Overview of Ito Calculus

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August 16, 2021

In this brief tutorial, I will discuss the basic mathematics of Stochastic Differential Equations (SDE). After this, I will discuss a couple of important applications.

1. Introduction to SDEs (§1)
2. Brownian motion (Ornstein-Uhlenbeck) (§2 & §6)
3. Kubo-Anderson model for spectral lineshape. (§3)
4. Financial Option pricing (Black Scholes Eq.)(§4)
5. Implementation in Mathematica (§5)

(the links are clickable!)

ODE vs SDE

We are usually accustomed to writing and solving differential equations in physics and chemistry.
For Example: Newton's equation of motion

$$\frac{d^2x}{dt^2} = F/m \tag{1}$$

Which we can easily solve given two initial conditions:

$$x(t) = Ft^2/2 + at + b \tag{2}$$

and we know a and b correspond to the initial position and velocity

ODE vs SDE

We can make it more complex by setting $F = -kx$ (harmonic oscillator)

$$\frac{d^2x}{dt^2} = -\frac{k}{m}x \tag{3}$$

and again, we solve this in a variety of ways and obtain that

$$x(t) = x(0)\cos(\omega t) \tag{4}$$
$$\omega = \sqrt{k/m} \tag{5}$$

This is a 2nd order ODE and we write it as two 1st order ODEs as

$$\frac{dx}{dt} = \frac{p}{m} \quad \text{and} \quad \frac{dp}{dt} = -kx \tag{6}$$

ODE vs SDE

A more compact way of doing this is in matrix form

$$\frac{d}{dt}\begin{pmatrix} x \\ p \end{pmatrix} = \begin{pmatrix} 0 & 1/m \\ -k & 0 \end{pmatrix}\begin{pmatrix} x \\ p \end{pmatrix} \tag{7}$$

Or in a more compact form

$$\dot{\mathbf{X}} = \mathbf{A} \cdot \mathbf{X} \tag{8}$$

where $\mathbf{X} = (x, p)^T$ is a vector and $\mathbf{A}$ is a matrix
When the matrix $\mathbf{A}$ does not depend upon $\mathbf{X}$, we have a 1st order linear ODE.
Or we can use *differential forms*

$$d\mathbf{X} = \mathbf{A}.\mathbf{X}dt \tag{9}$$

ODE vs SDE

To solve first-order ODE of the form,

$$\frac{dx}{dt} = g(t)f(x) \tag{10}$$

we usually do the following separation of variables trick

$$\frac{dx}{f(x)} = g(t)dt \tag{11}$$

then integrate

$$\int \frac{dx}{f(x)} = \int g(t)dt + C \tag{12}$$

you then determine C using the initial conditions after performing the integrations

ODE vs SDE

Another way, which will be useful for solving SDE's is to think in terms of the differentials
Suppose we have

$$dx = -\gamma x dt \tag{13}$$

This says "the value of x at time $t + dt$ is the value at time t plus dx"
In other words

$$x(t + dt) = x(t) - \gamma x(t)dt = (1 - \gamma dt)x(t) \tag{14}$$

We know

$$e^{-\alpha x} \approx 1 - \alpha x + \cdots \tag{15}$$

when x is small, so we write

$$x(t + dt) = e^{-\gamma dt}x(t) \tag{16}$$

ODE vs SDE

Every time we increment $x(t)$ to $x(t+dt)$, we multiply $x(t)$ by $e^{-\gamma dt}$.

$$x(t+ndt) = e^{-\gamma dt} \cdot e^{-\gamma dt} x(t) \tag{17}$$
$$= e^{-\gamma \sum_{i=1}^{n} dt} x(t) \tag{18}$$

I.e. if we set $\tau = ndt$, then

$$x(t+\tau) = (e^{-\gamma dt})^n x(t) = e^{-\gamma\tau} x(t) \tag{19}$$

Finally, if $\gamma = \gamma(t)$ depends upon time: $dx = -\gamma(t) x dt$, we have to perform an time-integration

$$x(t+\tau) = e^{-\int_t^{t+\tau} \gamma(s) ds} x(t) \tag{20}$$

ODE vs SDE

We now add one more level of complexity: a driving term.

$$\dot{x} = -\gamma x + f(t) \tag{21}$$

To solve: we first re-write this in terms of new variables

$$y(t) = x(t)e^{\gamma t} \tag{22}$$

The is defined so that if we ignored $f(t)$ and solved for $x(t)$, $y(t)$ would be a constant.

$$\frac{dy}{dt} = \left(\frac{dy}{dx}\right)\frac{dx}{dt} + \frac{dy}{dt} = e^{\gamma t} f(t) \tag{23}$$

ODE vs SDE

we now integrate!

