

# Stochastic density functional theory

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# Chapter 1

## Stochastic calculus and Langevin equations

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. The Ito formulation of stochastic calculus exposed here is one of the key points in the derivation of stochastic density functional theory. A digestible though rigorous introduction to stochastic calculus can be found in the book by Oksendal [1].

### 1.1 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

$$X_{(n+1)\Delta t} - X_{n\Delta t} = \Delta X_t = u(X_t)\Delta t + a(X_t)\Delta B_t \quad (1.1)$$

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  $\Delta B_t$  is Gaussian with zero mean so

$$\langle \Delta B_t \rangle = 0,$$

and we choose the variance to be

$$\langle [\Delta B_t]^2 \rangle = \Delta t.$$

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

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

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

$$\langle \Delta B_t \Delta B_{t'} \rangle = \langle \Delta B_t \rangle \langle \Delta B_{t'} \rangle = 0$$

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 coloured. 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

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

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)

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

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

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

The continuous diffusion equation in one dimension is

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

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

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

which has the general solution

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

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. If we define  $\Delta X_t = X_t - x_0$  the displacement of the process  $X_t$  with respect to its initial position  $x_0$  we have that its characteristic function is given by

$$\langle \exp[-ik\Delta X_t] \rangle = \exp(-Dk^2t),$$

Taylor expanding both sides to  $O(k^2)$  then gives

$$1 - ik\langle \Delta X_t \rangle - \frac{k^2}{2}\langle \Delta X_t^2 \rangle = 1 - Dk^2t$$

and so we see  $\langle \Delta X_t \rangle = 0$ , while the mean squared displacement is given by  $\langle \Delta X_t^2 \rangle = 2Dt$ .

## 1.2 The Ito Stochastic Calculus

Here we want to take the continuum limit of the stochastic equation (1.1). We see that by construction the noise term  $\Delta B_t$  is  $O(\sqrt{\Delta t})$  and so the term  $\Delta B_t^2$  is  $O(\Delta t)$  and so we need to keep it in deriving differential equations. Consider for a moment

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

We find that the mean of  $S$  is given by

$$\langle S \rangle = \sum_{i=1}^N \langle \Delta B_{i\Delta t}^2 \rangle = N\Delta t = t.$$

However we can use a specific Wick's theorem for Gaussian random variables to compute the averages which appear. The simplest case of Wick's theorem is the following. Consider a Gaussian random variable with pdf

$$p(x) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{x^2}{2\sigma^2}\right)$$

We would like to compute the moments  $\langle X^n \rangle$  for integer  $n$ . To do this we compute the generating function

$$\begin{aligned}
g(\lambda) &= \langle \exp(\lambda X) \rangle = \int_{-\infty}^{\infty} dx \exp(\lambda x) p(x) \\
&= \frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} dx \exp(\lambda x) \exp\left[-\frac{x^2}{2\sigma^2}\right] \\
&= \frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} dx \exp\left[-\frac{(x - \lambda\sigma^2)^2}{2\sigma^2} + \frac{\lambda^2\sigma^2}{2}\right] \\
&= \frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} dx' \exp\left[-\frac{x'^2}{2\sigma^2} + \frac{\lambda^2\sigma^2}{2}\right] = \exp\left[\frac{\lambda^2\sigma^2}{2}\right].
\end{aligned}$$

However Taylor expanding this  $g(\lambda) = \langle \exp(\lambda X) \rangle$  about  $\lambda = 0$  gives

$$\sum_{n=0}^{\infty} \frac{\lambda^n}{n!} \langle X^n \rangle = \sum_{m=0}^{\infty} \frac{\lambda^{2m} \sigma^{2m}}{m! 2^m}.$$

Now comparing the coefficients of  $\lambda$  on both sides of the above we see that

$$\langle X^n \rangle = 0 \text{ for } n \text{ odd,}$$

and for  $n = 2m$  even

$$\langle X^{2m} \rangle = \frac{\lambda^{2m} (2m)! \sigma^{2m}}{m! 2^m} = \sigma^{2m} (2m-1)(2m-3) \cdots 1.$$

Notice that  $(2m-1)(2m-3) \cdots 1$  the number of ways in which  $m$  distinct pairs can be formed from  $2m$  objects. If you label the objects from 1 to  $2m$  the first object has  $2m-1$  choices to be paired with, this leaves  $2m-2$  objects, the first of these can then be paired with a possible  $2m-3$  objects.

Wicks theorem for an even number  $2m$  of Gaussian random variables, each of average zero, states that

$$\langle A_1 A_2 \cdots A_{2m} \rangle = \sum_{\text{all pairs}} \prod_{\alpha} \langle A_{\alpha} A_{\sigma_{\alpha}} \rangle.$$

For instance for 4 Gaussian random variables we have

$$\langle A_1 A_2 A_3 A_4 \rangle = \langle A_1 A_2 \rangle \langle A_3 A_4 \rangle + \langle A_1 A_3 \rangle \langle A_2 A_4 \rangle + \langle A_1 A_4 \rangle \langle A_2 A_3 \rangle.$$

Now applying Wick's theorem gives

$$\begin{aligned}
\langle S^2 \rangle &= \sum_{ij=1}^N \langle \Delta B_{i\Delta t}^2 \Delta B_{j\Delta t}^2 \rangle \\
&= \sum_{ij=1}^N \langle \Delta B_{i\Delta t}^2 \rangle \langle \Delta B_{j\Delta t}^2 \rangle + 2 \langle \Delta B_{i\Delta t} \Delta B_{j\Delta t} \rangle^2 \\
&= \sum_{ij=1}^N \Delta t^2 + 2\delta_{ij} \Delta t^2 = t^2 + 2\frac{t^2}{N}
\end{aligned}$$

The variance of  $S$  is thus given by

$$\text{var}(S) = \langle S^2 \rangle - \langle S \rangle^2 = 2\frac{t^2}{N},$$

so in the limit of large  $N$  this means  $\text{var}(S) \rightarrow 0$  and so  $S = \langle S \rangle$  (this is basically the central limit theorem). The continuum stochastic differential equation Eq. (1.1) now becomes

$$dX_t = u(X_t)dt + a(X_t)dB_t$$

where  $\langle [dB_t]^2 \rangle = dt$ , further more we find from above that over any time interval  $t$ ,

$$\int_0^t dB_s^2 = \langle \int_0^t [dB_s]^2 \rangle = t,$$

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

$$[dB_t]^2 = dt. \tag{1.5}$$

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

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

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

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

where we have used Eq. (1.5). The SDE for  $f$  is then

$$df(X_t) = \frac{\partial f(X_t)}{\partial x} (u(X_t)dt + a(X_t)dB_t) + \frac{1}{2} \frac{\partial^2 f(X_t)}{\partial x^2} a^2(X_t)dt. \tag{1.6}$$

Because  $dB_t$  is chosen independently of the position  $X_t$ , taking the average of Eq. (1.6) (and dividing by  $dt$ ) yields

$$\left\langle \frac{df(X_t)}{dt} \right\rangle = \left\langle \frac{\partial f(X_t)}{\partial x} u(X_t) + \frac{1}{2} \frac{\partial^2 f(X_t)}{\partial x^2} a^2(X_t) \right\rangle$$

### 1.3 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

$$\langle f(X_t) \rangle_{x_0} = \int dx p(x, x_0; t) f(x),$$

the subscript  $x_0$  is just to remind us that the process starts at  $X_0 = x_0$ . Now take the time derivative of the above to get

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

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

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

This means that

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

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

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

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

$$\frac{\partial p(x, x_0; t)}{\partial t} = G^\dagger p(x, x_0; t). \quad (1.8)$$

The equation (1.8) 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

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



## 1.4 Generalisation to higher dimensions

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

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

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

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

we see that generator is given by

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

The corresponding Forward-Fokker-Planck equation is thus

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

## 1.5 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.

## 1.6 Physicists Brownian motion

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

$$m dV_t = -\gamma V_t dt + a dB_t,$$

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 Ornstein-Uhlenbeck process. The forces acting are: a friction term, with friction coefficient  $\gamma$  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  $\eta$  the liquid's viscosity.

Taking the average value of this equation shows that the average value of the velocity  $\langle V_t \rangle$  is zero. Consider now the variable  $S_t = V_t^2$ , we see that  $S_t$  obeys

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

Taking the average of this equation then gives

$$\langle dS_t \rangle = \left[ -2\frac{\gamma}{m} \langle S_t \rangle + \frac{a^2}{m^2} \right] dt.$$

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

$$\langle S_t \rangle = \frac{a^2}{2\gamma m}.$$

However equipartition of energy also tells us that

$$\left\langle \frac{1}{2} m V_t^2 \right\rangle = \frac{1}{2} k_B T \implies \frac{1}{2} m \langle S \rangle = \frac{a^2}{4\gamma},$$

this means the amplitude of the noise must be given by

$$a = \sqrt{2k_B T \gamma}.$$

This is an example of a fluctuation dissipation theorem that relates the dissipation, friction, in a system to the fluctuations - the noise.

## 1.7 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 normalised 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

$$\mathbf{J} = -D\nabla c,$$

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

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

we find the diffusion equation

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

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

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

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

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

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

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

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

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

so there is a dependency on the temperature  $T$  that can be very strong, especially for the viscosity  $\eta$  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

$$\mathbf{J}_T = -D_T c \nabla T,$$

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

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

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

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

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

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

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

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

Note that  $1/\gamma = \kappa$  where  $\kappa$  is called the mobility. The generator  $G$  is given by

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

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

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

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

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

where

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

is the canonical partition function which ensures the normalisation 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.

## 1.8 The Langevin equation

In the physics literature it is common to write stochastic equations in the form

$$\frac{dX}{dt} = u(X_t) + a(X_t)\eta(t)$$

where we have

$$\eta(t) = \frac{dB_t}{dt},$$

clearly  $\langle\eta(t)\rangle = 0$ . In order to determine the correlation function of  $\eta(t)$  defined as

$$c(t, t') = \langle\eta(t)\eta(t')\rangle,$$

consider the integral

$$I_f = \int dt \eta(t)f(t)$$

for an arbitrary function  $f$ . To start with, assuming  $f$  is independent of  $\eta$ , one has  $\langle I_f \rangle = 0$ , however

$$\langle I_f I_g \rangle = \iint dt dt' f(t)g(t')c(t, t'),$$

where  $g$  is another arbitrary function of  $t$ . Now we compute the same correlation function using the Ito calculus where

$$I_f = \int dB_t f(t),$$

from this we find

$$\langle I_f I_g \rangle = \int dt f(t)g(t) = \int dt dt' f(t)g(t')\delta(t - t').$$

and so we have that  $c(t, t') = \delta(t - t')$ . The process  $\eta(t)$  is called Gaussian white noise. Stochastic equations written in terms of white noise are called Langevin equations.

## Chapter 2

# Dynamics of the density field - stochastic density functional theory

In this section we see how, starting from the individual stochastic equations of motion for an interacting particle system we can derive an equation for the particle density distribution [2]. In the first part we will derive the stochastic equation for the density field in a direct way using Ito calculus. We will then see how the same equation can be derived using a path integral formulation starting from a lattice based model. While this latter method is less direct, it allows us to extend our results to systems where the overall particle number is not conserved, due to for example chemical reactions.

