy also tells us that

$$\mathbb{E}\left(\frac{1}{2}mV_t^2\right) = \frac{1}{2}k_B T \implies \frac{1}{2}m\mathbb{E}(S) = \frac{a^2}{4\gamma}, \quad (2.27)$$

this means the amplitude of the noise must be given by

$$a = \sqrt{2k_B T \gamma}. \quad (2.28)$$

This is an example of a fluctuation dissipation theorem that relates the dissipation, friction, in a system to the fluctuations - the noise. The position of the Brownian particle, if started from the origin, is given by

$$X_t = \int_0^t V_s ds, \quad (2.29)$$

the MSD is then

$$\mathbb{E}(X_t^2) = \int_0^t \int_0^t ds ds' \mathbb{E}(V_s V_{s'}), \quad (2.30)$$

so we need to know the correlation function of the velocity. We start by writing Eq. (2.23) as

$$md[V \exp(\frac{\gamma}{m}t)] = \exp(\frac{\gamma}{m}t)dB_t, \quad (2.31)$$

which we can integrate to give

$$V_t = V_0 \exp(-\frac{\gamma}{m}t) + \frac{1}{m} \int_0^t ds \exp\left(-\frac{\gamma}{m}(t-s)\right) dB_s. \quad (2.32)$$

This gives the correlation function for V to be

$$\mathbb{E}(V_t V_0) = \mathbb{E}(V_0^2) \exp(-\frac{\gamma}{m}t), \quad (2.33)$$

and if we assume that V_0 has the equilibrium steady state distribution we find

$$\mathbb{E}(V_t V_0) = \frac{k_B T}{m} \exp(-\frac{\gamma}{m}t). \quad (2.34)$$

Using time translational invariance of the equilibrium state we thus have $\mathbb{E}(V_s V_{s'}) = \frac{k_B T}{m} \exp(-\frac{\gamma}{m}|s - s'|)$ (so V is an example of a coloured noise). The term $\tau = m/\gamma$ is a relaxation time or persistence time for the velocity. This means that the velocity is more or less the same for the time τ and changes at times bigger than τ . The MSD is now given by (splitting the integral into the regions where $s < s'$ and $s > s'$ and using symmetry)

$$\begin{aligned} \mathbb{E}(X_t^2) &= 2 \frac{k_B T}{m} \int_0^t ds \int_0^s ds' \exp\left(-\frac{\gamma}{m}(s - s')\right) = 2 \frac{k_B T}{\gamma} \left[\int_0^t ds [1 - \exp(-\frac{\gamma}{m}s)] \right] \\ &= 2 \frac{k_B T}{\gamma} \left(t - \frac{m}{\gamma} [1 - \exp(-\frac{\gamma}{m}t)] \right). \end{aligned} \quad (2.35)$$

For short times we find that

$$E(X_t^2) = \frac{k_B T}{m} t^2, \quad (2.36)$$

this is the ballistic regime where the velocity is constant and has the Maxwell-Boltzmann distribution. At later times however we find

$$E(X_t^2) = 2 \frac{k_B T}{\gamma} t, \quad (2.37)$$

this means that the effective diffusion constant of the particle is given by

$$D = \frac{k_B T}{\gamma} \quad (2.38)$$

this is the famous Stokes-Einstein relation between the friction coefficient and diffusion constant. Notice that the correlation between the velocity can be written as

$$\mathbb{E}(V_s V_{s'}) = \frac{k_B T}{\gamma \tau} \exp(-\frac{1}{\tau}|s - s'|), \quad (2.39)$$

where inertia is small, *i.e.* $m \rightarrow 0$ we have $\tau \rightarrow 0$ and

$$g(s - s') = \frac{1}{\tau} \exp(-\frac{1}{\tau}|s - s'|) \rightarrow 2\delta(s - s').^{(4)} \quad (2.40)$$

⁽⁴⁾Exercise- prove this by looking at integrals of the form $\int ds' g(s - s') f(s')$

In this limit we find the mathematical version of Brownian motion. This limit is called the overdamped limit where the inertial or acceleration term in Eq. (2.23) can be neglected to give simply

$$-\gamma V_t dt + \sqrt{2k_B T \gamma} dB_t = 0 \implies V_t dt = dX_t = \sqrt{\frac{2k_B T}{\gamma}} dB_t. \quad (2.41)$$

2.4 The Generator and the Forward Fokker-Planck Equation

Consider the average value of an arbitrary function f evaluated at the point X_t for a stochastic process obeying an Ito SDE, started at x_0 at time $t = 0$, by definition

$$\mathbb{E}^{x_0}(f(X_t)) = \int dx p(x, x_0; t) f(x). \quad (2.42)$$

Now take the time derivative of the above to get

$$\begin{aligned} \mathbb{E}^{x_0} \left(\frac{df(X_t)}{dt} \right) &= \int dx \frac{\partial p(x, x_0; t)}{\partial t} f(x) = \mathbb{E}^x \left(\frac{\partial f(X_t)}{\partial x} u(X_t) + \frac{1}{2} \frac{\partial^2 f(X_t)}{\partial x^2} a^2(X_t) \right) \\ &= \int dx p(x, x_0; t) G f(x), \end{aligned} \quad (2.43)$$

where the operator G is called the generator and is defined by its action on a function f by

$$G f = \frac{1}{2} a^2(x) \frac{\partial^2 f(x)}{\partial x^2} + u(x) \frac{\partial f(x)}{\partial x}. \quad (2.44)$$

This means that

$$\int dx \frac{\partial p(x, x_0; t)}{\partial t} f(x) = \int dx p(x, x_0; t) G f(x). \quad (2.45)$$

Using the definition of the adjoint of G , denoted by G^\dagger , we can write that that

$$\int dx \frac{\partial p(x, x_0; t)}{\partial t} f(x) = \int dx G^\dagger p(x, x_0; t) f(x). \quad (2.46)$$

The above is true for any reasonable functions f and so we must have

$$\frac{\partial p(x, x_0; t)}{\partial t} = G^\dagger p(x, x_0; t). \quad (2.47)$$

The equation (2.47) is called the Forward-Fokker-Planck equation, it is called a forward equation because the partial differential equation is in terms of the variable x , the point at which the process ends up at time t . In one the dimensional systems studied here the generic Forward-Fokker-Planck equation is thus

$$\frac{\partial p(x, x_0; t)}{\partial t} = \frac{\partial^2}{\partial x^2} \left[\frac{a^2(x)}{2} p(x, x_0; t) \right] - \frac{\partial}{\partial x} [u(x) p(x, x_0; t)] \quad (2.48)$$

2.5 Generalization to higher dimensions

The generalization of Ito Calculus to higher dimensions is a straightforward exercise. The form of the SDE is

$$dX_i = u_i(\mathbf{X})dt + a_{ij}(\mathbf{X})dB_j \quad (2.49)$$

here the dB_i are independent stochastic increments for each spatial direction i . Here the Ito rule is $dB_i dB_j = \mathbb{E}(dB_i dB_j) = \delta_{ij} dt$. Recalling that the second order Taylor expansion in d dimensions (using the Einstein summation convention) is given by

$$f(\mathbf{x} + \mathbf{y}) = f(\mathbf{x}) + y_i \frac{\partial}{\partial x_i} f(\mathbf{x}) + \frac{1}{2} y_i y_j \frac{\partial^2 f(\mathbf{x})}{\partial x_i \partial x_j} + O(\mathbf{y}^3). \quad (2.50)$$

we see that generator is given by

$$Gf = \frac{1}{2} a_{ik}(\mathbf{x}) a_{jk}(\mathbf{x}) \frac{\partial^2 f(\mathbf{x})}{\partial x_i \partial x_j} + u_i(\mathbf{x}) \frac{\partial}{\partial x_i} f(\mathbf{x}). \quad (2.51)$$

The corresponding Forward-Fokker-Planck equation is thus

$$\frac{\partial p(\mathbf{x}, \mathbf{x}_0; t)}{\partial t} = \frac{\partial^2}{\partial x_i \partial x_j} \left[\frac{a_{ik}(x) a_{jk}(x)}{2} p(\mathbf{x}, \mathbf{x}_0; t) \right] - \frac{\partial}{\partial x_i} [u_i(\mathbf{x}) p(\mathbf{x}, \mathbf{x}_0; t)]. \quad (2.52)$$

2.6 A brief word on other forms of Stochastic Calculus.

There are other formulations of the stochastic calculus that differ from the Ito calculus in that the increment dB_t is correlated with the current particle position X_t . The most popular one is the Stratonovich version which looks like normal calculus without the second order derivative. Another version is the ant-Ito calculus, where some natural physical processes take their most simple form. However if we fix the Fokker-Planck equation the corresponding Ito, Stratonovich and anti-Ito processes will have the same statistics - only the stochastic equations will appear different. If the noise term does not depend on the position X_t , *i.e.* a_{ij} is constant, the process is independent of the version of the calculus used.

2.7 Links with physical descriptions of diffusion

In physics diffusion equations are often derived in terms of particle concentrations $c(\mathbf{x}; t)$, for particles that do not interact the concentration of particles evolves like the probability density function of a single particle and is only mathematically different in that it is not normalized to unity. In equilibrium, in the absence of external forces, tracer particles in a liquid or solid should have a uniform density which maximises the entropy of the system. If the distribution is not uniform the system will relax towards equilibrium, particles move

from regions where they are concentrated to regions where they are scarce. This means that a gradient of particle concentration should lead to a flow or current to redistribute the particles. Fick's first law states that

$$\mathbf{J} = -D\nabla c, \quad (2.53)$$

where D is the local collective diffusion constant which can depend on the environment. Along with the conservation equation

$$\frac{\partial c(\mathbf{x}, t)}{\partial t} + \nabla \cdot \mathbf{J} = 0, \quad (2.54)$$

we find the diffusion equation

$$\frac{\partial c(\mathbf{x}; t)}{\partial t} = \nabla \cdot D(\mathbf{x})\nabla c(\mathbf{x}; t). \quad (2.55)$$

From this we see that the generator for the corresponding SDE can be deduced by noting that

$$G^\dagger f = \nabla \cdot D(\mathbf{x})\nabla f \implies Gf = \nabla \cdot D(\mathbf{x})\nabla f = D(\mathbf{x})\nabla^2 f + \nabla D(\mathbf{x}) \cdot \nabla f \quad (2.56)$$

so here $G = G^\dagger$ so G is self adjoint. From G we can read off the Ito SDE corresponding to the Fick diffusion equation which is

$$d\mathbf{X}_t = \sqrt{2D(\mathbf{X}_t)}d\mathbf{B}_t + \nabla D(\mathbf{X}_t)dt. \quad (2.57)$$

This somewhat surprising result shows that, interpreted as an Ito process, a pure diffusion has a local drift or bias forcing it into regions where D is large ! Without this drift term the steady state distribution in a finite volume V is given by

$$p_s(\mathbf{x}) \propto \frac{1}{D(\mathbf{x})}, \quad (2.58)$$

rather than a uniform distribution. Physically, in regions where D is large the particle diffuses quickly and thus leaves them quickly, while it spends more time in regions where it diffuses slowly. The drift term is exactly the term necessary to counter this tendency by pushing particles back into the region of high diffusivity.