$$y(t) = y(0) + \int_0^t e^{\gamma s} f(s) ds. \tag{24}$$

And, now determine $x(t)$

$$x(t) = x_0 e^{-\gamma t} + \int_0^t e^{-\gamma(t-s)} f(s) ds \tag{25}$$

Similarly, if the coefficient is a function of time, we can write

$$\Gamma(t) = \int_0^t \gamma(s) ds$$

and obtain

$$x(t) = x_0 e^{-\Gamma(t)} + e^{-\Gamma(t)} \int_0^t e^{\Gamma(s)} f(s) ds \tag{26}$$

ODE vs SDE

One last trick.
We can also apply this technique for linear vector equations such as

$$\frac{d\mathbf{X}}{dt} = \mathbf{A} \cdot \mathbf{X} \tag{27}$$

Here, $\mathbf{A}$ is a $d \times d$ square matrix and we will assume that it is also Hermitian:

$$\mathbf{A} \cdot \mathbf{A}^{\dagger} = \mathbf{A}^{\dagger} \cdot \mathbf{A}$$

For this, we need to define a new vector, $\mathbf{Y} = \mathbf{U} \cdot \mathbf{X}$ by performing a linear transformation on the $\mathbf{X}$ where the (unitary) matrix $\mathbf{U}$ transforms $\mathbf{A}$ into a diagonal matrix:

$$D = \mathbf{U} \cdot \mathbf{A} \cdot \mathbf{U}^{\dagger} \tag{28}$$

with eigenvalues $\{\gamma_1, \cdots, \gamma_d\}$ which may be real or complex.

ODE vs SDE

The solution is now easy to obtain[1]

$$\mathbf{Y}(t) = e^{Dt}\mathbf{Y}(0) \tag{29}$$

where we understand that

$$e^{Dt} = \begin{pmatrix} e^{\lambda_1 t} & 0 & \dots & 0 \\ 0 & e^{\lambda_2 t} & \dots & 0 \\ \vdots & \vdots & \ddots & 0 \\ 0 & 0 & 0 & e^{\lambda_d t} \end{pmatrix} \tag{30}$$

So our solution for $\mathbf{X}(t)$ is then simply

$$\mathbf{X}(\mathbf{t}) = \left(\mathbf{U}^{\dagger} \cdot e^{Dt} \cdot \mathbf{U}\right) \cdot \mathbf{X}(0) \tag{31}$$

[1] we use this trick all the time in doing time-dependent quantum mechanics.

ODE vs SDE

The reason this works is that can write the ODE as

$$\frac{d}{dt}\mathbf{Y} = \mathbf{U} \cdot \mathbf{X} = D\mathbf{Y} = D(\mathbf{U} \cdot \mathbf{X}) \tag{32}$$

Thus,

$$\frac{d}{dt}\mathbf{X} = (\mathbf{U}^{\dagger} D \mathbf{U}) \cdot \mathbf{X} = \mathbf{A} \cdot \mathbf{X}. \tag{33}$$

Thus, write e^{At} as a power series

$$e^{\mathbf{A}t} = \sum_{n=0}^{\infty} \frac{(\mathbf{A}t)^n}{n!} = 1 + \mathbf{A}t + \frac{1}{2}(\mathbf{A}t)^2 + \cdots \tag{34}$$

$$= 1 + (\mathbf{U}^{\dagger} D \mathbf{U})t + \frac{1}{2}(\mathbf{U}^{\dagger} D \mathbf{U})(\mathbf{U}^{\dagger} D \mathbf{U})t^2 + \cdots \tag{35}$$

$$= \mathbf{U}^{\dagger} e^{Dt} \mathbf{U} \tag{36}$$

ODE vs SDE

Armed with this, we can add in a driving term

$$\frac{d}{dt}\mathbf{X} = \mathbf{A}\mathbf{X} + \mathbf{f}(t) \tag{37}$$

and immediately write the solution as

$$\mathbf{X}(t) = e^{\mathbf{A}t}\mathbf{X}(0) + \int_0^t e^{\mathbf{A}(t-s)}\mathbf{f}(s)ds \tag{38}$$

In all of this, we see that given $x(t)$ we can determine $x(t + dt)$ at the end of the time increment. Or, given $x(t)$, we can determine $x(t + \tau)$ by integrating the ODE.
This is purely *deterministic*.