### 2.1 Derivation of using stochastic density functional theory via Ito calculus

Here we give the derivation of the SDFT for a system composed of a fixed number of Brownian particles in interaction. Consider a system of  $N$  particles which is subject to a general time dependent potential  $U(\mathbf{x}, t)$

$$d\mathbf{X}_i = -\beta D \nabla U(\mathbf{X}_i, t) dt + \sqrt{2D} d\mathbf{B}_i$$

Starting from this system of  $N$  equations we will derive an equation for the density of the  $i$ th particle defined simply as

$$\rho_i(\mathbf{x}, t) = \delta(\mathbf{x} - \mathbf{X}_i).$$

The total density field is then given by

$$\rho(\mathbf{x}, t) = \sum_{i=1}^N \delta(\mathbf{x} - \mathbf{X}_i) = \sum_{i=1}^N \rho_i(\mathbf{x}, t).$$

We will play exactly the same game as in chapter 1 that we used to derive the Fokker-Planck equation, the key difference in the calculation is that we will not average over the noise. As in chapter 1 we write

$$A_i = f(\mathbf{X}_i) = \int \rho_i(\mathbf{x}, t) f(\mathbf{x}) d\mathbf{x},$$

and compute the evolution using the rules of Ito calculus to obtain

$$dA_i = df(\mathbf{X}_i) = \nabla f(\mathbf{X}_i) \cdot [-\beta D \nabla U(\mathbf{X}_i, t) dt + \sqrt{2D} d\mathbf{B}_i] + D \nabla^2 f(\mathbf{X}_i) dt$$

In terms of the density field of particle  $i$  this can be written as

$$dA_i = \int d\mathbf{x} \rho_i(\mathbf{x}, t) \left[ -\nabla f(\mathbf{x}) \cdot \beta D \nabla U(\mathbf{x}, t) + D \nabla^2 f(\mathbf{x}) dt + \nabla f(\mathbf{x}) \cdot \sqrt{2D} d\mathbf{B}_i \right]$$

and so integration by parts gives

$$dA_i = \int d\mathbf{x} f(\mathbf{x}) \left[ dt \beta D \nabla \cdot \rho_i(\mathbf{x}, t) \nabla U(\mathbf{x}) + dt D \nabla^2 \rho_i(\mathbf{x}, t) - \nabla \cdot [\rho_i(\mathbf{x}, t) \sqrt{2D} d\mathbf{B}_i] \right]$$

we also have

$$dA_i = \int d\mathbf{x} f(\mathbf{x}) d\rho_i(\mathbf{x}, t)$$

and so comparing these two equations we have

$$d\rho_i(\mathbf{x}, t) = dt \beta D \nabla \cdot \rho_i(\mathbf{x}, t) \nabla U(\mathbf{x}) + dt D \nabla^2 \rho_i(\mathbf{x}, t) - \nabla \cdot [\rho_i(\mathbf{x}, t) \sqrt{2D} d\mathbf{B}_i]$$

Now adding the equations for each  $i$  we find

$$d\rho(\mathbf{x}, t) = dt \beta D \nabla \cdot \rho(\mathbf{x}, t) \nabla U(\mathbf{x}) + dt D \nabla^2 \rho(\mathbf{x}, t) + d\Xi(\mathbf{x}, t)$$

where the noise is given by

$$d\Xi(\mathbf{x}, t) = - \sum_i \sqrt{2D} d\mathbf{B}_i \cdot \nabla [\rho_i(\mathbf{x}, t)].$$

The noise term appears problematic because it is not a function of  $\rho$  and depends explicitly on the individual density fields  $\rho_i(\mathbf{x})$ . However if we compute its correlation function we find

$$\langle d\Xi(\mathbf{x}, t) d\Xi(\mathbf{x}', t) \rangle = 2D \sum_i \nabla_{\mathbf{x}} [\rho_i(\mathbf{x}, t)] \cdot \nabla_{\mathbf{x}'} \cdot [\rho_i(\mathbf{x}', t)]$$

Now we use the simple identity

$$\rho_i(\mathbf{x}, t) \rho_i(\mathbf{x}', t) = \delta(\mathbf{X}_i(t) - \mathbf{x}) \delta(\mathbf{X}_i(t) - \mathbf{x}') = \delta(\mathbf{X}_i(t) - \mathbf{x}) \delta(\mathbf{x} - \mathbf{x}') = \rho_i(\mathbf{x}, t) \delta(\mathbf{x} - \mathbf{x}')$$

which allows us to write

$$\begin{aligned}
\langle d\Xi(\mathbf{x}, t)d\Xi(\mathbf{x}', t) \rangle &= 2Ddt \sum_i \nabla_{\mathbf{x}} \cdot \nabla_{\mathbf{x}'} [\rho_i(\mathbf{x}, t)\rho_i(\mathbf{x}', t)] \\
&= 2Ddt \sum_i \nabla_{\mathbf{x}} \cdot \nabla_{\mathbf{x}'} [\delta(\mathbf{x} - \mathbf{x}')\rho_i(\mathbf{x}, t)] = 2Ddt \nabla_{\mathbf{x}} \cdot \nabla_{\mathbf{x}'} [\delta(\mathbf{x} - \mathbf{x}')\rho(\mathbf{x}, t)] \\
&= -2Ddt \nabla_{\mathbf{x}} \cdot \rho(\mathbf{x}, t) \nabla_{\mathbf{x}} [\delta(\mathbf{x} - \mathbf{x}')],
\end{aligned}$$

the correlation function of the noise term thus depends only on the total density field  $\rho(\mathbf{x})$ . Writing the noise in the Langevin form

$$\xi(\mathbf{x}, t) = \dot{\Xi}(\mathbf{x}, t)$$

we find

$$\langle \xi(\mathbf{x}, t)\xi(\mathbf{x}', t') \rangle = -2D\delta(t - t') \nabla_{\mathbf{x}} \cdot \rho(\mathbf{x}, t) \nabla_{\mathbf{x}} [\delta(\mathbf{x} - \mathbf{x}')].$$

From the form of this correlation function we see that we can write the noise as

$$\xi(\mathbf{x}, t) = \nabla \cdot \sqrt{2D\rho(\mathbf{x}, t)} \boldsymbol{\eta}(\mathbf{x}, t)$$

where  $\boldsymbol{\eta}$  is a  $d$  dimensional vector field which is of the white noise form in both space and time, *i.e.*

$$\langle \eta_i(\mathbf{x}, t)\eta_j(\mathbf{x}', t') \rangle = 2D\delta_{ij}\delta(t - t')\delta(\mathbf{x} - \mathbf{x}').$$

For a system of particles interacting via a pairwise potential  $V(\mathbf{x})$  and an external potential  $v(\mathbf{x})$ , the overall potential seen by each particle can also be written as

$$U(\mathbf{x}, t) = v(\mathbf{x}) + \int d\mathbf{y} V(\mathbf{x} - \mathbf{y})\rho(\mathbf{y}, t).$$

This leads to the final closed equation for the density field

$$\dot{\rho}(\mathbf{x}, t) = D\nabla \cdot \left[ \nabla \rho(\mathbf{x}, t) + \beta \rho(\mathbf{x}, t)v(\mathbf{x}) + \beta \rho(\mathbf{x}, t) \int d\mathbf{y} \nabla V(\mathbf{x} - \mathbf{y})\rho(\mathbf{y}, t) \right] + \nabla \cdot \sqrt{2D\rho(\mathbf{x}, t)} \boldsymbol{\eta}(\mathbf{x}, t) \quad (2.2)$$

Now consider the following density functional

$$H[\rho] = T \int d\mathbf{x} \rho(\mathbf{x}) \ln[\rho(\mathbf{x})] + \int d\mathbf{x} v(\mathbf{x})\rho(\mathbf{x}) + \frac{1}{2} \int d\mathbf{x} d\mathbf{y} \rho(\mathbf{x}) V(\mathbf{x} - \mathbf{y})\rho(\mathbf{y}),$$

it has the form

$$H = E - TS$$

where  $E$  is the internal energy due to the interactions

$$E = \int d\mathbf{x} v(\mathbf{x})\rho(\mathbf{x}) + \frac{1}{2} \int d\mathbf{x} d\mathbf{y} \rho(\mathbf{x}) V(\mathbf{x} - \mathbf{y})\rho(\mathbf{y})$$



and  $S$  is the entropy given by

$$S = -T \int d\mathbf{x} \rho(\mathbf{x}) \ln[\rho(\mathbf{x})].$$

The SDFT (2.2) can then be written as

$$\dot{\rho}(\mathbf{x}, t) = D\beta \nabla \cdot \rho(\mathbf{x}) \nabla \frac{\delta H}{\delta \rho(\mathbf{x})} + \nabla \cdot \sqrt{2D\rho(\mathbf{x}, t)} \boldsymbol{\eta}(\mathbf{x}, t) \quad (2.3)$$

or alternatively as

$$\dot{\rho}(\mathbf{x}, t) = \kappa \nabla \cdot \rho(\mathbf{x}) \nabla \frac{\delta H}{\delta \rho(\mathbf{x})} + \nabla \cdot \sqrt{2\kappa T \rho(\mathbf{x}, t)} \boldsymbol{\eta}(\mathbf{x}, t)$$

where

$$\kappa = D\beta$$

is the particle mobility.

## 2.2 Recovering equilibrium statistical mechanics from SDFT

Clearly the system described by the SDFT derived above will enter into a steady state equilibrium distribution at late times (note non-conservative forces and driving can also be added and here the steady state will not be an equilibrium one).

Here we will find a functional equation rather than the usual partial differential - Fokker Planck- equation that one has for system with a finite number of degrees of freedom. When the degree of freedom is a function its self, we define the functional derivate  $\delta F / \delta \phi(\mathbf{x})$  via

$$F[\phi + \delta\phi] - F[\phi] = \int d\mathbf{x} \frac{\delta F}{\delta \phi(\mathbf{x})} \delta\phi(\mathbf{x}).$$

This is the extension to function spaces of the relation

$$F(\mathbf{x} + d\mathbf{x}) - F(\mathbf{x}) = \nabla F \cdot d\mathbf{x} = \sum_i \frac{\partial F}{\partial x_i} dx_i.$$

Using the rules of Ito calculus (clearly the noise field  $\nabla \cdot \sqrt{2\kappa T \rho(\mathbf{x}, t)} \boldsymbol{\eta}(\mathbf{x}, t)$  should be treated using Ito calculus ) we find the functional Fokker-Planck equation

$$\dot{P}[\rho] = \int d\mathbf{x} d\mathbf{x}' -D \frac{\delta^2}{\delta \rho(\mathbf{x}) \delta \rho(\mathbf{x}')} \nabla \cdot \rho(\mathbf{x}) \nabla \delta(\mathbf{x} - \mathbf{x}') P[\rho] - \int d\mathbf{x} \frac{\delta}{\delta \rho(\mathbf{x})} \left( D \nabla \cdot \rho(\mathbf{x}) \nabla \beta \frac{\delta H}{\delta \rho(\mathbf{x})} P \right)$$

In the first term, for  $\mathbf{x} \neq \mathbf{x}'$  we can push the  $\delta / \delta \rho(\mathbf{x}')$  through to act of  $P$  and find

$$\dot{P}[\rho] = \int d\mathbf{x} -D \frac{\delta}{\delta \rho(\mathbf{x})} \nabla \cdot \rho(\mathbf{x}) \nabla \frac{\delta P}{\delta \rho(\mathbf{x})} - \int d\mathbf{x} \frac{\delta}{\delta \rho(\mathbf{x})} \left( D \nabla \cdot \rho(\mathbf{x}) \nabla \beta \frac{\delta H}{\delta \rho(\mathbf{x})} P \right)$$

We cannot strictly do this at  $\mathbf{x} = \mathbf{x}'$  but we use take  $\nabla\delta(\mathbf{0}) = 0$  so everything is fine. After this step we see that the functional Fokker-Planck equation can be written as

$$\dot{P}[\rho] = - \int d\mathbf{x} \frac{\delta}{\delta\rho(\mathbf{x})} J[\rho, \mathbf{x}]$$

where  $J[\rho, \mathbf{x}]$  is the current functional defined by

$$\begin{aligned} J[\rho, \mathbf{x}] &= D\nabla \cdot \rho(\mathbf{x}) \nabla \frac{\delta P}{\delta\rho(\mathbf{x})} + D\nabla \cdot \rho(\mathbf{x}) \nabla \beta \frac{\delta H}{\delta\rho(\mathbf{x})} P \\ &= D\nabla \cdot \rho(\mathbf{x}) \left[ \frac{\delta P}{\delta\rho(\mathbf{x})} + \beta \frac{\delta H}{\delta\rho(\mathbf{x})} P \right] \end{aligned}$$