One way of obtaining a fluctuating diffusivity is by changing the temperature in the solvent or gas in which the particles diffuse. The Stokes-Einstein formula for the diffusivity is

$$D = \frac{k_B T}{\gamma} = \frac{k_B T}{6\pi R\eta(T)}, \quad (2.59)$$

so there is a dependency on the temperature T that can be very strong, especially for the viscosity η that can vary strongly with temperature, for example close to a liquid-glass transition. On top of this there is the effect of thermophoresis. In equilibrium the

temperature should be uniform and so a gradient in temperature can generate a current. This is the so called Soret effect where particles move along a temperature gradient. The current associated with a temperature gradient is given by

$$\mathbf{J}_T = -D_T c \nabla T, \quad (2.60)$$

its strength depends on the temperature gradient but also the local concentration of the particle number, the more particles there are the stronger the current. The factor D_T depends on the precise details of the interaction between the particles and the solvent. For example, smoke particles in a gas move away from regions of high temperature and D_T is thus positive. Physically this happens because, for a particle of finite size, the molecules on the hot side transfer more momentum than the molecules on the cooler side, thus pushing the particle away from regions of high temperature. For liquid solvents however, D_T can be negative.

If we write the overall diffusion equation including the currents coming from the concentration gradient and the temperature gradient we find⁽⁵⁾

$$\frac{\partial c(\mathbf{x}; t)}{\partial t} = \nabla \cdot (D(\mathbf{x}) \nabla c(\mathbf{x}, t) + D_T(\mathbf{x}) c(\mathbf{x}, t) \nabla T(\mathbf{x})). \quad (2.61)$$

Consider now a particle subject to an external force field in a solvent which exerts a random white noise force on the particle. The SDE for the velocity is

$$m d\mathbf{V}_t = -\gamma \mathbf{V}_t dt + \mathbf{F}(\mathbf{X}_t) dt + \sqrt{2k_B T \gamma} d\mathbf{B}_t. \quad (2.62)$$

In the over damped limit, $m \rightarrow 0$, this simplifies to give

$$d\mathbf{X}_t = \frac{1}{\gamma} \mathbf{F}(\mathbf{X}_t) dt + \sqrt{\frac{2k_B T}{\gamma}} d\mathbf{B}_t. \quad (2.63)$$

Often this sort of equation is written in terms of the bare diffusivity that the particle would have in the absence of the force, *i.e.* $D = k_B T / \gamma$ and so we have

$$d\mathbf{X}_t = \beta D \mathbf{F}(\mathbf{X}_t) dt + \sqrt{2D} d\mathbf{B}_t. \quad (2.64)$$

The generator G is given by

$$Gf = D \nabla^2 f + \beta D \mathbf{F} \cdot \nabla f, \quad (2.65)$$

where $\beta = 1/k_B T$, and from this we find the Fokker-Planck equation

$$\frac{\partial p(\mathbf{x}, \mathbf{x}_0, t)}{\partial t} = \nabla \cdot (D \nabla p(\mathbf{x}, \mathbf{x}_0, t) - D \beta \mathbf{F}(\mathbf{x}) p(\mathbf{x}, \mathbf{x}_0, t)). \quad (2.66)$$

⁽⁵⁾Exercise - write down the Ito SDE corresponding to this Fokker-Planck equation

In the case where \mathbf{F} is conservative, *i.e.* generated by a potential energy ϕ such that $\mathbf{F} = -\nabla\phi$ we see that the steady state distribution is given by the Gibbs Boltzmann distribution for the canonical ensemble

$$p_{eq}(\mathbf{x}) = \frac{\exp(-\beta\phi(\mathbf{x}))}{Z}, \quad (2.67)$$

where

$$Z = \int_V d\mathbf{x} \exp(-\beta\phi(\mathbf{x})), \quad (2.68)$$

is the canonical partition function which ensures the normalization of the probability density function over the finite volume V of the system. The solvent generating the stochastic noise exchanges energy with the particle and acts as the reservoir in the canonical ensemble.

2.8 First passage times

Imagine we have a problem where a molecule or colloid whose dynamics can be described by a SDE reacts when it hits a certain surface, given its starting point \mathbf{x} we can ask what is the average value of the time at which the particle arrives at the reactive surface? Denote by T the first passage time (FPT) to the surface Σ and define its average value, the mean first passage time (MFPT), starting from \mathbf{x} by $t(\mathbf{x}) = \mathbb{E}^{\mathbf{x}}(T)$. There are physical arguments based on fluxes to derive MFPTs but let's find the general equation probabilistically. If the particle starts at \mathbf{x} at time $t = 0$, in the following time interval dt the particle will move to $\mathbf{x} + d\mathbf{X}$ but also the time elapsed will increase by dt , this means that

$$t(\mathbf{x}) = \mathbb{E}(t(\mathbf{x} + d\mathbf{X})) + dt. \quad (2.69)$$

Now expanding $t(\mathbf{x} + d\mathbf{X})$ to second order in $d\mathbf{X}$ gives

$$t(\mathbf{x}) = t(\mathbf{x}) + Gt(\mathbf{x})dt + dt, \quad (2.70)$$

the $O(1)$ terms cancel and the remaining terms of $O(dt)$ then give

$$Gt(\mathbf{x}) = -1. \quad (2.71)$$

The only thing we need now are the boundary conditions, however if one starts on Σ then the first passage time to Σ is zero and so $t(\mathbf{x}) = 0$ on Σ are the boundary conditions. Consider a BM with diffusion constant D in one dimension started at some point $x \in [a, b]$, what is the expected hitting time of the edge of the interval? This means that

$$D \frac{\partial^2}{\partial x^2} t(x) = -1 \quad (2.72)$$

which has general solution $t(x) = -x^2/D + cx + d$, the boundary conditions then allow the determination of the constants of integration c and d to yield

$$t(x) = \frac{(b-x)(x-a)}{D}. \quad (2.73)$$

This result is interesting, it means that if b becomes large then the MPFT scales like b even if we start close to a . Most particles starting close to a will hit a within a finite time, however a few will go the wrong way and take a very long time to come back!⁽⁶⁾ Another question that helps elucidate the MFPT result above is whether the particle in question hits the point A or the point B first. One can imagine a problem with reactants in a two dimensional channel that stick to the upper or lower surfaces, from an initial concentration profile what proportion of the reactants get stuck to each surface? Denote by $P_a(x)$ the probability that the particle hits the point a before the point b . Again we just look at what happens in the first time step dt and write (consider a 1d problem - the generalisation to higher dimensions is straightforward)

$$P_a(x) = \mathbb{E}(P_a(x + dX)) = P_a(x) + GP_a(x)dt, \quad (2.74)$$

so we simply find $GP_a(x) = 0$. The boundary conditions are obviously $P_a(a) = 1$ and $P_a(b) = 0$. The solution is thus $P_a(x) = (b-x)/(b-a)$ ⁽⁷⁾. Now consider a particle diffusing in a potential in one dimension which is periodic with period L as shown in Fig. (2.84). The MFPT to points a and b starting from x obeys

$$D \frac{d^2}{dx^2} t(x) - D\beta \frac{d}{dx} \phi(x) \frac{d}{dx} t(x) = -1, \quad (2.75)$$

and this equation can be integrated to give

$$t(x) = -\frac{1}{D} \int_a^x dx' \exp(\beta\phi(x')) \int_a^{x'} dy \exp(-\beta\phi(y)) + A \int_a^x dx' \exp(\beta\phi(x')), \quad (2.76)$$

where in doing the last integration we have used $t(a) = 0$. The condition $t(b) = 0$ then gives the constant A and we obtain

$$t(x) = -\frac{1}{D} \int_a^x dx' \exp(\beta\phi(x')) \int_a^{x'} dy \exp(-\beta\phi(y)) + \left[\frac{1 \int_a^b dz \exp(\beta\phi(z)) \int_a^z dy \exp(-\beta\phi(y))}{\int_a^b dz \exp(\beta\phi(z))} \right] \int_a^x dx' \exp(\beta\phi(x')). \quad (2.77)$$

⁽⁶⁾Exercise - compute the mean first passage to a or b in presence of a uniform drift u

⁽⁷⁾Exercise - find P_a in presence of a uniform drift u

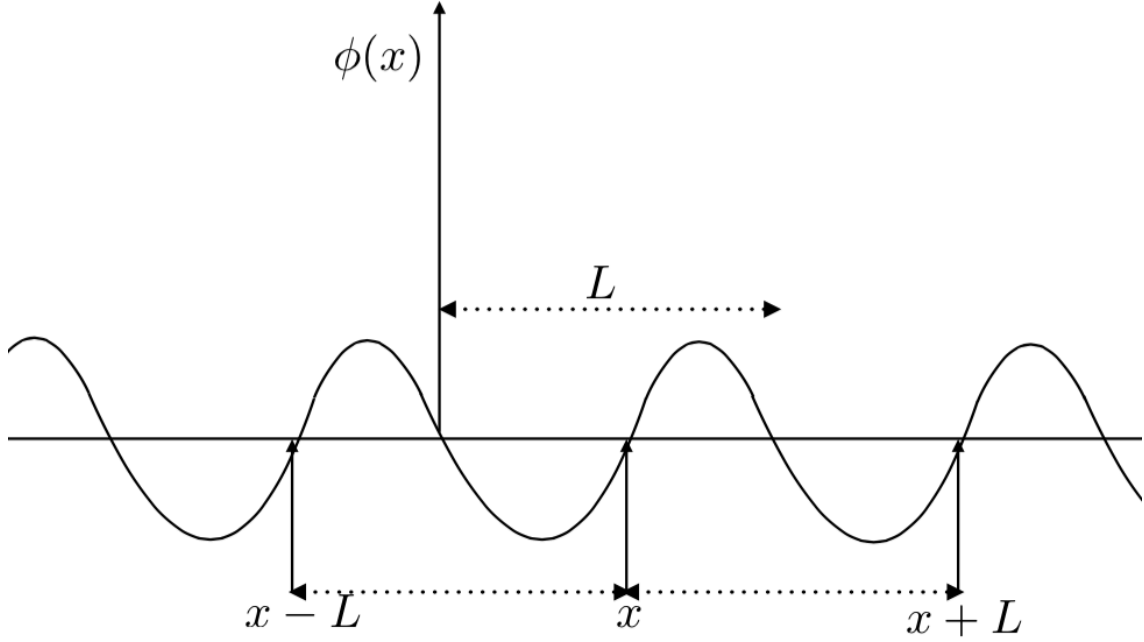


Figure 2.1: Periodic potential in one dimension

Now define by $t(x; L)$ the MFPT to move one period L to the left or the right of x , this means just choosing $a = x + L$ and $b = x - L$. This gives⁽⁸⁾

$$t(x, L) = \frac{1}{2D} \int_0^L dz \exp(\beta\phi(z)) \int_0^L dz \exp(-\beta\phi(z)), \quad (2.78)$$

remarkably we see that $t(x; L) = t(L)$ is independent of x . It is useful to visualize the coarse grained diffusion as a discrete random walk on the points nL - we say the discrete process is at the site nL until the continuous diffusion next arrives at $(n-1)L$ or $(n+1)L$, at which point the discrete process changes. This discrete random walk has no bias, it is equally likely to go to the left or right - we can see this by computing the probability that starting at x it hits $x + L$ before $x - L$. This probability of a positive step $P_+(x)$ (hitting $x + L$ before $x - L$) obeys

$$D \frac{d^2}{dx^2} P_+(x) - D\beta \frac{d}{dx} \phi(x) \frac{d}{dx} P_+(x) = 0, \quad (2.79)$$