Stochastic Equations

Suppose we write the differential as a *discrete* difference with a driving term as before

$$\Delta x(t_n) = x(t_n)\Delta t + f(t_n)\Delta t \quad (39)$$

We then get

$$x(t_n + \Delta t) = x(t_n) + \Delta x(t_n) \quad (40)$$

$$= x(t_n) + x(t_n)\Delta t + f(t_n)\Delta t \quad (41)$$

If we know $x(0)$

$$x(\Delta t) = x(0)(1 + \Delta t) + f(0)\Delta t \quad (42)$$

Stochastic Equations

What we're really interested in is the case where $f(t_n)$ is random. In other words, we select $f(t_n)$ some distribution at time t_n and replace it with y_n.

$$\Delta x(t_n) = x(t_n)\Delta t + y_n \Delta t \tag{43}$$

We can no longer determine what $x(\Delta t)$ will be

$$x(\Delta t) = x(0)(1 + \Delta t) + y_0 \Delta t \tag{44}$$

since y_0 is a random variable. For that matter, $x(0)$ my be random as well!
A SDE is obtained in the limit that $\Delta t \to 0$ of such stochastic *difference* equations.
But! we need to be very careful in taking this limit.

Gaussian increments

Wiener Process

Define the increment $\Delta W_n = y_n \Delta t$ and select the ΔW_n from a normal distribution:

$$P(\Delta W) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(\Delta W)^2/2\sigma^2} \tag{45}$$

where the variance $\sigma^2 = \Delta t$.
This produces a difference equation

$$\Delta x(t_n) = \Delta W_n \tag{46}$$

We can solve this by simply stringing together a series of gaussian increments starting at $x(0) = 0$

$$x_n = x(n\Delta t) = \sum_{i=0}^{n-1} \Delta W_i \tag{47}$$

Gaussian increments

Wiener Process

The sum of 2 gaussian random variables is also a gaussian random variable so we have that the mean and variance after n steps is

$$\mu = \langle x_n \rangle = 0 \tag{48}$$
$$V(x_n) = \langle (x_n - \langle x_n \rangle) \rangle = n\Delta t \tag{49}$$

And so,

$$P(x_n) = \frac{1}{\sqrt{2\pi n \Delta t}} e^{-x_n^2/(2n\Delta t)} \tag{50}$$

Gaussian increments

Wiener Process

For the SDE, we need to take $\Delta t \to 0$. So, we define $\Delta t = T/N$ for some total time interval divided into N same-sized steps and then take $N \to \infty$.
Thus,

$$x(T) = \lim_{N\to\infty} \sum_{i=0}^{N-1} \Delta W_n = \int_0^T dW(t) = W(T) \tag{51}$$

This defines a *stochastic integral*

$$\int_0^T dW(t) = W(T) \tag{52}$$

as the limit of the sum of an infinite string of random numbers. $W(T)$ itself is also a gaussian random number.

Gaussian increments

Wiener Process

The mean, $\mu = 0$ as we expect.
For the variance, we don't even need to take the limit.

$$V(x(T)) = \sum_{i=0}^{N-1} V(\Delta W_i) = \sum_{i=0}^{N-1} \Delta t = N\frac{T}{N} = T \tag{53}$$

Thus,

$$P(W(T)) = P(x(T)) = P(x, T) = \frac{1}{\sqrt{2\pi T}} e^{-x^2/(2T)} \tag{54}$$

Generally we write

$$W(T) = \int_0^T dW \tag{55}$$

Stochastic Differential Eqs

We can now incorporate the dW into our ODE and write a general SDE as

$$dx = f(x,t)dt + g(x,t)dW \tag{56}$$

The variance of dW is always proportional to dt, so any constant of proportionality can be absorbed into the definition of $g(x,t)$. Thus,

$$P(dW) = \frac{1}{\sqrt{2\pi dt}} e^{-(dW)^2/(2dt)} \tag{57}$$

We note something interesting here. In order for the term in the exponent to be unitless, we have to conclude that $(dW)^2 \propto dt$ and that the constant of proportionality is exactly equal to 1.

Ito Calculus

Ito's Lemma

We just concluded that

$$(dW)^2 = dt$$

Thus,

$$\left\langle \int_0^T (dW)^2 \right\rangle = \int_0^T \langle (dW)^2 \rangle = \int_0^T dt = T \tag{58}$$

This means that the integral over $(dW)^2$ is not random at all, in fact we have a surprising result

$$(dW)^2 = dt \tag{59}$$

This is called *Ito's Lemma* or Ito's rule, and it's our most useful tool for integrating SDEs.

Ito Calculus

Ito's formula.

Ito's lemma allows us to replace any term that is second order in dW with dt. Let's see how this works.
Suppose we have a simple function $y = x^2$ and we want the differential relation between y and x
Usual Calculus:

$$
\begin{aligned}
dy &= y(t+dt) - y(t) = x(t+dt)^2 - x(t)^2 && (60)\\
&= (x+dx)^2 - x^2 && (61)\\
&= x^2 + 2xdx + (dx)^2 - x^2 && (62)\\
dy &= 2xdx && (63)
\end{aligned}
$$

where in the last step, we dropped the $(dx)^2$ in the limit that $dx \to 0$.

Ito Calculus

Ito's formula.