We see that the steady state solution of this Fokker-Planck equation which has no current is given by

$$P[\rho] = \frac{1}{Z} \exp(-\beta H[\rho]),$$

the normalisation factor is the *partition function*

$$Z = \int d[\rho] \exp(-\beta H[\rho]).$$

You may feel that there are a number of things odd about the results derived above. Firstly the Hamiltonian  $H$  we see must appear in the partition function for the equilibrium statistical mechanics of the system looks suspiciously like the mean field Hamiltonian, this is however not the case as the mean field Hamiltonian is actually given by

$$H_{MF}[\bar{\rho}] = T \int d\mathbf{x} \bar{\rho}(\mathbf{x}) \ln[\bar{\rho}(\mathbf{x})] + \int d\mathbf{x} v(\mathbf{x}) \bar{\rho}(\mathbf{x}) + \frac{1}{2} \int d\mathbf{x} d\mathbf{y} \bar{\rho}(\mathbf{x}) V(\mathbf{x} - \mathbf{y}) \bar{\rho}(\mathbf{y}),$$

where  $\bar{\rho}(\mathbf{x})$  is the thermodynamic average of the density field. However the field theory has a very odd form, the entropy term is highly unusual compared to standard forms for field theories. We can analyse what happens in this field theory for homogeneous systems where the external potential  $v(\mathbf{x}) = 0$  by expanding the density field  $\rho(\mathbf{x})$  about its average bulk value, we write

$$\rho(\mathbf{x}) = \bar{\rho} + n(\mathbf{x})$$

where by definition

$$\int d\mathbf{x} n(\mathbf{x}) = 0.$$

Making the above change of variables we find

$$H[\rho] = T \int d\mathbf{x} (\bar{\rho} + n(\mathbf{x})) \ln(\bar{\rho} + n(\mathbf{x})) + \frac{1}{2} \int d\mathbf{x} d\mathbf{x}' (\bar{\rho} + n(\mathbf{x})) V(\mathbf{x} - \mathbf{x}') (\bar{\rho} + n(\mathbf{x}')),$$

and expanding to quadratic order in the density field fluctuations we find the quadratic Hamiltonian

$$H_{RPA} = \frac{1}{2} \int d\mathbf{x} d\mathbf{x}' n(\mathbf{x}) \Delta(\mathbf{x} - \mathbf{x}') n(\mathbf{x}').$$

where

$$\Delta(\mathbf{x} - \mathbf{x}') = \frac{T}{\bar{\rho}} \delta(\mathbf{x} - \mathbf{x}') + V(\mathbf{x} - \mathbf{x}').$$

This means that the correlation function for the fluctuations is

$$c(\mathbf{x}) = \langle n(\mathbf{x}) n(\mathbf{0}) \rangle = T \Delta^{-1}(\mathbf{x}),$$

where  $\Delta^{-1}(\mathbf{x})$  denotes the inverse operator in the sense that

$$\int d\mathbf{z} \Delta^{-1}(\mathbf{x} - \mathbf{z}) \Delta(\mathbf{z} - \mathbf{x}') = \delta(\mathbf{x} - \mathbf{x}').$$

In liquid theory the structure factor is defined via

$$\langle \tilde{n}(\mathbf{k}) \tilde{n}(\mathbf{k}') \rangle = (2\pi)^d \delta(\mathbf{k} + \mathbf{k}') S(\mathbf{k})$$

where

$$\tilde{n}(\mathbf{k}) = \int d\mathbf{x} n(\mathbf{x}) \exp(-i\mathbf{k} \cdot \mathbf{x}),$$

is the Fourier transform of the density fluctuations. Within the quadratic approximation made here we find that

$$S(\mathbf{k}) = \frac{T}{\tilde{\Delta}(\mathbf{k})} = \frac{T\bar{\rho}}{T + \bar{\rho}\tilde{V}(\mathbf{k})} = \frac{\bar{\rho}}{1 + \bar{\rho}\beta\tilde{V}(\mathbf{k})}.$$

This approximation for the structure factor is known as the random phase approximation [3]. In the theory of electrolytes it is known as the Debye-Hückel approximation.

## 2.3 Phenomenological derivation of SDFT

If a system of particles can be described by a free energy functional  $H[\rho]$  which minimised in equilibrium then clearly

$$\frac{\delta H[\rho]}{\delta \rho(\mathbf{x})} = 0.$$

Imagine that the system is not in equilibrium but we apply a fictive chemical potential  $\mu(\mathbf{x})$  which causes the system to be in equilibrium, this means that we minimize

$$J[\rho] = H[\rho] + \int d\mathbf{x} \mu(\mathbf{x}) \rho(\mathbf{x}),$$

and in equilibrium we should have

$$\mu(\mathbf{x}) = -\frac{\delta H[\rho]}{\delta \rho(\mathbf{x})}.$$

The local body force due to the potential  $\mu$  cancels that due to the action of the system on itself. Therefore the body force acting at a point  $\mathbf{x}$  is given by

$$\mathbf{f}(\mathbf{x}) = +\rho(\mathbf{x})\nabla\mu(\mathbf{x}),$$

If we assume that this force produces a current

$$\mathbf{j}(\mathbf{x}) = \kappa\mathbf{f}(\mathbf{x}),$$

where  $\kappa$  is the particle mobility, we find the diffusion equation

$$\begin{aligned} \dot{\rho}(\mathbf{x}, t) &= -\nabla \cdot \kappa f(\mathbf{x}) \\ &= -\nabla \cdot \kappa \rho(\mathbf{x}) \nabla \mu(\mathbf{x}) \\ &= \nabla \cdot \kappa \rho(\mathbf{x}) \nabla \frac{\delta H[\rho]}{\delta \rho(\mathbf{x})} \\ &= D\beta \nabla \cdot \rho(\mathbf{x}) \nabla \frac{\delta H[\rho]}{\delta \rho(\mathbf{x})}. \end{aligned}$$

However we know that there should be a noise term in this equation and in order to produce the correct equilibrium distribution, if the noise is white noise in time then it must be of the form derived in Eq. (2.3).

## 2.4 SDFT in the limit of small density fluctuations

If we return to the SDFT we can attempt to solve the resulting equations by linearising the equations about the bulk densities as in the RPA. Doing this yields

$$\dot{n}(\mathbf{x}, t) = D\nabla \cdot \left[ \nabla n(\mathbf{x}, t) + \beta\bar{\rho} \int d\mathbf{y} \nabla V(\mathbf{x} - \mathbf{y}) n(\mathbf{y}, t) \right] + \nabla \cdot \sqrt{2D\bar{\rho}}\boldsymbol{\eta}(\mathbf{x}, t),$$

where we have made use of the formula

$$\int d\mathbf{y} \nabla V(\mathbf{x} - \mathbf{y}) = \mathbf{0}.$$

A more subtle point is the use of  $\nabla \cdot \sqrt{2D\bar{\rho}}\boldsymbol{\eta}(\mathbf{x}, t)$  as the noise term. This is justified as with this choice the SDFT becomes

$$\dot{n}(\mathbf{x}, t) = \nabla \cdot D\bar{\rho} \nabla \frac{\delta H_{RPA}}{\delta n(\mathbf{x})} + \nabla \cdot \sqrt{2D\bar{\rho}}\boldsymbol{\eta}(\mathbf{x}, t).$$

The underlying equilibrium distribution is thus compatible with the use of the RPA for the equilibrium system and the resulting theory is a simple Gaussian theory. The theory is actually of what is known as the model B type for coarsening dynamics. Here the density fluctuations correspond to the order parameter. We see from the form of the theory that the integral of the order parameter is conserved.

This model B type theory has the form, in vector notation

$$\dot{\mathbf{x}} = -R\mathbf{A}\mathbf{x} + \boldsymbol{\xi},$$

where

$$\langle \xi_i(t)\xi_j(t') \rangle = 2\delta(t-t')R_{ij}.$$

The formal solution to this equation is

$$x_i(t) = \exp(-tRA)_{ik}x_k(0) + \int_0^t ds \exp(-tRA)_{ik} \exp(sRA)_{kl}\xi_l(s).$$

In the steady state (not necessarily equilibrium) regime the time dependent correlations function is given by (multiplying this equation by  $x_j(0)$  and averaging over the noise)

$$C_{ij}(t, 0) = C_{ij}(t) = \langle x_i(t)x_j(0) \rangle = \exp(-tRA)_{ik}C_{kj}(0).$$

To compute the equal time correlation start time at  $t = -\infty$  so the initial conditions are forgotten and so

$$x_i(t) = \int_{-\infty}^t ds \exp(-[t-s]RA)_{ik}\xi_k(s)$$

$$\begin{aligned} C_{ij}(t, t) &= \langle x_i(t)x_j(t) \rangle = \left\langle \int_{-\infty}^t ds ds' \exp(-[t-s]RA)_{ik}\xi_k(s) \exp(-[t-s']RA)_{jl}\xi_l(s') \right\rangle \\ &= 2 \int_{-\infty}^t ds ds' \exp(-[t-s]RA)_{ik} \exp(-[t-s']RA)_{jl} \delta(s-s') R_{kl} \\ &= 2 \int_{-\infty}^t ds \exp(-[t-s]RA)_{ik} R_{kl} \exp(-[t-s]RA)_{jl} \\ &= 2 \int_{-\infty}^t ds \exp(-[t-s]RA)_{ik} R_{kl} \exp(-[t-s]A^\dagger R^\dagger)_{kl}, \end{aligned}$$

where we have used the definition of the adjoint or transpose  $X_{ij}^\dagger = X_{ji}$  and used the properties

$$\exp(X)^\dagger = \exp(X^\dagger)$$

and

$$(XY)^\dagger = Y^\dagger X^\dagger.$$

In matrix notation we thus have

$$C(t, t) = 2 \int_{-\infty}^t ds \exp(-[t-s]RA)R \exp(-[t-s]A^\dagger R^\dagger).$$

However from the definition of  $R$  in terms of a noise correlator we obviously have  $R = R^\dagger$  and so

$$C(t, t) = 2 \int_{-\infty}^t ds \exp(-[t-s]RA)R \exp(-[t-s]A^\dagger R).$$

To get the equation for the steady state correlation function at equal times  $C_s = \lim_{t \rightarrow \infty} C(t, t)$  we take the derivative of this equation with respect to  $t$  and find

$$\dot{C}(t, t) = 0 = 2R - RAC_s - C_s A^\dagger R.$$

We therefore have

$$RAC_s + C_s A^\dagger R = 2T.$$

However from the definition of  $R$  in terms of a noise correlator we obviously have  $R = R^\dagger$ . In the case where  $A = A^\dagger$  we find the equipartition of energy result for a Gaussian model

$$C_s = A^{-1} = [\beta\Delta]^{-1} = T\Delta^{-1}$$

A time dependent static structure factor can be defined as

$$\langle \tilde{n}(\mathbf{k}, t) \tilde{n}(\mathbf{k}', 0) \rangle = (2\pi)^d S(\mathbf{k}, t) \delta(\mathbf{k} + \mathbf{k}'),$$

and with the approximations made for the linearised SDFT we find that as  $R = D\bar{\rho}k^2$  and so

$$S(\mathbf{k}, t) = S(\mathbf{k}) \exp\left(-\frac{\bar{\rho}Dk^2 t}{S(\mathbf{k})}\right). \quad (2.7)$$

## 2.5 Free Brownian particles

You may have noticed that even the basic SDFT in the absence of interactions seems difficult to solve. However we can obtain the exact two-point correlation function for non interacting Brownian motion directly. For noninteracting particles the equilibrium distribution in a finite volume  $V$  is uniform, we can thus write that  $\mathbf{X}_i(0) = \mathbf{x}_{i0}$  where  $\mathbf{x}_{i0}$  is a random variable with a uniform distribution over the volume  $V$ . We can then write  $\mathbf{X}_i(t) = \mathbf{x}_{i0} + \sqrt{2D}\mathbf{B}_i(t)$ , where  $\mathbf{B}_i$  are independent standard Brownian motions in  $d$  dimensions. The Fourier transform of the density field is then given by

$$\tilde{\rho}(\mathbf{k}) = \sum_i \exp\left(-i\mathbf{k} \cdot [\mathbf{x}_{i0} + \sqrt{2D}\mathbf{B}_i(t)]\right).$$