⁽⁸⁾Exercise - do the straightforward but tedious algebra to show Eq. (2.78)

this has the solution⁽⁹⁾ $P_+(x) = 1/2$, so the discrete random walk so constructed is unbiased. Physically this has to be true but the maths is reassuring! We can actually use the mean first passage time distribution to compute the effective diffusion constant in this system. If the discrete random walk takes N steps during the time t it has a MSD (started from the origin)

$$\mathbb{E}(X_t^2) = L^2 N. \quad (2.80)$$

However $N \times t(L) = t$, the number of jumps made times the average time to jump must equal the total time (at late times) and so

$$\mathbb{E}(X_t^2) = L^2 \frac{t}{t(L)} = 2D_e t, \quad (2.81)$$

thus the effective diffusion constant D_e is given by

$$D_e = \frac{L^2}{2t(L)} = \frac{D}{\frac{1}{L} \int_0^L dz \exp(\beta\phi(z)) \frac{1}{L} \int_0^L dz \exp(-\beta\phi(z))}. \quad (2.82)$$

This result can be written in terms of the spatial averages

$$\langle \exp(\pm\beta\phi(z)) \rangle_s = \frac{1}{L} \int_0^L dz \exp(\pm\beta\phi(z)), \quad (2.83)$$

to give

$$D_e = \frac{D}{\langle \exp(\beta\phi) \rangle_s \langle \exp(-\beta\phi) \rangle_s}. \quad (2.84)$$

Using Jensen's inequality one can show that $D_e < D$ so the diffusion is always slowed down by the presence of a potential⁽¹⁰⁾ - this is due to the trapping in the minima of the potential. It is also amusing to note that the effective diffusion constant in the potential ϕ is identical to that in the inverted potential $-\phi$.

Using the expression for the MPFT Eq. (2.78) we can analyse what happens at low temperature. This means that β is large and so the integral

$$I_- = \int_0^L dz \exp(-\beta\phi(z)) \quad (2.85)$$

can be approximated about its minimal value occurring at z_{\min} (assuming it is unique). To do the integral we write $z = z_{\min} + \zeta$ and Taylor expand about z_{\min} to get

$$\begin{aligned} I_- &\approx \int_0^L d\zeta \exp\left(-\beta\phi(z_{\min}) - \frac{\beta}{2}\phi''(z_{\min})\zeta^2\right) \\ &\approx \int_{-\infty}^{\infty} d\zeta \exp\left(-\beta\phi(z_{\min}) - \frac{\beta}{2}\phi''(z_{\min})\zeta^2\right) = \sqrt{\frac{2\pi}{\beta\phi''(z_{\min})}} \exp(-\beta\phi(z_{\min})) \end{aligned} \quad (2.86)$$

⁽⁹⁾Exercise - prove this

⁽¹⁰⁾Exercise - find out what Jensen's inequality is and use it to prove $D_e < D$

The same method of calculation estimates I_+ from the contribution of the maximum of ϕ at the point z_{\max} and gives

$$I_+ \approx \sqrt{\frac{2\pi}{\beta|\phi''(z_{\max})|}} \exp(\beta\phi(z_{\max})). \quad (2.87)$$

We thus obtain the *Arrhenius law* for thermally activated energy barrier crossing

$$t(L) \approx \tau_0 \exp(\beta\Delta\phi), \quad (2.88)$$

where $\Delta\phi = \phi(z_{\max}) - \phi(z_{\min})$ is the biggest energy barrier the particle has to cross. The factor τ_0 is a time scale given by

$$\tau_0 = \frac{2\pi}{D\beta} \frac{1}{\sqrt{|\phi''(z_{\max})|\phi''(z_{\min})|}}, \quad (2.89)$$

we see that it depends on the details of the dynamics, the temperature, and the local curvature of the potential at the absolute maximum and minimum. At low temperatures the particle spends all its time trying to cross the barrier and the result becomes essentially independent of L .

Chapter 3

Diffusion in media with variable diffusivity

Here we consider the effective diffusivity of media with a locally varying diffusion constant $D(\mathbf{x})$ containing tracer particles which diffuse according to the diffusion equation

$$\frac{\partial}{\partial t}p(\mathbf{x}; t) = \nabla D(\mathbf{x}) \cdot \nabla p(\mathbf{x}; t). \quad (3.1)$$

The most important transport coefficients in heterogeneous media are the effective drift \mathbf{V}_e determined from the mean displacement

$$\mathbb{E}^{\mathbf{x}_0}(\mathbf{X}_t - \mathbf{x}_0) \sim \mathbf{V}_e t. \quad (3.2)$$

For large t and for isotropic systems the effective diffusion constant D_e is given by the dispersion about the mean displacement

$$\mathbb{E}^{\mathbf{x}_0}((\mathbf{X}_t - \mathbf{x}_0)^2) - [\mathbb{E}^{\mathbf{x}_0}(\mathbf{X}_t - \mathbf{x}_0)]^2 \sim 2dD_e t. \quad (3.3)$$

For systems which are not isotropic (say layered systems), the effective diffusion is characterized by an effective diffusion tensor D_{eij} . The effective diffusion tensor takes the form $D_{eij} = D_e \delta_{ij}$ when the system has a rotational invariance in the statistical sense. This means that at late times and seen on large length scales, a diffusing cloud of particles moves with average velocity \mathbf{V}_e while its size increases as $\sqrt{D_e t}$. If we consider a periodic system, where $D(\mathbf{x})$ is periodic over a unit cell Ω , and consider a steady states situation for the distribution of \mathbf{X} modulo Ω , we can show that the drift in this problem should be zero. Integrating the Ito SDE Eq. (2.57) for the process described by Eq. (3.1) we find the mean displacement to be

$$\mathbf{X}_t - \mathbf{x}_0 = \int_0^t ds \nabla D(\mathbf{X}_s) + \int_0^t d\mathbf{B}_s \sqrt{2D(\mathbf{X}_s)}; \quad (3.4)$$

upon taking the average this gives

$$\mathbb{E}(\mathbf{X}_t - \mathbf{x}_0) = \int_0^t ds \mathbb{E}(\nabla D(\mathbf{X}_s)). \quad (3.5)$$

However, D just depends on the position of \mathbf{X} modulo the periodic cell Ω which we denote as \mathbf{Y} and we assume that \mathbf{Y} is in equilibrium. In terms of the process \mathbf{Y} we have

$$\mathbb{E}(\mathbf{X}_t - \mathbf{x}_0) = \int_0^t ds \mathbb{E}(\nabla D(\mathbf{Y}_s)) \quad (3.6)$$

The Forward Fokker-Planck equation for \mathbf{Y} is the same as for \mathbf{X} except that it is restricted to Ω and has periodic boundary conditions. The steady state distribution is constant $p_s(\mathbf{y}) = 1/|\Omega|$ and using this the gives

$$\mathbb{E}(\mathbf{X}_t - \mathbf{x}_0) = \int_0^t ds \int_{\Omega} d\mathbf{y} p_s(\mathbf{y}) \nabla D(\mathbf{y}) = \int_0^t ds \frac{1}{|\Omega|} \int_{\Omega} d\mathbf{y} \nabla D(\mathbf{y}) = 0 \quad (3.7)$$

by periodicity. For a general SDE of the form Eq. (2.49), if the local diffusivity and drift are periodic on a unit cell Ω and we assume we start with \mathbf{X} modulo Ω in the steady state with distribution $p_s(\mathbf{y})$ on Ω , the mean displacement is given by

$$\mathbb{E}(\mathbf{X}_t - \mathbf{x}_0) = \mathbf{V}_e t, \quad (3.8)$$

for all times t , where the effective drift is given by

$$\mathbf{V}_e = \int_{\Omega} d\mathbf{y} p_s(\mathbf{y}) \mathbf{u}(\mathbf{y}). \quad (3.9)$$

Clearly in an isotropic system the effective drift is $\mathbf{0}$ as there is no preferred direction.

3.1 Links with electrical and porous media

The computation of the effective diffusion constant is greatly simplified by considering the link with a number of old, but important, physics, problems. Consider an isotropic dielectric medium with dielectric constant $\epsilon(\mathbf{x})$ which varies in space. A well studied example of such a dielectric medium is one of a background medium with dielectric constant ϵ , containing dielectric spheres of dielectric constant ϵ' placed randomly (having an isotropic distribution) in the medium.