The average over particle positions involves a first over the  $\mathbf{x}_{i0}$  denoted by  $\langle \cdot \rangle_0$  and a second over the  $\mathbf{B}_i$  denoted by  $\langle \cdot \rangle_B$ . Note that

$$\langle \exp(-i\mathbf{k} \cdot \mathbf{x}_0) \rangle_0 = \frac{1}{V} \int_V d\mathbf{x} \exp(-i\mathbf{k} \cdot \mathbf{x}_0),$$

and for large  $V$  we can use

$$\int_V d\mathbf{x} \exp(-i\mathbf{k} \cdot \mathbf{x}_0) \rightarrow (2\pi)^d \delta(\mathbf{k}).$$

This gives

$$\langle \tilde{\rho}(\mathbf{k}) \rangle = \frac{1}{V} \sum_i (2\pi)^d \delta(\mathbf{k}) = \bar{\rho} (2\pi)^d \delta(\mathbf{k})$$

where  $\bar{\rho} = N/V$  is the particle density. The correlation function of the density is given by

$$\langle \tilde{\rho}(\mathbf{k}, t) \tilde{\rho}(\mathbf{k}, 0) \rangle = \frac{1}{V} \langle (2\pi)^d \delta(\mathbf{k} + \mathbf{k}') \sum_i \exp(-i\mathbf{k} \cdot \sqrt{2D} \mathbf{B}_i(t)) \rangle_B + \frac{1}{V^2} (2\pi)^{2d} \delta(\mathbf{k}) \delta(\mathbf{k}') \sum_{i \neq j} 1.$$

For large  $N$  this gives

$$\langle \tilde{\rho}(\mathbf{k}, t) \tilde{\rho}(\mathbf{k}, 0) \rangle = \bar{\rho} (2\pi)^d \delta(\mathbf{k} + \mathbf{k}') \exp(-\mathbf{k}^2 D t) + \bar{\rho}^2 (2\pi)^{2d} \delta(\mathbf{k}) \delta(\mathbf{k}'),$$

and so we find

$$\langle \tilde{n}(\mathbf{k}, t) \tilde{n}(\mathbf{k}, 0) \rangle = \bar{\rho} (2\pi)^d \delta(\mathbf{k} + \mathbf{k}') \exp(-\mathbf{k}^2 D t).$$

Therefore using this result at  $t = 0$  we find

$$S(\mathbf{k}) = \bar{\rho},$$

and that the result of the approximation using the linear order of the density fluctuations Eq. (2.7) is exact. Even for particles in interaction it can be shown that Eq. (2.7) is exact to first order in  $t$  as at short time Brownian motion dominates over the drift caused by the interactions.

## 2.6 Generalisation to different species of particles

It is straightforward to generalise the derivation of SDF/T for a single particle species to that for several types of particle, if  $\rho_\alpha(\mathbf{x})$  denotes the density field of particles of type  $\alpha$  then

$$\dot{\rho}_\alpha = \nabla \cdot D_\alpha \rho_\alpha \nabla \frac{\delta \beta H}{\delta \rho_\alpha(\mathbf{x})} + \nabla \cdot \sqrt{2D_\alpha \rho_\alpha} \boldsymbol{\eta}_\alpha,$$

where  $\boldsymbol{\eta}_\alpha$  are spatio-temporal vector white noise fields of zero mean and with correlation function

$$\langle \eta_{\alpha i}(\mathbf{x}, t) \eta_{\alpha i}(\mathbf{x}', t') \rangle = \delta_{\alpha\beta} \delta_{ij} \delta(t - t') \delta(\mathbf{x} - \mathbf{x}').$$

If the particle type  $\alpha$  is subject to an external potential  $v_\alpha$  and there is a pairwise interaction of the form  $V_{\alpha\beta}$  between particle types  $\alpha$  and  $\beta$  then  $H$  is given by

$$H = \int d\mathbf{x} \sum_{\alpha} T \rho_{\alpha}(\mathbf{x}) \ln [\rho_{\alpha}(\mathbf{x})] + \frac{1}{2} \sum_{\alpha\beta} \int \int d\mathbf{x} d\mathbf{y} \rho_{\beta}(\mathbf{x}) V_{\alpha\beta}(\mathbf{x}-\mathbf{y}) \rho_{\beta}(\mathbf{y}) - \int d\mathbf{x} \sum_{\alpha} v_{\alpha}(\mathbf{x}) \rho_{\alpha}(\mathbf{x}).$$

## 2.7 The Martin-Siggia-Rose path integral

Consider a discrete stochastic differential equation, in  $d$  dimensions, of the form,

$$\frac{\Delta X_i}{\Delta t} = u_i(\mathbf{X}_t) + a_{ij}(\mathbf{X}_t) \frac{\Delta B_{it}}{\Delta t}$$

The probability to observe the trajectory  $\mathbf{x}_{t_0}, \mathbf{x}_{t_1} \cdots \mathbf{x}_{t_N}$  can be written as

$$P(\mathbf{x}_0, \mathbf{x}_{t_1} \cdots \mathbf{x}_{t_N}) = \langle \prod_i \delta(\mathbf{X}_{t_i} - \mathbf{x}_{t_i}) \rangle,$$

where the average here indicates the average over the Brownian increments. Now if we are lucky we can solve the equation for the  $\mathbf{X}_{t_i}$  to write

$$\mathbf{X}_{t_i} = \mathbf{X}_{t_i} \left( \frac{\Delta B_{it_0}}{\Delta t}, \dots, \frac{\Delta B_{it_{i-1}}}{\Delta t}, \mathbf{x}_0 \right)$$

so we explicitly have an expression for each  $\mathbf{X}_{t_i}$  as a function of the noise and the initial position  $\mathbf{x}_0$ . However this is not necessarily the case, and we may have to live with the implicit stochastic equation for the  $\mathbf{X}_{t_i}$ . Consider the probability of observing  $\mathbf{x}_{t_1}$  after the first time step given we start at  $\mathbf{x}_0$  at  $t = 0$ . The implicit equation for  $\mathbf{X}_{t_1}$  is

$$A_i(\mathbf{X}_{t_1}) = \frac{X_{it_1}}{\Delta t} - \frac{x_{i0}}{\Delta t} - u_i(\mathbf{x}_0) - a_{ij}(\mathbf{x}_0) \frac{\Delta B_{it_0}}{\Delta t} = 0$$

Now we recall

$$\delta(\mathbf{A}(\mathbf{x}) - \mathbf{A}(\mathbf{X})) = |\det T|^{-1} \delta(\mathbf{x} - \mathbf{X}).$$

where  $T_{ij} = \partial A_i / \partial x_j$  is the local linear transformation. However we see here that  $\det T = [\Delta t]^d$ . The determinant is thus independent of the path. However as  $\mathbf{A}(\mathbf{X}_{t_1}) = 0$  we have

$$\begin{aligned} P(\mathbf{x}_0, \mathbf{x}_{t_1}) &= \langle \prod_i \delta(\mathbf{X}_{t_1} - \mathbf{x}_{t_1}) \rangle = \text{Const.} \langle \delta(A(\mathbf{x}_{t_1})) \rangle \\ &= \text{Const.} \langle \delta \left( \frac{\mathbf{x}_{t_1}}{\Delta t} - \frac{\mathbf{x}_0}{\Delta t} - u_i(\mathbf{x}_0) + a_{ij}(\mathbf{x}_0) \frac{\Delta B_{it_0}}{\Delta t} \right) \rangle. \end{aligned}$$



Iterating this and taking the continuum limit gives

$$P([\mathbf{x}_t], [t]) = \mathcal{N} \left\langle \prod_{t,i} \delta(\dot{x}_i(t) - u_i(\mathbf{x}(t)) - \xi_i(t)) \right\rangle,$$

where  $\xi_i(t) = a_{ij}(\mathbf{x}(t))\eta_j(t)$  is the noise and  $\langle \cdot \rangle$  indicates the average over the noise. Note in the above derivation it is essential that we have used the the Ito prescription where the noise is independent of the current position. The term  $\mathcal{N}$  is simply a normalisation factor.

The next step involves expressing the delta functions as Fourier transforms, using the formula

$$\delta(\mathbf{x}) = \frac{1}{(2\pi)^d} \int d\mathbf{k} \exp(-i\mathbf{k} \cdot \mathbf{x})$$

Using this for each delta function with  $\mathbf{k} = \Delta t \hat{\mathbf{x}}$  then gives

$$P([\mathbf{x}_t], [t]) = \mathcal{N} \left\langle \int \prod_t \frac{\Delta t d\hat{\mathbf{x}}(t)}{(2\pi)^d} \exp \left( -i \sum_t \Delta t \hat{\mathbf{x}}(t) \cdot [\dot{\mathbf{x}}(t) - \mathbf{u}(\mathbf{x}(t)) - \boldsymbol{\xi}(t)] \right) \right\rangle,$$

so we can take the continuous limit to find

$$P([\mathbf{x}_t], [t]) = \mathcal{N}' \left\langle \int d[\hat{\mathbf{x}}] \exp \left( -i \int_0^t ds \hat{\mathbf{x}}(s) \cdot [\dot{\mathbf{x}}(s) - \mathbf{u}(\mathbf{x}(s)) + \boldsymbol{\xi}(s)] \right) \right\rangle.$$

Now we can average over the noise, we use the identity

$$\left\langle \exp \left( -i \int_0^t ds \mathbf{f}(s) \cdot \boldsymbol{\eta}(s) \right) \right\rangle = \exp \left( -\frac{1}{2} \int_0^t ds \mathbf{f}(s) \cdot \mathbf{f}(s) \right),$$

to find

$$\begin{aligned} P([\mathbf{x}_t], [t]) &= \mathcal{N}' \int d[\hat{\mathbf{x}}] \exp \left( \int_0^t ds -i \hat{\mathbf{x}}(s) \cdot [\dot{\mathbf{x}}(s) - \mathbf{u}(\mathbf{x}(s))] - \frac{1}{2} a^\dagger(\mathbf{x}(s)) \hat{\mathbf{x}}(s) \cdot a^\dagger(\mathbf{x}(s)) \hat{\mathbf{x}}(s) \right) \\ &= \mathcal{N}' \int d[\hat{\mathbf{x}}] \exp \left( \int_0^t ds -i \hat{\mathbf{x}}(s) \cdot [\dot{\mathbf{x}}(s) - \mathbf{u}(\mathbf{x}(s))] - \frac{1}{2} \hat{\mathbf{x}}(s) \cdot a(\mathbf{x}(s)) a^\dagger(\mathbf{x}(s)) \hat{\mathbf{x}}(s) \right). \end{aligned}$$

For the SDFT we have

$$P([\rho], [t]) = \mathcal{N}' \int d[\hat{\rho}] \exp \left( \int ds d\mathbf{x} -i \hat{\rho}(\mathbf{x}, s) [\dot{\rho}(\mathbf{x}, s) - D\beta \nabla \rho(\mathbf{x}, s) \cdot \nabla \frac{\delta H}{\delta \rho(\mathbf{x})}] - \int d\mathbf{x} ds D\rho(\mathbf{x}, s) [\nabla \hat{\rho}(\mathbf{x}, s)]^2 \right) \quad (2.10)$$

## Chapter 3

# SDFT and extensions via path integral methods

### 3.1 Path integral for continuous time discrete lattice processes

Constructing path integrals for discrete dynamical variables, for example Ising spins, can be very difficult. The traditional approach is the Doi-Peliti formalism [4] which is very technical. Here I present a simple and elegant method which is very general and I find somewhat easier [5, 6]. This method was used to derive the basic SDFT and can be generalised, for example to models where the particle number is not conserved.

Consider a model on a lattice in  $d$  dimensions on which we place identical (for the moment) interacting particles. We define the number of particles on the lattice site  $i$  by  $n_i$  and define the vector  $\mathbf{n} = (n_1, n_2, \dots, n_K)$  where  $K$  is the total number of sites. We consider continuous time dynamics where the rate per unit time at which the particle configuration changes from  $\mathbf{n}$  to  $\mathbf{n} + \Delta\mathbf{n}$  is given by  $W(\mathbf{n}, \Delta\mathbf{n})$ , the values of  $\Delta\mathbf{n}$  for which  $W(\mathbf{n}, \Delta\mathbf{n})$  is non-zero defines the possible changes in the system at any given time for a given configuration  $\mathbf{n}$ . The probability that the system moves from the state  $\mathbf{n}$  to  $\mathbf{n} + \Delta\mathbf{n}$  between the time  $t$  and  $t + \Delta t$  is given by  $W(\mathbf{n}, \Delta\mathbf{n})\Delta t$ . The probability that two moves happen in  $[t, t + \Delta t]$  is of order  $\Delta t^2$  and becomes zero when  $\Delta t \rightarrow 0$ , *i.e.* in the true continuous time limit. The joint probability density to observe the trajectory  $\mathbf{n}(t)$  is given by

$$P[[t], [\mathbf{n}(t)]] = \langle \prod_t \delta(\mathbf{n}(t) - \mathbf{N}(t)) \rangle,$$

where we denote by  $\mathbf{N}(t)$  the random variable describing the number of particles at the lattice sites and  $\langle \cdot \rangle$  denotes the average over this process. Note that the notation  $[t], [\mathbf{n}(t)]$  indicates the probability of  $\mathbf{n}(t_1), \mathbf{n}(t_2) \dots \mathbf{n}(t)$  at the corresponding times  $t_1, t_2, \dots t$ .

We can now write

$$P(t, \mathbf{n}(t)) = \left\langle \int \prod_t \frac{d\hat{\mathbf{n}}(t)}{(2\pi)^K} \exp \left( -i \sum_t \hat{\mathbf{n}}(t) \cdot [\mathbf{n}(t) - \mathbf{N}(t)] \right) \right\rangle,$$

where we have used the Fourier representation of the Dirac delta function. If we only use the Fourier representation on the last time step we find that for a total time  $t + \Delta t$  that we have

$$P([t+\Delta t], [\mathbf{n}(t+\Delta t)]) = P([t], [\mathbf{n}(t)]) \left\langle \int \frac{d\hat{\mathbf{n}}(t+\Delta t)}{(2\pi)^K} \exp(-i\hat{\mathbf{n}}(t+\Delta t) \cdot [\mathbf{n}(t+\Delta t) - \mathbf{N}(t+\Delta t)]) \right\rangle,$$

and where the last average above is over the dynamics between  $t$  and  $t + \Delta t$  given that  $\mathbf{N}(t) = \mathbf{n}(t)$  at time  $t$ .

We see that  $\mathbf{N}(t + \Delta t) = \mathbf{n}(t) + \Delta \mathbf{n}$  with probability  $W(\mathbf{n}(t), \Delta \mathbf{n})\Delta t$ , however  $\mathbf{N}(t + \Delta t) = \mathbf{n}(t)$  with probability  $\prod_{\Delta \mathbf{n}} (1 - W(\mathbf{n}(t), \Delta \mathbf{n})\Delta t)$ , *i.e.* this is because the probability that a given jump  $\mathbf{n}(t) \rightarrow \mathbf{n}(t) + \Delta \mathbf{n}$  does not occur is  $(1 - W(\mathbf{n}(t), \Delta \mathbf{n})\Delta t)$  and so the probability that non occurs among the possible jumps is given by the product. Therefore, to order  $\Delta t$ , the probability that there is no jump is  $1 - \sum_{\Delta \mathbf{n}} W(\mathbf{n}(t), \Delta \mathbf{n})\Delta t$ . Using these probabilities we find

$$\begin{aligned} P([t + \Delta t], [\mathbf{n}(t + \Delta t)]) &= \\ P([t], [\mathbf{n}(t)]) &\int \frac{d\hat{\mathbf{n}}(t + \Delta t)}{(2\pi)^K} \exp(-i\hat{\mathbf{n}}(t + \Delta t) \cdot \mathbf{n}(t + \Delta t)) \langle \exp(i\hat{\mathbf{n}}(t + \Delta t) \cdot \mathbf{N}(t + \Delta t)) \rangle \\ &= P([t], [\mathbf{n}(t)]) \int \frac{d\hat{\mathbf{n}}(t + \Delta t)}{(2\pi)^K} \exp(-i\hat{\mathbf{n}}(t + \Delta t) \cdot \mathbf{n}(t + \Delta t)) \times \\ &\quad \exp(i\hat{\mathbf{n}}(t + \Delta t) \cdot \mathbf{n}(t)) \left[ 1 - \sum_{\Delta \mathbf{n}} W(\mathbf{n}(t), \Delta \mathbf{n})\Delta t \right] + \Delta t \sum_{\Delta \mathbf{n}} \exp(i\hat{\mathbf{n}}(t + \Delta t) \cdot [\mathbf{n}(t) + \Delta \mathbf{n}]) W(\mathbf{n}(t), \Delta \mathbf{n}). \end{aligned}$$

We now write  $\mathbf{n}(t) = \mathbf{n}(t + \Delta t) - \dot{\mathbf{n}}(t + \Delta t)\Delta t$  and find that to order  $\Delta t$  we have

$$\begin{aligned} P([t + \Delta t], [\mathbf{n}(t + \Delta t)]) &= P([t], [\mathbf{n}(t)]) \times \\ &\int \frac{d\hat{\mathbf{n}}(t + \Delta t)}{(2\pi)^K} \exp \left( -i\Delta t \hat{\mathbf{n}}(t + \Delta t) \cdot \dot{\mathbf{n}}(t + \Delta t) + \Delta t \sum_{\Delta \mathbf{n}} [\exp(i\hat{\mathbf{n}}(t + \Delta t) \cdot \Delta \mathbf{n}) - 1] W(\mathbf{n}(t + \Delta t), \Delta \mathbf{n}) \right). \end{aligned}$$

Iterating this and taking the continuum limit we find that path integral representation

$$\begin{aligned} P([t], [\mathbf{n}(t)]) &= \mathcal{N} \int d[\hat{\mathbf{n}}(t)] \exp \left( \int dt -i\hat{\mathbf{n}}(t) \cdot \dot{\mathbf{n}}(t) + \sum_{\Delta \mathbf{n}} [\exp(i\hat{\mathbf{n}}(t) \cdot \Delta \mathbf{n}) - 1] W(\mathbf{n}(t), \Delta \mathbf{n}) \right), \\ &= \mathcal{N} \int d[\hat{\mathbf{n}}(t)] \exp(S[\hat{\mathbf{n}}(t), \mathbf{n}(t)]) \end{aligned}$$

and  $\mathcal{N}$  is a normalisation constant. The nice thing about this formula is that all the possible changes  $\Delta \mathbf{n}$  appear additively and so the effect of each possible type of move can be considered one by one, each giving an additive contribution to the action  $S$  defined above.

### 3.2 A system of free random walkers

To start with let's consider a system of non-interacting particles which can hop to between nearest neighbours  $\langle i, j \rangle$  on a discrete lattice. If there are  $n_i$  particles at site  $i$  then each particle can hop with rate  $\gamma$  to a neighbouring site  $j$ . Let us consider the change  $\Delta \mathbf{n}$  corresponding to moving a particle at site  $i$  to a neighbouring site  $j$ . The total rate of this happening is given by  $W = n_i \gamma$  as each particle hops independently of the other particles at the site. Note that if no particle is present ( $n_i = 0$ ) then  $W = 0$  and the move cannot occur. The  $\Delta \mathbf{n}$  associated with this change is  $\mathbf{n} = -\mathbf{e}_i + \mathbf{e}_j$  (where  $\mathbf{e}_i$  denotes the basis vectors such that  $\mathbf{n} = \sum_i \mathbf{n}_i \mathbf{e}_i$ ), so the site  $i$  loses a particle and the site  $j$  gains a particle. For this change we find

$$W(\mathbf{n}(t), \Delta \mathbf{n}) = \gamma n_i(t) \Delta_{ij},$$

where  $\Delta_{ij} = 1$  if the sites  $i$  and  $j$  are connected, *i.e.* it is the connectivity matrix of the underlying lattice. In the path integral this gives a contribution

$$(\exp(i\hat{\mathbf{n}}(t) \cdot \Delta \mathbf{n}) - 1) W(\mathbf{n}(t), \Delta \mathbf{n}) = (\exp(-i\hat{n}_i + i\hat{n}_j) - 1) \gamma n_i(t) \Delta_{ij}$$

We now take the limit where the lattice size  $a \rightarrow 0$ . The auxiliary field is rewritten  $\hat{n}_i \rightarrow \hat{\rho}(\mathbf{x})$  and we write  $n_i = a^d \rho(\mathbf{x})$ . Using this we can write  $\hat{n}_j = \hat{\rho}(\mathbf{x}) + \hat{\rho}(\mathbf{x} + a\mathbf{e}_{ij})$  where  $\mathbf{e}_{ij}$  is the unit vector between the sites  $i$  and  $j$ . This gives

$$\begin{aligned} & \sum_{\langle i, j \rangle} (\exp(-i\hat{n}_i + i\hat{n}_j) - 1) \gamma n_i(t) \Delta_{ij} \\ & \approx a^{-d} \int d\mathbf{x} \sum_j \left( i[\hat{\rho}(\mathbf{x} + a\mathbf{e}_{ij}) - \hat{\rho}(\mathbf{x})] - \frac{1}{2}[\hat{\rho}(\mathbf{x} + a\mathbf{e}_{ij}) - \hat{\rho}(\mathbf{x})]^2 \right) \gamma \rho(\mathbf{x}) a^d. \end{aligned}$$

We should notice here that we have kept the second order term in the expansion of  $\exp(-i\hat{n}_i + i\hat{n}_j)$  as although the first term is superficially of order  $a$ , the sum involved makes it of order  $a^2$  and thus of the same order as the second term. On a square lattice, in the first term of the sum we see that the contribution from the two lattice vectors in the direction  $x$  is given to leading order in  $a$  by from the Taylor expansion,

$$\hat{\rho}(\mathbf{x} + a\mathbf{e}_x) - \hat{\rho}(\mathbf{x}) + \hat{\rho}(\mathbf{x} - a\mathbf{e}_x) - \hat{\rho}(\mathbf{x}) \approx a^2 \frac{\partial^2}{\partial x^2} \hat{\rho}(\mathbf{x}),$$

we also have

$$\sum_j [\hat{\rho}(\mathbf{x} + a\mathbf{e}_{ij}) - \hat{\rho}(\mathbf{x})]^2 \rho(\mathbf{x}) \approx 2a^2 [\nabla \hat{\rho}(\mathbf{x})]^2.$$

Putting this all together then gives

$$P([t], [\rho(\mathbf{x}, t)]) = \mathcal{N} \int d[\hat{\rho}(\mathbf{x}, t)] \exp \left( \int d\mathbf{x} dt - i\hat{\rho}(\mathbf{x}, t)\dot{\rho}(\mathbf{x}, t) + ia^2\gamma\rho(\mathbf{x}, t)\nabla^2\hat{\rho}(\mathbf{x}, t) - a^2\gamma[\nabla\hat{\rho}(\mathbf{x})]^2\rho(\mathbf{x}) \right).$$

Note that  $\gamma a^2 = D$  is the effective diffusion constant. Integrating the second term by parts allows us to write

$$P([t], [\rho(\mathbf{x}, t)]) = \mathcal{N} \int d[\hat{\rho}(\mathbf{x}, t)] \exp \left( \int d\mathbf{x} dt - i\hat{\rho}(\mathbf{x}, t)[\dot{\rho}(\mathbf{x}, t) - D\nabla^2\rho(\mathbf{x}, t)] - D[\nabla\hat{\rho}(\mathbf{x})]^2\rho(\mathbf{x}) \right).$$