The effective dielectric constant is defined as follows, applying an electric potential across the medium generates an average electric field

$$\langle \mathbf{E} \rangle_s = \frac{1}{V} \int d\mathbf{x} \mathbf{E}(\mathbf{x}), \quad (3.10)$$

the effective dielectric constant is then defined via

$$\epsilon_e \langle \mathbf{E} \rangle_s = \langle \epsilon(\mathbf{x}) \mathbf{E}(\mathbf{x}) \rangle_s. \quad (3.11)$$

The full computation of ϵ_e requires using the existence of the electric potential

$$\mathbf{E}(\mathbf{x}) = -\nabla \phi(\mathbf{x}), \quad (3.12)$$

and Poisson's equation in a dielectric medium

$$\nabla \cdot \mathbf{D} = 0, \quad (3.13)$$

where $\mathbf{D}(\mathbf{x}) = \epsilon(\mathbf{x}) \mathbf{E}(\mathbf{x})$ is the electric displacement. Mathematically identical problems include the computation of the effective conductivity of a heterogeneous conductor with local conductivity $\sigma(\mathbf{x})$. It is determined via the relation

$$\sigma_e \langle \mathbf{E} \rangle_s = \langle \sigma(\mathbf{x}) \mathbf{E}(\mathbf{x}) \rangle_s, \quad (3.14)$$

here again

$$\mathbf{E}(\mathbf{x}) = -\nabla \phi(\mathbf{x}), \quad (3.15)$$

and Ohms law gives the electric current as $\mathbf{j}(\mathbf{x}) = \sigma(\mathbf{x}) \mathbf{E}(\mathbf{x})$. In the steady state, charge conservation gives

$$\nabla \cdot \mathbf{j} = 0. \quad (3.16)$$

Finally the effective permeability of a porous media with respect to incompressible fluid flow is defined via

$$\kappa_e \langle \nabla P \rangle_s = \langle \kappa(\mathbf{x}) \nabla P(\mathbf{x}) \rangle_s, \quad (3.17)$$

where $\kappa(\mathbf{x})$ is the local permeability of the medium, related to the pore sizes and their geometries in rocks, and P is the local pressure. The velocity field of the fluid flow in the steady state is given by Darcy's law (which is phenomenological and supported by measurements on water bearing rocks in aquifers and oil bearing rocks in oil reservoirs)

$$\mathbf{u} = \kappa(\mathbf{x}) \nabla P(\mathbf{x}), \quad (3.18)$$

and the final equation comes from the incompressibility of the fluid flow

$$\nabla \cdot \mathbf{u} = 0. \quad (3.19)$$

These are all static problems while the problem of diffusion is clearly time dependent. However it can be shown that D_e is given by

$$D_e \langle \nabla p \rangle_s = \langle D(\mathbf{x}) \nabla p(\mathbf{x}) \rangle_s, \quad (3.20)$$

where $p(\mathbf{x})$ obeys

$$\nabla \cdot D(\mathbf{x}) \nabla p(\mathbf{x}). \quad (3.21)$$

This steady state diffusion problem corresponds to applying a concentration gradient across the medium, it relates the concentration gradient to the current via

$$D_e \langle \nabla p \rangle = -\langle \mathbf{J} \rangle, \quad (3.22)$$

where $\mathbf{J}(\mathbf{x}) = -D(\mathbf{x})\nabla p(\mathbf{x})$. As all these problems are mathematically equivalent, if you can solve one you can solve them all.

3.2 Diffusion with variable diffusivity in one dimension

In one dimension the steady state equation

$$\frac{d}{dx} D(x) \frac{d}{dx} p(x) = 0 \quad (3.23)$$

has the simple first integral

$$D(x) \frac{d}{dx} p(x) = -J \quad (3.24)$$

where the current J is constant, this means that

$$\langle D \frac{d}{dx} p \rangle_s = -J \quad (3.25)$$

but also

$$\langle \frac{d}{dx} p \rangle_s = -J \langle D^{-1} \rangle \quad (3.26)$$

Now using Eq. (3.20) gives

$$D_e \langle \frac{d}{dx} p \rangle_s = -J D_e \langle D^{-1} \rangle_s = \langle D \frac{d}{dx} p \rangle_s = -J, \quad (3.27)$$

and so

$$D_e = \langle D^{-1} \rangle_s^{-1}, \quad (3.28)$$

the average on the right hand side above is the harmonic mean of the local diffusivity $D(x)$.

3.3 Wiener bounds

The effective diffusion constant, in any dimension d , is constrained by the Wiener bounds

$$\langle D^{-1} \rangle_s^{-1} \leq D_e \leq \langle D \rangle_s. \quad (3.29)$$

we thus see that in one dimension the lower Wiener bound gives the exact result.

3.4 Exact result in two dimensions

The general solution of the steady state diffusion equation

$$\nabla \cdot D(x, y) \nabla p(x, y) = 0 \quad (3.30)$$

can be written in terms of another function $p'(x, y)$ via

$$D(x, y) \nabla p(x, y) = D(x, y) \begin{pmatrix} \frac{\partial}{\partial x} p(x, y) \\ \frac{\partial}{\partial y} p(x, y) \end{pmatrix} = D_0 \begin{pmatrix} -\frac{\partial}{\partial y} p'(x, y) \\ \frac{\partial}{\partial x} p'(x, y) \end{pmatrix}, \quad (3.31)$$

this can be rearranged to give

$$D'(x, y) \nabla p'(x, y) = D'(x, y) \begin{pmatrix} \frac{\partial}{\partial x} p'(x, y) \\ \frac{\partial}{\partial y} p'(x, y) \end{pmatrix} = D_0 \begin{pmatrix} \frac{\partial}{\partial y} p(x, y) \\ -\frac{\partial}{\partial x} p(x, y) \end{pmatrix}, \quad (3.32)$$

where $D'(x, y) = D_0^2/D(x, y)$. So we see that p' also obeys a steady state diffusion equation

$$\nabla \cdot D'(x, y) \nabla p'(x, y) = 0. \quad (3.33)$$

Now consider the case where $D'(x, y) \equiv D(x, y)$, that is to say they are statistically equivalent or are the same fields up to a translation; this means that we must have $D_e = D'_e$. Taking the spatial averages of Eqs. (3.31) and (3.32) gives

$$D_e \begin{pmatrix} \langle \frac{\partial}{\partial x} p(x, y) \rangle_s \\ \langle \frac{\partial}{\partial y} p(x, y) \rangle_s \end{pmatrix} = D_0 \begin{pmatrix} -\langle \frac{\partial}{\partial y} p'(x, y) \rangle_s \\ \langle \frac{\partial}{\partial x} p'(x, y) \rangle_s \end{pmatrix}, \quad (3.34)$$

and

$$D_e \begin{pmatrix} \langle \frac{\partial}{\partial x} p'(x, y) \rangle_s \\ \langle \frac{\partial}{\partial y} p'(x, y) \rangle_s \end{pmatrix} = D_0 \begin{pmatrix} \langle \frac{\partial}{\partial y} p(x, y) \rangle_s \\ -\langle \frac{\partial}{\partial x} p(x, y) \rangle_s \end{pmatrix}. \quad (3.35)$$

The only way in which these two equations can be satisfied together is if $D_e = D_0$ ⁽¹⁾. As an example consider the case where $D = D_0 \exp(-\beta\phi(x, y))$ where ϕ is a Gaussian random field of zero mean (a non-zero mean can however be trivially absorbed into the definition of D_0), with a correlation function which is isotropic

$$\langle \phi(\mathbf{x})\phi(\mathbf{y}) \rangle = \Delta(\mathbf{x} - \mathbf{y}), \quad (3.36)$$

if the correlation function is short range the effective diffusion constant is *self averaging* in the sense that the diffusion samples all realizations of the field ϕ after sufficiently long times and is thus independent of the realization of the field ϕ . Clearly the field ϕ has the same statistics as the field $-\phi$ and so $D_0 \exp(-\beta\phi) \equiv D_0 \exp(\beta\phi)$ and so here we have $D' = D_0^2/D \equiv D$ and consequently

$$D_e = D_0. \quad (3.37)$$

⁽¹⁾Exercise - prove this

As another example, consider a checkerboard material with diffusivity D_1 in the black squares and D_2 on the white squares. It is not obvious that the diffusion tensor takes the isotropic form $D_{eij} = D_e \delta_{ij}$, however if one diagonalizes the diffusion tensor it will take the form

$$D_e = \begin{pmatrix} \lambda & 0 \\ 0 & \mu \end{pmatrix}, \quad (3.38)$$

however a rotation by $\pi/2$ must give the same diffusion tensor and thus $\lambda = \mu$ and so $D_{eij} = D_e \delta_{ij}$ (this argument applies to any system repeated over a square lattice). Using the duality result one can show that⁽²⁾ $D_e = D_0 = \sqrt{D_1 D_2}$.

3.5 Links between diffusion with varying diffusivity and diffusion in a potential

There is a remarkable link between diffusion in a potential and diffusion in a medium of varying diffusivity. Consider a medium where $D(\mathbf{x}) = D_0 \exp(-\beta\phi(\mathbf{x}))$, in terms of the potential ϕ the Ito SDE is

$$d\mathbf{X}_t = \sqrt{2D_0 \exp(-\beta\phi(\mathbf{X}_t))} d\mathbf{B}_t - D_0 \beta \exp(-\beta\phi(\mathbf{X}_t)) \nabla\phi(\mathbf{X}_t) dt. \quad (3.39)$$

The MSD for this diffusivity problem is defined by

$$\mathbb{E}((\mathbf{X}_t - \mathbf{x}_0)^2) \sim 2dD_e^{dif} t. \quad (3.40)$$

Now consider the introduction of a new random time defined by

$$\tau = \int_0^t \exp(-\beta\phi(\mathbf{X}_s)) ds, \quad (3.41)$$

and measure the time for the process \mathbf{X} in terms of τ , this gives

$$d\mathbf{X}_\tau = \sqrt{2D_0} dB_\tau - D_0 \beta \nabla\phi(\mathbf{X}_\tau) d\tau. \quad (3.42)$$

This is true because trivially

$$d\tau = \exp(-\beta\phi(\mathbf{X}_t)) dt. \quad (3.43)$$

Less trivially

$$[dB_\tau]^2 = d\tau = \exp(-\beta\phi(\mathbf{X}_t)) dt, \quad (3.44)$$

but on the other hand we see

$$[\sqrt{\exp(-\beta\phi(\mathbf{X}_t))} d\mathbf{B}_t]^2 = \exp(-\beta\phi(\mathbf{X}_t)) dt = [dB_\tau]^2. \quad (3.45)$$

⁽²⁾Exercise - prove this

The diffusivity process when written in terms of the *random time variable* τ is a process diffusing in a potential ϕ at inverse temperature β with a bare diffusion constant D_0 . This means that

$$\mathbb{E}((\mathbf{X}_\tau - \mathbf{x}_0)^2) \sim 2dD_e^{pot}\mathbb{E}(\tau), \quad (3.46)$$

where D_e^{pot} denotes the effective diffusion constant for diffusion in a potential. There is an average value $\mathbb{E}(\tau)$ on the right hand side because τ is random. However the original process \mathbf{X}_t modulo the period has a uniform distribution in the steady state over the unit cell, this means for large times we have

$$\mathbb{E}(\tau) = \mathbb{E}\left(\int_0^t \exp(-\beta\phi(\mathbf{X}_s)) ds\right) \sim t\langle \exp(-\beta\phi(\mathbf{x})) \rangle_s, \quad (3.47)$$

and so, comparing equations (3.41) and (3.46), we find

$$D_e^{pot}\langle \exp(-\beta\phi(\mathbf{x})) \rangle_s = D_e^{dif}. \quad (3.48)$$