### 3.3 Particles in a potential

Imagine now that the particles are subjected to an potential  $U$ , which can either be externally imposed or is due to the interaction with other particles. Again the dynamics is due to particles moving between neighbouring sites. If we were applying Glauber dynamics for instance, the rates for a single particle to move from a site  $i$  to a neighbouring site  $j$  must be modified to respect detailed balance. The rate of going from site  $i$  to  $j$   $\gamma_{ij}$  and the rate of going from  $j$  to  $i$  obey

$$\frac{\gamma_{ij}}{\gamma_{ji}} = \exp(-\beta U(j) + \beta U(i)),$$

if we compute the overall energy change for interacting particles with pairwise interactions the total energy change is indeed  $\Delta E = U(j) - U(i)$ . A simple, symmetric, way of choosing the modified rates is to take

$$\gamma_{ij} = \gamma \exp \left( -\frac{\beta}{2}U(j) + \frac{\beta}{2}U(i) \right).$$

With this choice we find that for the move in question

$$(\exp(i\hat{\mathbf{n}}(t) \cdot \Delta \mathbf{n}) - 1) W(\mathbf{n}(t), \Delta \mathbf{n}) = (\exp(-i\hat{n}_i + i\hat{n}_j) - 1) \gamma \exp \left( -\frac{\beta}{2}U(j) + \frac{\beta}{2}U(i) \right) n_i(t) \Delta_{ij}$$

and going to the continuum limit

$$\begin{aligned} & \sum_{\langle i, j \rangle} (\exp(-i\hat{n}_i + i\hat{n}_j) - 1) \gamma \exp \left( -\frac{\beta}{2}U(j) + \frac{\beta}{2}U(i) \right) n_i(t) \Delta_{ij} \\ & \approx a^{-d} \int d\mathbf{x} \sum_j \left( i[\hat{\rho}(\mathbf{x} + a\mathbf{e}_{ij}) - \hat{\rho}(\mathbf{x})] - \frac{1}{2}[\hat{\rho}(\mathbf{x} + a\mathbf{e}_{ij}) - \hat{\rho}(\mathbf{x})]^2 \right) \left( 1 - \frac{\beta}{2}U(\mathbf{x} + a\mathbf{e}_{ij}) + \frac{\beta}{2}U(\mathbf{x}) \right) \gamma \rho(\mathbf{x}) a^d, \end{aligned}$$

With respect to the free case there is one new term of order  $a^2$  coming from the first term of the first bracket above and the second two terms of the second bracket above which depend on the potential  $U$ . This term is explicitly

$$\begin{aligned} & \int d\mathbf{x} \sum_j i[\hat{\rho}(\mathbf{x} + a\mathbf{e}_{ij}) - \hat{\rho}(\mathbf{x})] \left( -\frac{\beta}{2}U(\mathbf{x} + a\mathbf{e}_{ij}) + \frac{\beta}{2}U(\mathbf{x}) \right) \gamma\rho(\mathbf{x}) \approx \\ & \approx -i\frac{\gamma\beta a^2}{2} \int d\mathbf{x} \sum_j \nabla\hat{\rho}(\mathbf{x}) \cdot \mathbf{e}_{ij} \nabla U(\mathbf{x}) \cdot \mathbf{e}_{ij} \rho(\mathbf{x}) \\ & = -i\beta\gamma a^2 \int d\mathbf{x} \nabla\hat{\rho}(\mathbf{x}) \cdot \nabla U(\mathbf{x}) \rho(\mathbf{x}) = i\beta\gamma a^2 \int d\mathbf{x} \hat{\rho}(\mathbf{x}) \nabla \cdot [\nabla U(\mathbf{x}) \rho(\mathbf{x})], \end{aligned}$$

where we applied the divergence theorem.

With this extra term we find

$$\begin{aligned} P([t], [\rho(\mathbf{x}, t)]) = \\ \mathcal{N} \int d[\hat{\rho}(\mathbf{x}, t)] \exp \left( \int d\mathbf{x} dt - i\hat{\rho}(\mathbf{x}, t)[\dot{\rho}(\mathbf{x}, t) - D\nabla^2\rho(\mathbf{x}, t) - D\beta\nabla \cdot [\nabla U(\mathbf{x})\rho(\mathbf{x})]] - D[\nabla\hat{\rho}(\mathbf{x})]^2\rho(\mathbf{x}) \right). \end{aligned}$$

For an interacting particle system with no external potential we have

$$U(\mathbf{x}, t) = \int d\mathbf{y} V(\mathbf{x} - \mathbf{y}) \rho(\mathbf{y}, t),$$

and we have exactly the same MSR path integral as derived from the SDFT in Eq. (2.10)

### 3.4 Models with annihilation and destruction of particles

We can also have systems where particles disappear or transform into two particles. In the first case  $\Delta n_i = -1$  at the site  $i$  and zero elsewhere the rate of this happening is  $\gamma_d n_i$  and thus we find

$$(\exp(i\hat{\mathbf{n}}(t) \cdot \Delta\mathbf{n}) - 1) W(\mathbf{n}(t), \Delta\mathbf{n}) = (\exp(-i\hat{n}_i) - 1) \gamma_d n_i(t),$$

this gives an additional term in the path integral action of the form

$$S_d = \int dt \sum_i (\exp(-i\hat{n}_i(t)) - 1) \gamma_d n_i(t),$$

which in the continuum formulation becomes

$$S_d = \int dt d\mathbf{x} (\exp(-i\hat{\rho}(\mathbf{x}, t)) - 1) \gamma_d \rho(\mathbf{x}, t),$$

If each particle can split into two, independently of the configuration of the others, then  $\Delta n_i = 1$  at each site  $i$  and the change occurs with the rate  $\gamma_s n_i$  and we thus find

$$(\exp(i\hat{\mathbf{n}}(t) \cdot \Delta \mathbf{n}) - 1) W(\mathbf{n}(t), \Delta \mathbf{n}) = (\exp(i\hat{n}_i) - 1) \gamma_s n_i(t),$$

giving contribution to the action

$$S_s = \int dt \sum_i (\exp(i\hat{n}_i) - 1) \gamma_s n_i(t),$$

and for the continuum limit

$$S_s = \int dt d\mathbf{x} (\exp(i\hat{\rho}(\mathbf{x}, t)) - 1) \gamma_s \rho(\mathbf{x}, t).$$

Another possibility is that a pair of particles at the same site annihilate one another. This happens with rather  $\gamma_a n_i(n_i - 1)$  as the rate must be proportional to the number of possible pairs that can annihilate, in addition  $\Delta n_i = -2$ . Here we have

$$(\exp(i\hat{\mathbf{n}}(t) \cdot \Delta \mathbf{n}) - 1) W(\mathbf{n}(t), \Delta \mathbf{n}) = (\exp(-2i\hat{n}_i) - 1) \gamma_a n_i(t)(n_i(t) - 1),$$

this gives an annihilation term

$$S_a = \int dt \sum_i (\exp(-2i\hat{n}_i) - 1) \gamma_a n_i(t)(n_i(t) - 1),$$

and in the continuum limit

$$S_a = \int dt d\mathbf{x} (\exp(-2i\hat{\rho}(\mathbf{x}, t)) - 1) \gamma_a \rho(\mathbf{x}, t)(\rho(\mathbf{x}, t)a^d - 1).$$

## Chapter 4

# Applications to electrolyte conductivity

Here we see how SDFT can be used to predict the conductivity of electrolyte solutions, this approach gives a very concise method to reproduce results obtained by Onsager [7], and also allows a considerable number of extensions to more general potential interactions and lower dimensional systems [8].

### 4.1 Naive estimation of electrical conductivity

Here we will consider a simplified Brownian model for electrolyte solutions. The ions are treated as over damped Brownian particles and hydrodynamic effects due to the solvent are neglected. Consider a solution made up of  $K$  ionic species  $\alpha$  of valencies  $z_\alpha$ , bulk densities  $\bar{\rho}_\alpha$ , in the presence of an externally applied electric field  $\mathbf{E}$ .

The equation of motion for a single ion of type  $\alpha$  is

$$\frac{d\mathbf{X}}{dt} = \kappa_\alpha \mathbf{f} + \sqrt{2T\kappa_\alpha} \boldsymbol{\eta},$$

where  $\mathbf{f}$  is the force acting on the ion and  $\kappa_\alpha$  is its mobility. The average speed of the ion is thus

$$\left\langle \frac{d\mathbf{X}}{dt} \right\rangle = \mathbf{V} = \kappa_\alpha \langle \mathbf{f} \rangle$$

If we ignore the interaction due to the other ions, the only force acting on the ion is that due to the electric field, and so

$$\mathbf{f} = qz_\alpha \mathbf{E},$$

where  $q$  is the basic unit of charge  $q = e$ .

$$\mathbf{V} = \kappa_\alpha q z_\alpha \mathbf{E}.$$



The number current of particles of type  $\alpha$  is thus

$$\mathbf{j}_\alpha = \bar{\rho}_\alpha \kappa_\alpha q z_\alpha \mathbf{E},$$

the contribution to the electric current  $\mathbf{J}_\alpha$  from species  $\alpha$  is obtained by multiplying the number current by the charge of the particles  $q_\alpha = z_\alpha q$  and thus

$$\mathbf{J}_\alpha = \bar{\rho}_\alpha \kappa_\alpha q^2 z_\alpha^2 \mathbf{E}.$$

The total electric current is thus

$$\mathbf{J} = \sum_\alpha \mathbf{J}_\alpha = \left[ \sum_\alpha \bar{\rho}_\alpha \kappa_\alpha q^2 z_\alpha^2 \right] \mathbf{E}.$$

The conductivity, in an isotropic system, is defined via

$$\mathbf{J} = \sigma(E) \mathbf{E}, \tag{4.1}$$

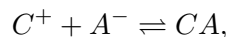
where  $E = |\mathbf{E}|$  and so here we find

$$\sigma(E) = \sigma_0 = \sum_\alpha \bar{\rho}_\alpha \kappa_\alpha q^2 z_\alpha^2, \tag{4.2}$$

which is a standard textbook result.

## 4.2 The first and second Wien effect

The simple computation carried out above predicts that the electrical conductivity does not depend on the strength of the electric field. However experiments carried out by Wien in the early 1900s showed that the conductivity actually increases with the strength of the electric field. The first Wien effect was seen in what are called strong electrolytes where most of the ions are dissociated from each other. For monovalent electrolytes the chemical reaction



has an equilibrium between the free ions and the bound salt molecules. In strong electrolytes (for instance *NaCl*) the equilibrium concentration of the salt molecule is very low and we can assume that all the salt molecules are dissociated (very close to 100%). In strong electrolytes the 1st Wien effect is observed, as the field is increased the conductivity increases. The approximation we made in the previous section was to neglect the interactions between the particles. Intuitively a cations will tend to be surrounded by anions even if it is not bound to a anion, when an electric field is applied the cations are pulled one way and the anions the other, as they were in equilibrium before the application of the field, when they are moved apart there is a self interaction term which resists the applied electric

field (called the reaction field) which tries to pull them together again, this reaction field thus means that the total electric field experienced by an ion is less than the applied field and thus the effective field in Eq. (4.1) is smaller and the conductivity is thus reduced. As the field increases the reaction field becomes smaller and the reduction is less important.

In weak electrolytes, for example carbonic acid  $H_2CO_3$ , between 1 and 10% of the molecules disassociate. While the mechanism present in the first Wien effect clearly also plays an effect here, the presence of the electric field shifts the equilibrium distribution in favouring the disassociation reaction. This increases the bulk densities of the ionic species  $\bar{\rho}_\alpha$  in Eq. (4.2) and so the conductivity increases.

### 4.3 The first Wien effect via SDFT

Consider a system where the interactions between the ions are given by

$$V_{\alpha\beta}(\mathbf{x}) = q^2 z_\alpha z_\beta G_0(\mathbf{x}) + U_{\alpha\beta}(\mathbf{x}).$$

where

$$\epsilon \nabla^2 G_0(\mathbf{x}) = -\delta(\mathbf{x})$$

is the electrostatic Green's function generating the Coulomb interaction between the particles and other interactions, for instance hard core repulsion are included in  $U_{\alpha\beta}$ .

We write the SDFT in terms of particle currents

$$\begin{aligned} \dot{\rho}_\alpha &= -\nabla \cdot \mathbf{j}_\alpha, \\ \mathbf{j}_\alpha &= -T \kappa_\alpha \nabla \rho_\alpha + \kappa_\alpha \rho_\alpha \mathbf{f}_\alpha + (\kappa_\alpha \rho_\alpha)^{1/2} \boldsymbol{\eta}_\alpha, \end{aligned} \quad (4.3)$$

where the force acting on a particle of type  $\alpha$  is given by

$$\mathbf{f}_\alpha = z_\alpha q \mathbf{E} - \sum_\beta \nabla V_{\alpha\beta} * \rho_\beta, \quad (4.4)$$

where  $*$  denotes the convolution over spatial variables. The second term above includes the electrostatic reaction field.

Therefore we find the average electrical current is given by

$$\langle \mathbf{J} \rangle = q \sum_\alpha z_\alpha \langle \mathbf{j}_\alpha \rangle$$

The first term above is the naive conductivity derived above where we neglected the interactions (the second term). Using Eqs.(4.3) and (4.4) in the definition of the current gives

$$\langle \mathbf{J} \rangle = q^2 \left( \sum_\alpha z_\alpha^2 \kappa_\alpha \bar{\rho}_\alpha \right) \mathbf{E} - q \sum_{\alpha,\beta} z_\alpha \kappa_\alpha \langle \rho_\alpha \nabla V_{\alpha\beta} * \rho_\beta \rangle.$$

Now we write the theory in terms of fluctuations about the bulk or average ionic densities and define the correlation matrix of the density fluctuations:

$$\begin{aligned} n_\alpha(\mathbf{x}, t) &= \rho_\alpha(\mathbf{x}, t) - \bar{\rho}_\alpha, \\ C_{\alpha\beta}(\mathbf{x}) &= \langle n_\alpha(\mathbf{x}, t) n_\beta(0, t) \rangle. \end{aligned}$$

In terms of the correlation matrix  $C_{\alpha\beta}$  we find

$$\langle \mathbf{J} \rangle = \sigma_0 \mathbf{E} - q \sum_{\alpha, \beta} z_\alpha \kappa_\alpha \int C_{\alpha\beta}(\mathbf{x}) \nabla V_{\alpha\beta}(\mathbf{x}) d\mathbf{x}.$$

The linearised approximation to the SDFT is now given by

$$\dot{n}_\alpha = T \kappa_\alpha \nabla^2 n_\alpha - \kappa_\alpha z_\alpha q \mathbf{E} \cdot \nabla n_\alpha + \kappa_\alpha \bar{\rho}_\alpha \nabla^2 \left[ \sum_{\beta} V_{\alpha\beta} * n_\beta \right] + (\kappa_\alpha \bar{\rho}_\alpha)^{1/2} \nabla \cdot \boldsymbol{\eta}_\alpha.$$

The dynamics takes a simpler form in Fourier space:

$$\dot{\tilde{n}}_\alpha(\mathbf{k}) = -\kappa_\alpha (T k^2 + i z_\alpha q \mathbf{E} \cdot \mathbf{k}) \tilde{n}_\alpha(\mathbf{k}) - \kappa_\alpha \bar{\rho}_\alpha k^2 \sum_{\beta} \tilde{V}_{\alpha\beta}(\mathbf{k}) \tilde{n}_\beta(\mathbf{k}) + \tilde{\xi}_\alpha(\mathbf{k}, t), \quad (4.5)$$

where the Gaussian noise  $\xi_\alpha(\mathbf{k}, t)$  has the correlation matrix

$$\langle \tilde{\xi}_\alpha(\mathbf{k}, t) \tilde{\xi}_\beta(\mathbf{k}', t') \rangle = 2(2\pi)^d T \kappa_\alpha \bar{\rho}_\alpha k^2 \delta_{\alpha\beta} \delta(t - t') \delta(\mathbf{k} + \mathbf{k}').$$

In terms of the two component vector

$$N(\mathbf{x}, t) = \begin{pmatrix} n_+(\mathbf{x}, t) \\ n_-(\mathbf{x}, t) \end{pmatrix},$$

and defining the matrices

$$\begin{aligned} \tilde{R}(\mathbf{k}) &= k^2 \begin{pmatrix} \bar{\rho}_+ \kappa_+ & 0 \\ 0 & \bar{\rho}_- \kappa_- \end{pmatrix}, \\ \tilde{A}(\mathbf{k}) &= T \begin{pmatrix} \frac{1}{\bar{\rho}_+} \left( 1 + i \frac{z_+ q \mathbf{E} \cdot \mathbf{k}}{T k^2} \right) + \frac{\tilde{V}_{++}(k)}{T} & \frac{\tilde{V}_{+-}(k)}{T} \\ \frac{\tilde{V}_{+-}(k)}{T} & \frac{1}{\bar{\rho}_-} \left( 1 + i \frac{z_- q \mathbf{E} \cdot \mathbf{k}}{T k^2} \right) + \frac{\tilde{V}_{--}(k)}{T} \end{pmatrix}, \end{aligned}$$

the evolution Eq. (4.5) becomes

$$\partial_t \tilde{N} = -\tilde{R} \tilde{A} \tilde{N} + \tilde{\Xi}.$$

The correlation function of the Gaussian noise  $\tilde{\Xi}(\mathbf{k}, t)$  is given by

$$\langle \tilde{\Xi}(\mathbf{k}, t)_\alpha \tilde{\Xi}_\beta(\mathbf{k}', t') \rangle = 2(2\pi)^d T \tilde{R}_{\alpha\beta}(k) \delta(\mathbf{k} + \mathbf{k}') \delta(t - t').$$

The density fluctuation correlation matrix  $C_{\alpha\beta}(\mathbf{x})$  is invariant by translation and is defined by

$$C(\mathbf{x}) = \langle N_\alpha(\mathbf{x}) N_\beta(\mathbf{0}) \rangle,$$

and in Fourier space, the correlation is given by

$$\begin{aligned} \langle \tilde{N}(\mathbf{k})_\alpha \tilde{N}_\beta(\mathbf{k}') \rangle &= \int e^{-i\mathbf{k}\cdot\mathbf{x} - i\mathbf{k}'\cdot\mathbf{x}'} C_{\alpha\beta}(\mathbf{x} - \mathbf{x}') d\mathbf{x} d\mathbf{x}' \\ &= \int e^{-i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{x} + i\mathbf{k}'\cdot\mathbf{u}} C_{\alpha\beta}(\mathbf{u}) d\mathbf{x} d\mathbf{u} \\ &= (2\pi)^d \delta(\mathbf{k} + \mathbf{k}') \tilde{C}_{\alpha\beta}(\mathbf{k}). \end{aligned}$$

Using the results of section (2.4), in the stationary regime,  $\tilde{C}$  satisfies

$$\tilde{R} \tilde{A} \tilde{C} + \tilde{C} \tilde{A}^* \tilde{R} = 2T \tilde{R}.$$

where we have used the relations  $\tilde{R}(-\mathbf{k})^T = \tilde{R}(\mathbf{k})$  and  $\tilde{A}(-\mathbf{k})^T = \tilde{A}(\mathbf{k})^*$ . In the absence of the electric field, the system would be in thermal equilibrium and  $\tilde{A}$  would be self-adjoint; in this case one finds  $\tilde{C} = T \tilde{A}^{-1}$ , and one recovers the standard Debye-Hückel approximation for the density fluctuation correlation function. In the presence of an electric field, we have to solve the system of equations (4.3). For  $M$  distinct ionic species we obtain a system of  $M(M+1)/2$  equations. If we consider the simplest case of two species we thus have three linear equations to solve.

Writing  $\rho_\pm \kappa_\pm = r_\pm$  and  $\tilde{A} = T \begin{pmatrix} a & b \\ b & c \end{pmatrix}$ , solving for the components of the correlation function leads to

$$\tilde{C} = \frac{2}{(a+a^*)(c+c^*)|r_+a+r_-c^*|^2 - b^2[r_+(a+a^*)+r_-(c+c^*)]^2} \times \begin{pmatrix} (c+c^*)|r_+a+r_-c^*|^2 & -b(r_+a^*+r_-c)[r_+(a+a^*)+r_-(c+c^*)] \\ -b(r_+a+r_-c^*)[r_+(a+a^*)+r_-(c+c^*)] & (a+a^*)|r_+a+r_-c^*|^2 \end{pmatrix}.$$

Notice that the correlation function's off diagonal components satisfy  $\tilde{C}_{+-}(\mathbf{k}) = \tilde{C}_{-+}^*(\mathbf{k})$ , or equivalently  $\tilde{C}_{+-}(\mathbf{k}) = \tilde{C}_{-+}(-\mathbf{k})$ , which in real space corresponds to  $C_{+-}(\mathbf{x}) = C_{-+}(-\mathbf{x})$ , which is a symmetry condition pointed out by Onsager. This is because the symmetry  $\mathbf{x} \rightarrow -\mathbf{x}$  is broken by the electric field (in the direction of the field), however reversing the direction of the field but at the same time swapping the charges generates a physically identical situation.

The average electrical current, which is given by Eq. (4.3), reads

$$\mathbf{J} = \sigma_0 \mathbf{E} + q \sum_{\alpha, \beta} \kappa_\alpha z_\alpha \int i \mathbf{k} \tilde{V}_{\alpha\beta}(-\mathbf{k}) \tilde{C}_{\alpha\beta}(\mathbf{k}) \frac{d\mathbf{k}}{(2\pi)^d}.$$

Recall here that the correction to the bare current is given by the average of the interaction term which was neglected upon linearizing the full SDFT, thus our expansion is only valid when the computed correction is small. From the expression for the current we can define the field dependent conductivity via

$$\mathbf{J} = \sigma(E) \mathbf{E} = [\sigma_0 + \Delta\sigma(E)] \mathbf{E},$$

where we assumed that the system is isotropic. We find that the correction to the bare conductivity is given by

$$\begin{aligned} \Delta\sigma(E) = & -\frac{q^2 \bar{\rho}_+ \bar{\rho}_- (\kappa_+ z_+ - \kappa_- z_-)^2}{(\kappa_+ + \kappa_-) T^2} \\ & \times \int \frac{\frac{k_\parallel^2}{k^2} \tilde{V}_{+-}^2 \left( 1 + \frac{\kappa_+ \bar{\rho}_+ \tilde{V}_{++} + \kappa_- \bar{\rho}_- \tilde{V}_{--}}{(\kappa_+ + \kappa_-) T} \right)}{\left( 1 + \frac{\bar{\rho}_+ \tilde{V}_{++}}{T} \right) \left( 1 + \frac{\bar{\rho}_- \tilde{V}_{--}}{T} \right) \left( \left[ 1 + \frac{\kappa_+ \bar{\rho}_+ \tilde{V}_{++} + \kappa_- \bar{\rho}_- \tilde{V}_{--}}{(\kappa_+ + \kappa_-) T} \right]^2 + \left[ \frac{(\kappa_+ z_+ - \kappa_- z_-) q E k_\parallel}{(\kappa_+ + \kappa_-) T k^2} \right]^2 \right)} \frac{d\mathbf{k}}{(2\pi)^d}, \\ & -\frac{\bar{\rho}_+ \bar{\rho}_- \tilde{V}_{+-}^2}{T^2} \left( 1 + \frac{\kappa_+ \bar{\rho}_+ \tilde{V}_{++} + \kappa_- \bar{\rho}_- \tilde{V}_{--}}{(\kappa_+ + \kappa_-) T} \right)^2 \end{aligned}$$

where  $k_\parallel$  denotes the component of the vector  $\mathbf{k}$  in the direction of  $\mathbf{E}$  (the third line of the equation belongs to the denominator of the integrand).

We notice from Eq. (4.3) that the correction  $\Delta\sigma(E)$  is zero when  $\kappa_+ z_+ = \kappa_- z_-$ . In this case, the two ionic types move with the same average velocity  $\mathbf{v} = q \kappa_\pm z_\pm \mathbf{E}$  due to an applied uniform field and the density fluctuation correlation keeps its equilibrium form, which is isotropic and does not modify the average electric field felt by an ion.