Using this results we immediately recover the result Eq. (2.84) for the diffusion constant in a one dimensional potential from the much easier calculation of the diffusion constant of a medium with variable diffusivity. However in the case of potentials such that $\phi \equiv -\phi$ we can use Eq. (3.48) and Eq. (3.37) to obtain the effective diffusion constant in, a class of, two dimensional random potentials as

$$D_e = \frac{D_0}{\langle \exp(-\beta\phi(\mathbf{x})) \rangle_s}. \quad (3.49)$$

If the potential ϕ is Gaussian of zero mean with correlation function having a finite correlation length ξ , for instance

$$\Delta(\mathbf{x}) = \exp\left(-\frac{|\mathbf{x}|}{\xi}\right), \quad (3.50)$$

we can approximate the spatial average in the denominator of Eq. (3.49) by the ensemble average ⁽³⁾ which only depends on $\Delta(0)$ to obtain

$$\langle \exp(-\beta\phi(\mathbf{x})) \rangle_s = \int d\phi \frac{1}{\sqrt{2\pi\Delta(0)}} \exp\left(-\frac{\phi^2}{2\Delta(0)}\right) \exp(-\beta\phi) = \exp(\beta^2\Delta(0)), \quad (3.51)$$

and so

$$D_e = D_0 \exp\left(-\frac{\beta^2}{2}\Delta(0)\right), \quad (3.52)$$

the appearance of β^2 in the exponential above is called super-Arrhenius behavior. It is quite surprising that this result only depends on the correlation function of the random field at coinciding points and not the full functional form.

⁽³⁾Exercise prove this by showing computing the variance of the random variable $X = \langle \exp(-\beta\phi(\mathbf{x})) \rangle_s - \langle \exp(-\beta\phi(\mathbf{x})) \rangle$ for a large system of area A , how quickly does $\Delta(\mathbf{x})$ have to decay for it to be true?

If one takes a Gaussian random potential in one dimension, Eq. (2.84) yields the effective diffusion coefficient

$$D_e = D_0 \exp(-\beta^2 \Delta(0)). \quad (3.53)$$

3.6 Dynamical transition in squared Gaussian potentials

Interestingly one can use this result to demonstrate the existence of a dynamical transition in two dimensions in the case where, among other models, the potential ϕ is given by

$$\phi(\mathbf{x}) = \frac{\alpha}{2} \psi^2(\mathbf{x}) - \frac{\alpha}{2} \psi'^2(\mathbf{x}), \quad (3.54)$$

where ψ and ψ' are Gaussian random fields with the same distribution (models with effective potentials which are Gaussian squared occur for the diffusion of dipoles in random electric fields and for models of the glass transition). Clearly by construction $\phi \equiv -\phi$ and so we can use our previous results to show

$$D_e = \frac{D_0}{\langle \exp\left(\frac{\beta\alpha}{2} \psi'^2(\mathbf{x}) - \frac{\beta\alpha}{2} \psi^2(\mathbf{x})\right) \rangle_s}. \quad (3.55)$$

As before, for a short range isotropic correlation function, for the fields ψ and ψ' , we can approximate the spatial average in the denominator of Eq. (3.55) by the ensemble average to obtain

$$\langle \exp\left(\frac{\beta\alpha}{2} \psi'^2(\mathbf{x}) - \frac{\beta\alpha}{2} \psi^2(\mathbf{x})\right) \rangle_s = \iint \frac{d\psi d\psi'}{2\pi\Delta(0)} \exp\left(-\frac{1}{2\Delta(0)} \psi'^2 - \frac{1}{2\Delta(0)} \psi^2 + \frac{\beta\alpha}{2} \psi'^2 - \frac{\beta\alpha}{2} \psi^2\right). \quad (3.56)$$

The integral over ψ' diverges when $\beta\alpha > 1/\Delta(0)$ and so the diffusion constant vanishes in the low temperature phase $\beta > \beta_c = 1/(\alpha\Delta(0))$. For $\beta < \beta_c$ we find⁽⁴⁾

$$D_e = D_0 \left(1 - \frac{\beta}{\beta_c}\right)^{\frac{1}{2}} \left(1 + \frac{\beta}{\beta_c}\right)^{\frac{1}{2}}. \quad (3.57)$$

Near the transition temperature T_c , the diffusion constant vanished as $D_e \sim (T - T_c)^{\frac{1}{2}}$. Below T_c the diffusion is anomalous and sub-diffusive, the MSD behaves as t^α , where $\alpha \neq 1$ (hence the term anomalous) and where $\alpha < 1$ (hence the term sub-diffusive).

A useful application of the relationship Eq. (3.48) is that the diffusion in a potential at low temperatures, especially near a dynamical transition from diffusion to sub-diffusion, obviously becomes very slow and as a particle must diffuse a large distance, the order of a few correlation lengths, to sample the potential and attain its asymptotic value simulations must be run for a very long time. However if one simulates the related diffusivity problem, the dynamics is much faster as there is no trapping in the diffusivity problem (the steady state distribution is uniform). The link between the diffusivity and potential problem is not widely known and has not really been exploited in numerical simulations.

⁽⁴⁾Exercise - prove this

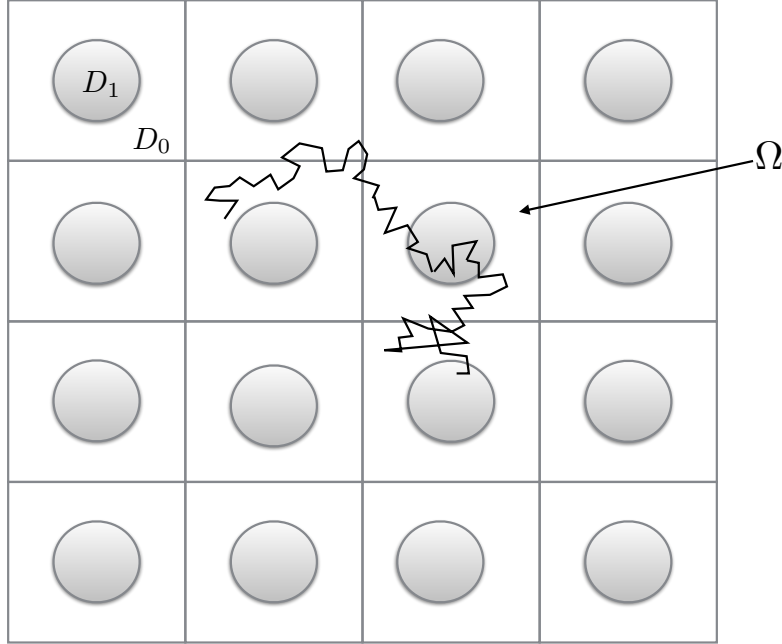


Figure 3.1: Discs of diffusivity D_1 arranged on a square lattice in a background medium of diffusivity D_0

3.7 The Maxwell formula for diffusion in systems with spherical inclusions

Consider a system with a uniform background of diffusivity D_0 with spherical inclusions of radius R having diffusivity D_1 . The spheres can be arranged on a regular lattice for example as shown in Fig. (3.1), or randomly (and may or may not overlap). The precise packing of the spheres will influence the effective diffusivity. However for dilute systems, where the density of spheres per unit volume is small, the correlations between sphere positions do not contribute to first order in the density. The basic idea is that we carry out the computation of the average current for a single sphere in a finite volume Ω , where the coordinate origin is taken to be at the center of the sphere. Away from the surface of

the spherical inclusion the, steady state diffusion equation

$$\nabla \cdot D(\mathbf{x})\nabla p(\mathbf{x}) = 0 \quad (3.58)$$

becomes

$$\nabla^2 p(\mathbf{x}) = 0. \quad (3.59)$$

Integrating Eq. (3.58) over an infinitesimal pillbox lying either side of the spheres's surface (exactly as one does in electrostatics) gives the boundary condition

$$D(\mathbf{x})\mathbf{n} \cdot \nabla p(\mathbf{x})|_{|\mathbf{x}|=R^+} = D(\mathbf{x})\mathbf{n} \cdot \nabla p(\mathbf{x})|_{|\mathbf{x}|=R^-}, \quad (3.60)$$

where R_{\pm} denotes values infinitesimally smaller/greater than R and \mathbf{n} is the unit vector normal to the sphere's surface. As ∇p must have a non-zero average value we must have

$$\nabla p \sim \mathbf{u} \text{ for } |\mathbf{x}| \rightarrow \infty, \quad (3.61)$$

where \mathbf{u} is constant. The mathematical problem is equivalent to that of a dielectric sphere in a uniform applied electric field, and you have probably seen it before in this context. The general solution outside the sphere is

$$p(\mathbf{x}) = \mathbf{u} \cdot \mathbf{x} + p_e(\mathbf{x}), \quad (3.62)$$

where $p_e(\mathbf{x}) \rightarrow 0$ as $|\mathbf{x}| \rightarrow \infty$ is a solution to $\nabla^2 p_e = 0$. Inside the sphere

$$p(\mathbf{x}) = \mathbf{u} \cdot \mathbf{x} + p_i(\mathbf{x}), \quad (3.63)$$

where $\nabla^2 p_i = 0$ and p_i remains finite as $|\mathbf{x}| \rightarrow 0$. In d dimensions the general solution is given by

$$p(\mathbf{x}) = \mathbf{u} \cdot \mathbf{x} + A\mathbf{u} \cdot \nabla \frac{1}{r^{d-2}} = \mathbf{u} \cdot \mathbf{x} - A(d-2)\mathbf{u} \cdot \frac{\mathbf{x}}{r^d}, \quad (3.64)$$

where $r = |\mathbf{x}|$ and have used, that for $r > 0$,

$$\nabla^2 \frac{1}{r^{d-2}} = 0. \quad (3.65)$$

Matching the solution at $|\mathbf{x}| = R$ shows that p_i must have the form

$$p_i(\mathbf{x}) = B\mathbf{u} \cdot \mathbf{x}. \quad (3.66)$$

Continuity of the solution at $|\mathbf{x}| = R$ gives

$$1 - (d-2)\frac{A}{R^d} = B. \quad (3.67)$$

We now note that

$$\nabla_i p = u_i + Au_j \nabla_i \nabla_j \frac{1}{r^{d-2}} = u_i - \frac{A(d-2)}{r^d} u_j \left[\delta_{ij} - d \frac{x_i x_j}{r^2} \right], \quad (3.68)$$

and using this in Eq. (3.60) gives

$$B = 1 - (d-1)(d-2) \frac{A}{R^d}. \quad (3.69)$$

The solution of these two equations is

$$A = R^d \left[\frac{(D_1 - D_0)}{(d-2)(D_1 + (d-1)D_0)} \right] \quad (3.70)$$

$$B = \frac{dD_0}{(D_1 + (d-1)D_0)}. \quad (3.71)$$

We now compute

$$\begin{aligned} \langle \nabla p \rangle_s &= \frac{1}{\Omega} \int_{\Omega} d\mathbf{x} \nabla p(\mathbf{x}) \\ &= \mathbf{u} \left(1 - \frac{V_d(R)}{|\Omega|} + B \frac{V_d(R)}{|\Omega|} \right), \end{aligned} \quad (3.72)$$

where Ω is the volume containing the sphere and $V_d(R)$ the volume of the sphere of radius R in d dimensions. The integrals in the exterior region proportional to A turn out to be zero from isotropy. Similarly

$$\begin{aligned} \langle D \nabla p \rangle_s &= \frac{1}{\Omega} \int_{\Omega} d\mathbf{x} D(\mathbf{x}) \nabla p(\mathbf{x}) \\ &= \mathbf{u} \left(D_0 \left[1 - \frac{V_d(R)}{|\Omega|} \right] + B D_1 \frac{V_d(R)}{|\Omega|} \right). \end{aligned} \quad (3.73)$$

Now using Eq. (3.20) yields

$$D_e(1 - c + Bc) = D_0(1 - c) + B D_1 c, \quad (3.74)$$

where $c = V_d(R)/|\Omega|$ is the volume fraction of the spheres. Solving this then gives

$$D_e = D_0 \frac{\alpha + d - 1 + c(d-1)(\alpha-1)}{\alpha + d - 1 - c(\alpha-1)}, \quad (3.75)$$

where $\alpha = D_1/D_0$. For $d = 3$ the above is the classical result of Maxwell for a system of dielectric spheres. The expression is only technically correct to $O(c)$, at order c^2 the precise distribution of the spheres, not just the volume fraction, should intervene. Having said that the Maxwell formula works pretty well up to unreasonably large densities for a wide range of dielectric/diffusivity contrasts. Computing the dielectric and electric properties of systems of metamaterials is becoming increasingly important as today one can build quite elaborate systems and design their optical properties via both the choice of materials in the composite and the geometries employed.

3.8 Diffusion in a system of hard spherical obstacles

A system of hard spherical obstacles can be obtained by choosing a potential $\phi(\mathbf{x})$ which is zero outside the spheres and takes the value ϵ inside the spheres, taking the limit $\epsilon \rightarrow \infty$ then ensures that the particles are excluded from the volume occupied by the spheres. If we consider a diffusivity problem where $D(\mathbf{x}) = D_0 \exp(-\beta\phi(\mathbf{x}))$ we obtain $\alpha = \exp(-\beta\epsilon)$. We also have that

$$\langle \exp(-\beta\phi) \rangle_s = 1 - c + c\alpha \quad (3.76)$$

and so using the link between the diffusivity and potential problem Eq. (3.48) and the diffusion constant for the particle is given by

$$D_e^{pot} = \frac{\alpha + d - 1 + c(d - 1)[\alpha - 1]}{[\alpha + d - 1 - c(\alpha - 1)][1 - c + c\alpha]}. \quad (3.77)$$

In the limit of hard spheres (HS) $\alpha \rightarrow 0$ and we find

$$D_e^{HS} = \frac{1}{1 + \frac{c}{d-1}} \approx 1 - \frac{c}{d-1}. \quad (3.78)$$

Chapter 4

Perturbation methods for systems with random drift

Here we consider the the diffusivity in systems where a tracer is transported due to a constant molecular, or bare, diffusivity and advection due to a random drift $\lambda \mathbf{u}(\mathbf{x}, t)$ which can depend on time. The term λ is a parameter which is assumed to be small and that will be used to generate a perturbation expansion for the effective diffusivity about the bare value D_0 . The SDE is given by

$$d\mathbf{X}_t = \lambda \mathbf{u}(\mathbf{X}_t) dt + \sqrt{2D_0} d\mathbf{B}_t. \quad (4.1)$$

The Fokker-Planck equation for a particle started at $\mathbf{x} = \mathbf{0}$ at $t = 0$ (we can take $\mathbf{x} = \mathbf{0}$ without loss of generality is a statistically homogeneous system) can be written as

$$\frac{\partial}{\partial t} p(\mathbf{x}, t) = D_0 \nabla^2 p(\mathbf{x}, t) - \lambda \nabla \cdot [\mathbf{u}(\mathbf{x}, t) p(\mathbf{x}, t)] + \delta(\mathbf{x}) \delta(t). \quad (4.2)$$

The delta function at $t = 0$ creates the initial condition $p(\mathbf{x}, 0) = \delta(\mathbf{x})$ for the diffusion equation in the time region $t > 0$. The space-time Fourier transform of the solution to the Fokker-Planck equation is defined by

$$\tilde{p}(\mathbf{k}, \omega) = \int_{-\infty}^{\infty} dt \exp(-i\omega t) \int d\mathbf{x} \exp(-i\mathbf{k} \cdot \mathbf{x}) p(\mathbf{x}, t). \quad (4.3)$$

Using the inverse Fourier transform representation for $p(\mathbf{x}, t)$

$$p(\mathbf{x}, t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \exp(i\omega t) \int \frac{d\mathbf{k}}{(2\pi)^d} \exp(i\mathbf{k} \cdot \mathbf{x}) \tilde{p}(\mathbf{k}, \omega) \quad (4.4)$$

and the corresponding result for \mathbf{u} , and also noting the identity

$$\int_{-\infty}^{\infty} dx \exp(ipx) = 2\pi \delta(p), \quad (4.5)$$

taking the space-time Fourier transform of Eq. (4.2) gives⁽¹⁾

$$i\omega\tilde{p}(\mathbf{k}, \omega) = -D_0k^2\tilde{p}(\mathbf{k}, \omega) - i\lambda \int \frac{d\nu d\mathbf{q}}{(2\pi)^{d+1}} \mathbf{k} \cdot \tilde{\mathbf{u}}(\mathbf{q}, \omega - \nu)\tilde{p}(\mathbf{k} - \mathbf{q}, \nu) + 1, \quad (4.6)$$

which can be written as

$$\tilde{p}(\mathbf{k}, \omega) = \tilde{p}_0(\mathbf{k}, \omega) - i\lambda p_0(\mathbf{k}, \omega) \int \frac{d\nu d\mathbf{q}}{(2\pi)^{d+1}} \mathbf{k} \cdot \tilde{\mathbf{u}}(\mathbf{q}, \nu)\tilde{p}(\mathbf{k} - \mathbf{q}, \omega - \nu), \quad (4.7)$$

where

$$\tilde{p}_0(\mathbf{k}, \omega) = \frac{1}{D_0k^2 + i\omega}, \quad (4.8)$$

is called the free-diffusion propagator⁽²⁾ - it is the solution of Eq. (4.6), when $\lambda = 0$ and is the solution about which the perturbation theory is constructed. In a system which has an effective diffusion constant (but we will restrict ourselves to cases where the effective drift $\mathbf{V}_e = \mathbf{0}$) the solution to the Fokker-Planck equation for large t and \mathbf{x} should have the normal diffusive form but with an effective diffusion equation. In Fourier space this means

$$\tilde{p}(\mathbf{k}, \omega) \sim \frac{1}{D_e k^2 + i\omega} \text{ for } k, \omega \rightarrow 0, \quad (4.9)$$

from which we see that D_e can be read off from the static ($\omega = 0$) part of the diffusion propagator via

$$\tilde{p}(\mathbf{k}, 0) \sim \frac{1}{D_e k^2} \text{ for } k \rightarrow 0. \quad (4.10)$$

4.1 Non-averaged perturbation theory

Here we develop a perturbation expansion for the solution of the diffusion equation for an arbitrary realization of the drift \mathbf{u} . The perturbation theory is developed diagrammatically using Feynman diagrams. We represent the free diffusion propagator $\tilde{p}_0(\mathbf{k}, \omega)$ as a line with a *four-momentum* $\mathbf{K} = (\mathbf{k}, \omega)$ flowing through it as shown in Fig. (4.1), while the full propagator $\tilde{p}(\mathbf{k}, \omega)$ is shown using a thick line as in (4.2).

The Eq. (4.7) for the full diffusion propagator $\tilde{p}(\mathbf{k}, \omega)$ is represented diagrammatically in Fig. (4.3). The Feynman diagram of the *vertex* interaction represented by the second term on the right hand side of Eq. (4.7) is the second diagram on the right hand side of Fig. (4.3). The squiggly line represents $-i\lambda \mathbf{k} \cdot \tilde{\mathbf{u}}(\mathbf{Q})/(2\pi)^{d+1}$ - (the scalar product is of $\tilde{\mathbf{u}}$ the upward momentum leaving the vertex with \mathbf{k} the incoming *spatial or three momentum*) and the upward four moment \mathbf{Q} is integrated over. Notice that the total four momentum

⁽¹⁾Exercise - prove this

⁽²⁾Exercise - invert the Fourier transform and show that it yield the solution $p_0(\mathbf{x}, t) = \exp(-\mathbf{x}^2/(4D_0t))/(4\pi D_0t)^{\frac{d}{2}}$ for $t > 0$, what happens for $t < 0$?

$$\tilde{p}_0(\mathbf{k}, \omega) = \begin{array}{c} \mathbf{K} \\ \longrightarrow \\ \mathbf{K} = (\mathbf{k}, \omega) \end{array}$$

Figure 4.1: Feynman diagram representation of free diffusion propagator

$$\tilde{p}(\mathbf{k}, \omega) = \begin{array}{c} \mathbf{K} \\ \longrightarrow \\ \mathbf{K} = (\mathbf{k}, \omega) \end{array}$$

Figure 4.2: Feynman diagram representation of full diffusion propagator

is conserved, we have \mathbf{K} flowing in and \mathbf{Q} flowing up and out through the squiggly line and $\mathbf{K} - \mathbf{Q}$ flowing out through the thick line. Think of the propagators as a hose pipe in a garden watering system, the squiggly lines are open irrigation pipes through which (water) four-momentum can leave or enter the main hosepipe.

Iterating the equation expressed by Fig. (4.3) generates what is called a Neumann expansion for the full propagator and yields to $O(\lambda^4)$ the diagrams shown in Fig. (4.4).