At zero field, the correction to the conductivity is given by

$$\begin{aligned} \Delta\sigma(0) = & -\frac{q^2 \bar{\rho}_+ \bar{\rho}_- (\kappa_+ z_+ - \kappa_- z_-)^2}{d(\kappa_+ + \kappa_-) T^2} \\ & \times \int \frac{\tilde{V}_{+-}(k)^2}{\left[ 1 + \frac{\bar{\rho}_+ \tilde{V}_{++}(k) + \bar{\rho}_- \tilde{V}_{--}(k)}{T} + \frac{\bar{\rho}_+ \bar{\rho}_- (\tilde{V}_{++}(k) \tilde{V}_{--}(k) - \tilde{V}_{+-}(k)^2)}{T^2} \right] \left[ 1 + \frac{\kappa_+ \bar{\rho}_+ \tilde{V}_{++}(k) + \kappa_- \bar{\rho}_- \tilde{V}_{--}(k)}{(\kappa_+ + \kappa_-) T} \right]} \frac{d\mathbf{k}}{(2\pi)^d}. \end{aligned}$$

## 4.4 Zero field conductivity for purely electrostatic interactions

If the interaction is purely electrostatic, i.e., only the first term is present in Eq. (4.3), our result at zero field Eq. (4.3) reduces to

$$\Delta\sigma(0) = -\frac{q^6 \bar{\rho}_+ \bar{\rho}_- z_+^2 z_-^2 (\kappa_+ z_+ - \kappa_- z_-)^2}{d(\kappa_+ + \kappa_-) T^2} \int \frac{\tilde{G}_0(\mathbf{k})^2}{\left(1 + \frac{q^2(z_+^2 \bar{\rho}_+ + z_-^2 \bar{\rho}_-) \tilde{G}_0(\mathbf{k})}{T}\right) \left(1 + \frac{\sigma_0 \tilde{G}_0(\mathbf{k})}{(\kappa_+ + \kappa_-) T}\right)} \frac{d\mathbf{k}}{(2\pi)^d}.$$

We now define,

$$\begin{aligned} m_{\pm}^2 &= \frac{\bar{\rho}_{\pm} z_{\pm}^2 q^2}{\epsilon T} \\ m^2 &= m_+^2 + m_-^2 \\ m'^2 &= \frac{\kappa_+ m_+^2 + \kappa_- m_-^2}{\kappa_+ + \kappa_-} = \frac{\sigma_0}{\epsilon T (\kappa_+ + \kappa_-)}. \end{aligned}$$

Here  $\ell_D = 1/m$  is the Debye screening length, it is the correlation length of the charge density fluctuations in the absence of an electric field.

$$\frac{\Delta\sigma(0)}{\sigma_0} = -\frac{q^2}{d\epsilon T} \frac{m_+^2 m_-^2 (\kappa_+ z_+ - \kappa_- z_-)^2}{m'^2 (\kappa_+ + \kappa_-)^2} \int \frac{1}{\left([\epsilon \tilde{G}_0(\mathbf{k})]^{-1} + m^2\right) \left([\epsilon \tilde{G}_0(\mathbf{k})]^{-1} + m'^2\right)} \frac{d\mathbf{k}}{(2\pi)^d}.$$

In the case where all the charges are mobile in an electroneutral system,  $\sum_{\alpha} z_{\alpha} \bar{\rho}_{\alpha} = 0$  and thus

$$\frac{m_+^2 m_-^2 (\kappa_+ z_+ - \kappa_- z_-)^2}{m'^2 (\kappa_+ + \kappa_-)^2} = -z_+ z_- m'^2,$$

leading to a simpler form for the correction:

$$\frac{\Delta\sigma(0)}{\sigma_0} = \frac{q^2 z_+ z_- m'^2}{d\epsilon T} \int \frac{1}{\left([\epsilon \tilde{G}_0(\mathbf{k})]^{-1} + m^2\right) \left([\epsilon \tilde{G}_0(\mathbf{k})]^{-1} + m'^2\right)} \frac{d\mathbf{k}}{(2\pi)^d}.$$

In a homogeneous  $d$ -dimensional space with solvent dielectric permittivity  $\epsilon$ , the electrostatic Green function is given by  $\tilde{G}_0(\mathbf{k}) = (\epsilon k^2)^{-1}$  and the conductivity correction (Eq. 4.4) becomes

$$\frac{\Delta\sigma(0)}{\sigma_0} = -\frac{q^2}{d\epsilon T} \frac{m_+^2 m_-^2 (\kappa_+ z_+ - \kappa_- z_-)^2}{m'^2 (\kappa_+ + \kappa_-)^2} \int \frac{1}{(k^2 + m^2)(k^2 + m'^2)} \frac{d\mathbf{k}}{(2\pi)^d}.$$

We note that while  $m$  is the usual inverse Debye screening length, which only depends on static quantities, the inverse length scale  $m'$  depends generally explicitly on the dynamical properties of the system via the mobilities  $\kappa_{\alpha}$ . However, for a monovalent electrolyte

$(z_{\pm} = \pm 1)$ ,  $m' = m/\sqrt{2}$  and is thus independent of the ionic mobilities. Furthermore, we note that the correction to the bare conductivity is always negative. Explicit evaluation for dimensions  $d = 1$  to 3 yields

$$\begin{aligned} \left(\frac{\Delta\sigma(0)}{\sigma_0}\right)_{d=3} &= -\frac{q^2}{12\pi\epsilon T} \frac{m_+^2 m_-^2 (\kappa_+ z_+ - \kappa_- z_-)^2}{m'^2 (\kappa_+ + \kappa_-)^2} \frac{1}{m + m'}, \\ \left(\frac{\Delta\sigma(0)}{\sigma_0}\right)_{d=2} &= -\frac{q^2}{4\pi\epsilon T} \frac{m_+^2 m_-^2 (\kappa_+ z_+ - \kappa_- z_-)^2}{m'^2 (\kappa_+ + \kappa_-)^2} \frac{\log\left(\frac{m}{m'}\right)}{m^2 - m'^2}, \\ \left(\frac{\Delta\sigma(0)}{\sigma_0}\right)_{d=1} &= -\frac{q^2}{2\epsilon T} \frac{m_+^2 m_-^2 (\kappa_+ z_+ - \kappa_- z_-)^2}{m'^2 (\kappa_+ + \kappa_-)^2} \frac{1}{mm'(m + m')}. \end{aligned}$$

For an electroneutral system where all charges are mobile, the correction is given by

$$\begin{aligned} \left(\frac{\Delta\sigma}{\sigma_0}\right)_{d=3} &= \frac{q^2 z_+ z_-}{12\pi\epsilon T} \frac{m'^2}{m + m'}, \\ \left(\frac{\Delta\sigma}{\sigma_0}\right)_{d=2} &= \frac{q^2 z_+ z_-}{4\pi\epsilon T} \frac{\log\left(\frac{m}{m'}\right)}{\left(\frac{m}{m'}\right)^2 - 1}, \\ \left(\frac{\Delta\sigma}{\sigma_0}\right)_{d=1} &= \frac{q^2 z_+ z_-}{2\epsilon T} \frac{m'}{m(m + m')}. \end{aligned}$$

We now recall that the validity of the linearization of the SDFT can be checked a posteriori by verifying that the correction to the average current or conductivity is small. In all dimensions this condition is satisfied holds if the electrostatic coupling constant  $\Gamma = \frac{q^2 z_+ z_-}{2\pi\epsilon T}$  is small, but the dependence on the density depends on the dimension. For example, for monovalent ions:

- For  $d = 3$ , the correction is proportional to  $\sqrt{\bar{\rho}}$  and is small if  $\bar{\rho}$  is small.
- For  $d = 2$ , the magnitude of the correction is purely controlled by the coupling constant  $\Gamma$ , which is dimensionless here, and does not depend on the density. In  $d = 2$  it is well known that there is a transition from a weak coupling conducting phase to a strong coupling dielectric phase (where the charge carriers exist only in bound pairs) – the Kosterlitz-Thouless transition. The weak coupling approach applied here is clearly only valid in the conducting phase.
- For  $d = 1$ , the correction is proportional to  $1/\sqrt{\bar{\rho}}$  and is thus small at high densities, however the long range nature of the electric field generated by one dimensional charges means that the one dimensional problem is not very realistic.

## 4.5 Field dependence for monovalent salts

Here we examine the case of monovalent salts (with no background charge,  $z_+ = -z_- = 1$  and  $\bar{\rho}_+ = \bar{\rho}_- = \rho$ ), which turns out to be the simplest case where one can obtain completely analytical results for the conductivity at any applied field. We define the inverse Debye length  $m$  and dimensionless electric field  $\mathbf{F}$  by

$$m^2 = \frac{2\bar{\rho}q^2}{\epsilon T},$$

$$\mathbf{F} = \frac{q}{mT}\mathbf{E},$$

and as the system is electroneutral we have written  $\bar{\rho}_\pm = \bar{\rho}$ . For this case the correlation function is given by

$$\tilde{C}(\mathbf{k}) = \frac{\bar{\rho}}{\left(1 + \frac{m^2}{2k^2}\right) \left[1 + \frac{m^2}{k^2} + \left(\frac{m\mathbf{k}\cdot\mathbf{F}}{k^2}\right)^2\right]} \begin{pmatrix} \left(1 + \frac{m^2}{2k^2}\right)^2 + \left(\frac{m\mathbf{k}\cdot\mathbf{F}}{k^2}\right)^2 & \frac{m^2}{2k^2} \left(1 + \frac{m^2}{2k^2} - i\frac{m\mathbf{k}\cdot\mathbf{F}}{k^2}\right) \\ \frac{m^2}{2k^2} \left(1 + \frac{m^2}{2k^2} + i\frac{m\mathbf{k}\cdot\mathbf{F}}{k^2}\right) & \left(1 + \frac{m^2}{2k^2}\right)^2 + \left(\frac{m\mathbf{k}\cdot\mathbf{F}}{k^2}\right)^2 \end{pmatrix}$$

The field dependent conductivity is given by

$$\frac{\sigma(F)}{\sigma_0} = 1 - \frac{m^d}{2\bar{\rho}} \int \frac{u_{\parallel}^2}{(2u^2 + 1)(u^4 + u^2 + F^2u_{\parallel}^2)} \frac{d\mathbf{u}}{(2\pi)^d},$$

where, again, the subscript  $\parallel$  denotes the component parallel to the electric field  $\mathbf{E}$ . For a finite field and a dimension  $d = 3$ , we need to evaluate the integral

$$I = \int \frac{u_{\parallel}^2}{(2u^2 + 1)(u^4 + u^2 + F^2u_{\parallel}^2)} \frac{d\mathbf{u}}{(2\pi)^3} = \frac{1}{2\pi^2} \int_0^\infty du \int_0^1 dv \frac{u^2 v^2}{(2u^2 + 1)(u^2 + 1 + F^2v^2)}.$$

The integral over  $u$  gives

$$I = \frac{1}{8\pi} \int_0^1 \frac{2(1 + F^2v^2) - \sqrt{2}\sqrt{1 + F^2v^2}}{(1 + 2F^2v^2)\sqrt{1 + F^2v^2}} v^2 dv$$

$$= \frac{1}{16\pi F^3} \left[ F\sqrt{1 + F^2} - \arctan\left(\frac{F}{\sqrt{1 + F^2}}\right) - \sqrt{2}F + \arctan(\sqrt{2}F) \right].$$

This gives the final result

$$\frac{\sigma(F)}{\sigma_0} = 1 - \frac{m^3}{32\pi\bar{\rho}F^3} \left[ F\sqrt{1 + F^2} - \arctan\left(\frac{F}{\sqrt{1 + F^2}}\right) - \sqrt{2}F + \arctan(\sqrt{2}F) \right].$$

The first term in brackets is dominant at large fields and the correction decays as  $1/F$ . The correction decays as the applied field increases, which is the so called Wien effect in simple strong electrolytes and we asymptotically recover the formula for the bare conductivity without interactions, the driving by the field thus kills all correlations.



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