4.2 Disorder averaged perturbation theory

To proceed we assume that the effective diffuse constant is self averaging and that it can be read off from the disorder averaged propagator $\langle p(\mathbf{k}, \omega) \rangle$. We will assume that the field \mathbf{u} is Gaussian with zero mean and with a short-range correlation function, which is invariant under translations in space and time, given by

$$\langle u_i(\mathbf{x}, t) u_j(\mathbf{x}', t') \rangle = C_{ij}(\mathbf{x} - \mathbf{x}', t - t'). \quad (4.11)$$

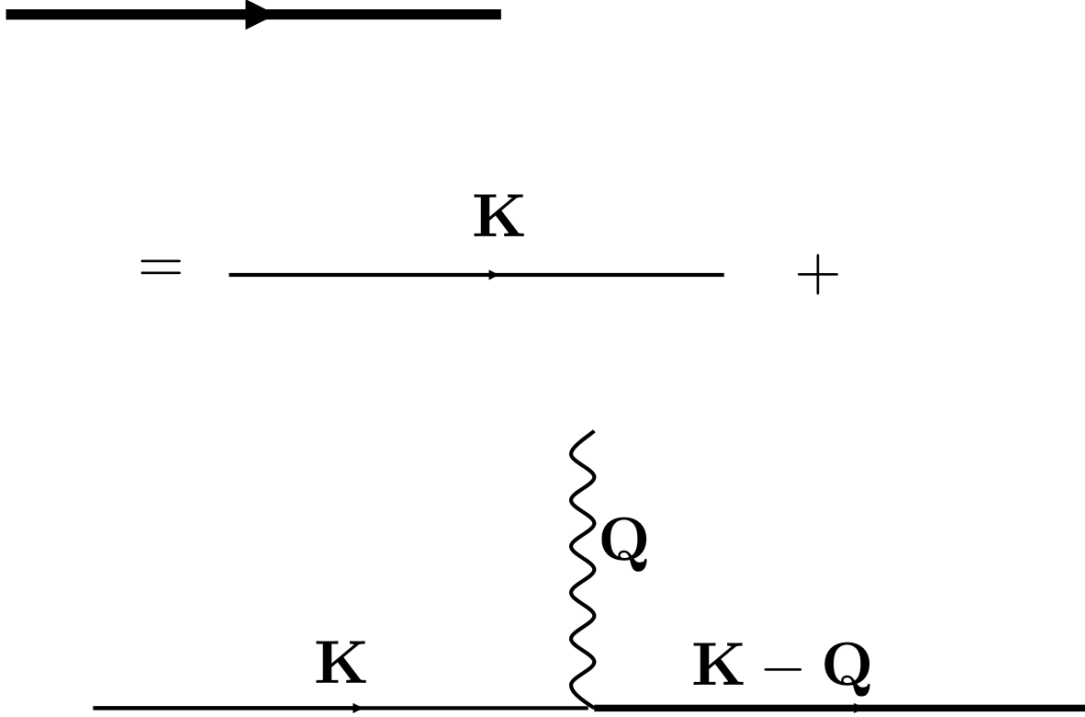


Figure 4.3: Feynman diagram representation of Eq. (4.7).

From this is is easy to see that the correlation function of the Fourier transform of the drift field is given by

$$\langle u_i(\mathbf{k}, \omega) u_j(\mathbf{k}', \omega') \rangle = (2\pi)^{d+1} \delta(\mathbf{k} + \mathbf{k}') \delta(\omega + \omega') \tilde{C}_{ij}(\mathbf{k}, \omega). \quad (4.12)$$

In four vector notation this looks simpler and reads

$$\langle \tilde{u}_i(\mathbf{K}) \tilde{u}_j(\mathbf{K}') \rangle = (2\pi)^{d+1} \delta(\mathbf{K} + \mathbf{K}') \tilde{C}_{ij}(\mathbf{K}), \quad (4.13)$$

where $\mathbf{K} = (\mathbf{k}, \omega)$. If we write

$$\tilde{p}(\mathbf{K}) = \tilde{p}_0(\mathbf{K}) + \tilde{p}_1(\mathbf{K}) + \tilde{p}_2(\mathbf{K}) + \tilde{p}_3(\mathbf{K}) + \tilde{p}_4(\mathbf{K}) + \dots, \quad (4.14)$$

where $p_n(\mathbf{K})$ denotes the terms $O(\lambda^n)$ we can carry out the averaging term by term. Clearly $\langle p_1(\mathbf{K}) \rangle = 0$ and $\langle p_n(\mathbf{K}) \rangle = 0$ for any n which is odd as \mathbf{u} is on average zero because there is a statistical symmetry associated with $\mathbf{u} \rightarrow -\mathbf{u}$. The first non-zero term, on average, for

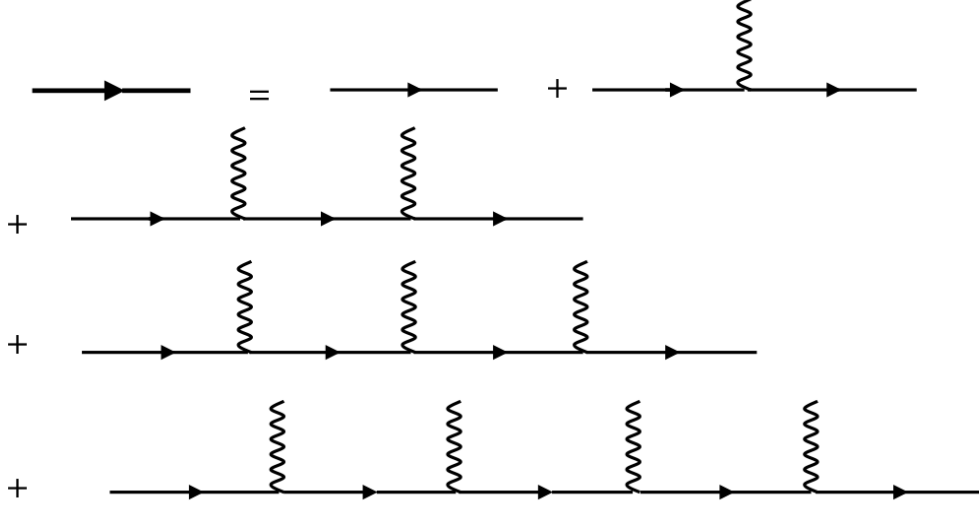


Figure 4.4: Diagrammatic expansion of $p(\mathbf{k}, \omega)$ obtained from solving Eq. (4.7)

$n > 1$ is the term

$$\begin{aligned}
\langle p_2(\mathbf{K}) \rangle &= (-i\lambda)^2 p_0(\mathbf{K}) \int \frac{d\mathbf{Q}d\mathbf{Q}'}{(2\pi)^{2d+2}} k_i(k_j - q_j) \tilde{C}_{ij}(\mathbf{Q})(2\pi)^{d+1} \delta(\mathbf{Q} + \mathbf{Q}') p_0(\mathbf{K} - \mathbf{Q}) p_0(\mathbf{K} - \mathbf{Q} - \mathbf{Q}') \\
&= (-i\lambda)^2 p_0(\mathbf{K}) \int \frac{d\mathbf{Q}}{(2\pi)^{d+1}} k_i(k_j - q_j) \tilde{C}_{ij}(\mathbf{Q}) p_0(\mathbf{K} - \mathbf{Q}) p_0(\mathbf{K}).
\end{aligned} \tag{4.15}$$

We see that taking the average imposes that \mathbf{Q} the four momentum leaving the first vertex is equal to $-\mathbf{Q}'$ the four momentum leaving the second vertex. In terms of the irrigation picture it means that rather than flowing out of the main hose pipe and being lost, the four momentum flows back in at the next vertex. Diagrammatically this is shown in Fig (4.5), the irrigation hose pipe connecting the two vertices in the main hosepipe, shown as a dashed line, along with the main part of the hosepipe below it, carries a factor of

$$(-i\lambda)^2 \int \frac{d\mathbf{Q}}{(2\pi)^{d+1}} k_i(k_j - q_j) \tilde{C}_{ij}(\mathbf{Q}) p_0(\mathbf{K} - \mathbf{Q}) \tag{4.16}$$

The average value of the $O(\lambda^4)$ term $\langle \tilde{p}_4(\mathbf{k}, \omega) \rangle$ (without the four momenta shown) is shown in Fig (4.6). Note that all the diagrams in Fig. (4.6) factorize and the first factorizes twice, such terms can be resummed. Diagrams that do not factorise in this way are called

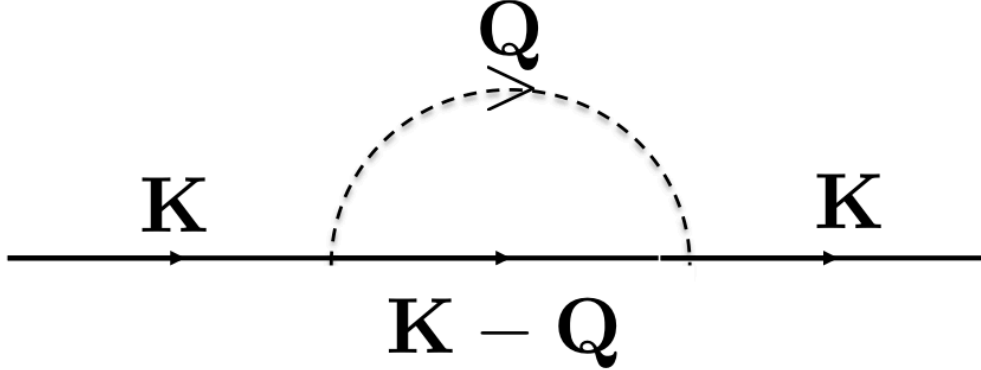


Figure 4.5: Order λ^2 contribution to $\langle p(\mathbf{k}, \omega) \rangle = \langle p_2(\mathbf{k}, \omega) \rangle$.

one particle irreducible diagrams (a terminology coming from particle physics). The full propagator can thus be written as a geometric series

$$\begin{aligned} \tilde{p}(\mathbf{K}) &= p_0(\mathbf{K}) + p_0(\mathbf{K})\Sigma(\mathbf{K})p_0(\mathbf{K}) + p_0(\mathbf{K})\Sigma(\mathbf{K})p_0(\mathbf{K})\Sigma(\mathbf{K})p_0(\mathbf{K}) + \dots \\ &= \frac{p_0(\mathbf{K})}{1 - \Sigma(\mathbf{K})p_0(\mathbf{K})} = \frac{1}{p_0^{-1}(\mathbf{K}) - \Sigma(\mathbf{K})} \end{aligned} \quad (4.17)$$

where $\Sigma(\mathbf{K})$ is the sum of one-particle irreducible diagrams. The first two terms in the perturbation expansion for $\Sigma(\mathbf{k})$ are shown in Fig (4.7). Examining Eq. (4.10) shows that the effective diffusion constant can be deduced from $\Sigma(\mathbf{k})$ via

$$D_e = D_0 - \lim_{k \rightarrow 0} \frac{\Sigma(\mathbf{k}, 0)}{k^2}. \quad (4.18)$$

The term $\Sigma_2(\mathbf{K})$ is given by Eq. (4.19) and so

$$\Sigma_2(\mathbf{k}, 0) = (-i\lambda)^2 \int \frac{d\mathbf{q}d\nu}{(2\pi)^{d+1}} \frac{k_i(k_j - q_j)\tilde{C}_{ij}(\mathbf{q}, \nu)}{D_0(\mathbf{k} - \mathbf{q})^2 - i\nu} \quad (4.19)$$

To extract the diffusion constant requires some additional assumptions. Firstly the correlation function transform $\tilde{C}_{ij}(\mathbf{K})$ must have a tensorial structure which is determined by the symmetries of the random field. If we look at quenched random fields, that do not

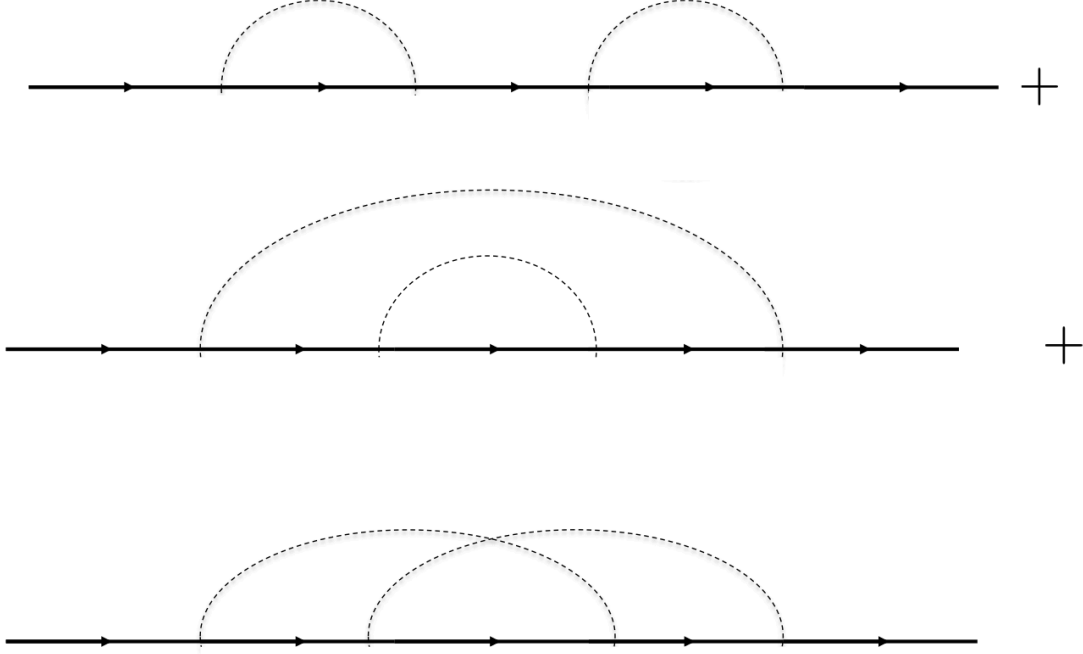


Figure 4.6: Order λ^4 contribution to $\langle p(\mathbf{k}, \omega) \rangle = \langle p_4(\mathbf{k}, \omega) \rangle$.

depend on time, such as frozen random potentials of steady state random fluid flows, we can write that in general

$$\tilde{C}_{ij}(\mathbf{q}, \nu) = (2\pi)\delta(\nu) \left[q_i q_j \tilde{\Delta}_P(q) + [q^2 \delta_{ij} - q_i q_j] \tilde{\Delta}_I(q) \right] \quad (4.20)$$

The contribution proportional to $\tilde{\Delta}_P$ comes from a drift \mathbf{u}_P created by a random potential ϕ_P , where as the term proportional to $\tilde{\Delta}_I$ comes from an independent incompressible fluid flow \mathbf{u}_I . Note that both the correlation functions $\tilde{\Delta}_I$ and $\tilde{\Delta}_P$ must be positive for the correlation function given to correspond to a real Gaussian process - the correlation tensor function must be positive definite. The tensor structure ensures that the flow is divergence-less, which in Fourier space reads $\mathbf{q} \cdot \tilde{\mathbf{u}}_I(\mathbf{q}) = 0$. This gives a contribution

$$\Sigma_{2P}(\mathbf{k}, 0) = -\lambda^2 \int \frac{d\mathbf{q}}{(2\pi)^d} \frac{k_i(k_j - q_j)q_i q_j \tilde{\Delta}_P(q)}{D_0(\mathbf{k} - \mathbf{q})^2} \quad (4.21)$$

coming from the potential. We now use that for small k

$$\frac{k_i(k_j - q_j)q_i q_j}{(\mathbf{k} - \mathbf{q})^2} \approx \frac{k_i k_j q_i q_j}{q^2} - \frac{k_i q_i q^2}{q^2} \left(1 + \frac{2q_k k_k}{q^2} \right) = -\frac{k_i k_j q_i q_j}{q^2} - k_i q_i. \quad (4.22)$$

$$\Sigma_2(\mathbf{K}) = \text{---} \overbrace{\hspace{1.5cm}}^{\text{---}} \text{---}$$

$$\Sigma_4(\mathbf{K}) = \text{---} \overbrace{\hspace{2.5cm}}^{\text{---}} \text{---} \overbrace{\hspace{1.5cm}}^{\text{---}} \text{---} \text{---} \quad +$$

$$\text{---} \overbrace{\hspace{1.5cm}}^{\text{---}} \text{---} \overbrace{\hspace{1.5cm}}^{\text{---}} \text{---} \text{---}$$

Figure 4.7: Order λ^2 and λ^4 contribution to $\Sigma(\mathbf{K})$

The last term gives no contribution to the integral in Eq. (4.21) as it is odd in q_i and the remaining $O(k^2)$ contribution to the integral is given by

$$\Sigma_{2P}(\mathbf{k}, 0) = k_i k_j \frac{\lambda^2}{D_0} \int \frac{d\mathbf{q}}{(2\pi)^d} \tilde{\Delta}_P(q) \frac{q_i q_j}{q^2}. \quad (4.23)$$

The integral

$$I_{ij} = \int \frac{d\mathbf{q}}{(2\pi)^d} \tilde{\Delta}_P(q) \frac{q_i q_j}{q^2} \quad (4.24)$$

is clearly proportional to δ_{ij} , *i.e.* $I_{ij} = \delta_{ij} R$, summing over $i = j$ in d dimensions then gives

$$I_{ii} = dR = \int \frac{d\mathbf{q}}{(2\pi)^d} \tilde{\Delta}_P(q) \frac{q^2}{q^2} = \Delta_P(0), \quad (4.25)$$

(remember that with the Einstein summation convention $I_{ii} = \sum_{i=1}^d I_{ii}$) and therefore

$$\Sigma_{2P}(\mathbf{k}, 0) = k^2 \frac{\lambda^2}{D_0 d} \Delta_P(0), \quad (4.26)$$

when $\Delta_P(0)$ is finite and hence, if there is only the potential term present,

$$D_e = D_0 \left(1 - \frac{\lambda^2}{D_0^2 d} \Delta_P(0)\right). \quad (4.27)$$

To this level in perturbation theory we see that the effective diffusion constant for diffusion in a random potential only depends on the potential's correlation function at coinciding points - this is in agreement with the exact results we have obtained earlier (setting $\lambda = D_0 \beta$ via the Stokes-Einstein relation) in one [Eq. (3.53)] and two [Eq. (3.52)] dimensions. The effect of the potential is to slow down diffusion with respect to the bare diffusion constant. A similar calculation⁽³⁾ shows that the term coming from the incompressible part of the velocity field yields

$$\Sigma_{2I}(\mathbf{k}, 0) = k^2 \frac{\lambda^2}{D_0} \left(1 - \frac{1}{d}\right) \int \frac{d\mathbf{q}}{(2\pi)^d} \Delta_I(\mathbf{q}) = -k^2 \frac{\lambda^2}{D_0} \Delta_I(0) \left(1 - \frac{1}{d}\right), \quad (4.28)$$

thus for a purely incompressible field we find

$$D_e = D_0 \left(1 + \frac{\lambda^2}{D_0^2} \Delta_I(0) \left[1 - \frac{1}{d}\right]\right), \quad (4.29)$$

when $\Delta_I(0)$ is finite. Purely incompressible flow thus increases the effective diffusivity - this is physically because there is no trapping and the tracer is convected by the flow. For both the potential and incompressible case the perturbation theory diverges badly in the limit $D_0 \rightarrow 0$. We know that when $D_0 = 0$ there is no diffusion, the tracer just stays at a local minimum. However the incompressible flow generates an effective diffusivity even in the absence of a bare or molecular diffusivity (as can be seen in numerical simulations). As the perturbation theory builds up to corrections to D_e as a power series in λ^2 we see that writing Eq. (4.29) as

$$D_e = D_0 + \frac{\lambda^2}{D_e} \Delta_I(0) \left[1 - \frac{1}{d}\right], \quad (4.30)$$

is also correct to $O(\lambda^2)$. This idea can be justified more rigorously and is an example of *self consistent perturbation theory*. The idea is to do perturbation theory about the free propagator with the effective self diffusion constant rather than the bare one, this formalism can be pushed to higher orders in perturbation theory. In Eq. (4.30) we can set $D_0 = 0$ and obtain

$$D_e = \lambda \sqrt{\Delta_I(0) \left[1 - \frac{1}{d}\right]}, \quad (4.31)$$

this simple result actually works remarkably well when compared to numerical simulations in $d = 3$. The expressions for the $O(\lambda^4)$ terms Σ_4 can be written down easily⁽⁴⁾, however the resulting integrals often need to be evaluated numerically.

⁽³⁾Exercise- do the calculation

⁽⁴⁾Exercise - Give the integral expressions for $\Sigma_4(\mathbf{k}, \omega)$ in terms of \tilde{C}_{ij} , don't try and evaluate the integrals

Note that the integrals

$$\Delta_{P/I}(0) = \int \frac{d\mathbf{q}}{(2\pi)^d} \Delta_{P/I}(\mathbf{q}), \quad (4.32)$$

may not exist due to long range correlations (which correspond to divergences at small q), in this case the diffusion constant diverges and this signals that the diffusion becomes anomalous, that is to say

$$\mathbb{E}(\mathbf{X}_t^2) \sim t^\alpha \quad (4.33)$$

where $\alpha \neq 1$. Systems where $\alpha < 1$ are called sub-diffusive, while the case $\alpha > 1$ is called super-diffusive. In many cases the exponent α can be computed using renormalisation group techniques.