But, suppose that x obeys a SDE.

$$dx = f dt + g dW \tag{64}$$

Now we have

$$dy = 2x dx + (dx)^2 \tag{65}$$

$$= 2x(f dt + g dW) + g^2 (dW)^2 \tag{66}$$

$$= (2xf + g^2) dt + 2xg dW \tag{67}$$

(again, we can drop $(dt)^2$ in the limit of $dt \to 0$.)

Ito Calculus

Ito's formula.

For an arbitrary SDE, we can write

$$dy = \left(\frac{dy}{dx}\right) dx + \frac{1}{2}\left(\frac{d^2y}{dx^2}\right)(dx)^2 \tag{68}$$

and if y also carries an explicit time dependence

$$dy = \left(\frac{dy}{dx}\right) dx + \left(\frac{dy}{dt}\right) dt + \frac{1}{2}\left(\frac{d^2y}{dx^2}\right)(dx)^2 \tag{69}$$

We now use these equations in solving two useful SDEs.

The Ornstein-Uhlenbeck Equation

Additive Noise

Let's now consider how to integrate SDEs by looking at one of the more commonly encountered case in which the noise is added to some linear ODE.

$$dx = -\gamma x dt + g dW \tag{70}$$

The solution of deterministic part is $x_t = x_o e^{-\gamma t}$ so we make the substitution: $y = e^{\gamma t} x$

Approach 1: Write out the differential

$$\begin{aligned} dy &= y(x(t+dt), t+dt) - y(t) && (71) \\ &= y(x+dx, t+dt) - y(t) && (72) \\ &= (x+dx)e^{\gamma(t+dt)} - xe^{\gamma t} && (73) \\ &= xe^{\gamma t}\gamma dt + e^{\gamma t}(1+\gamma t)dx && (74) \\ &= \gamma y dt + e^{\gamma t} dx && (75) \end{aligned}$$

The Ornstein-Uhlenbeck Equation

Additive Noise

Approach 2: use Ito Formula

$$dy = \left(\frac{dy}{dx}\right) dx + \left(\frac{dy}{dt}\right) dt + \frac{1}{2}\left(\frac{d^2y}{dx^2}\right)(dx)^2 \tag{76}$$

Our substitution was $y = xe^{\gamma t}$.

$$dy = e^{\gamma t} dx + \gamma y dt \tag{77}$$

and we arrive at the relation in 1 step.

The Ornstein-Uhlenbeck Equation

Additive Noise

Using either approach, we have

$$\begin{aligned} dy &= \gamma y dx + e^{\gamma t} dx && (78) \\ &= \gamma y dx + e^{\gamma t}(-\gamma x dt + g dW) && (79) \\ &= g e^{\gamma t} dW && (80) \end{aligned}$$

Now we're good to go!

$$y(t) - y(0) = g \int_0^t e^{\gamma s} dW(s) \tag{81}$$

Substitute this back, $x = ye^{-\gamma t}$

$$x(t) = e^{-\gamma t} x(0) + g \int_0^t e^{-\gamma(t-s)} dW(s) \tag{82}$$

The Ornstein-Uhlenbeck Equation

Additive Noise

Finally, we can make both γ and g explicit functions of time and we arrive at the final solution

$$x(t) = e^{-\Gamma(t)}x(0) + \int_0^t e^{\Gamma(s)-\Gamma(t)}g(s)dW(s) \tag{83}$$

where

$$\Gamma(t) = \int_0^t \gamma(s)ds \tag{84}$$

Geometric Brownian motion

Multiplicative Noise

In this case, we consider a SDE in which the noise multiplies the variable x

$$dx = -\gamma x dt + g x dW \tag{85}$$

My preferred approach is to make the substition $y = \ln(x)$ and use Ito's formula, so let's do that.

$$dy = -(\gamma + g^2/2)dt + g dW \tag{86}$$

Thus,

$$y(t) - y(0) = -(\gamma + g^2/2)t + gW(t) \tag{87}$$

I.e.

$$x(t) = \exp(-(\gamma + g^2/2)t + gW(t))x(0) \tag{88}$$

Stochastic integration

The general integral

$$I(t) = \int_0^t f(s)dW(s) \tag{89}$$

where $f(t)$ is some function of t is a gaussian random variable (since dW is the Wiener process).
The variance, however, is deterministic

$$V(I(t)) = \int_0^t f^2(s)ds \tag{90}$$

where we've used Ito's lemma. Our only requirement is that $f^2(s)$ be integrable over $0 \leq s \leq t$

Brownian Motion

A Brief Historical review

- 1827: Robert Brown reports on the erratic motion of pollen grains in water.
- 1905: Einstein provides theoretical explanation
- 1908: Langevin provides an independent and alternative explanation
- 1940: Development of Ito calculus

Erratic motion[2] is due to fact that the liquid is composed of molecules that are in constant motion, randomly colliding with the pollen grain.

[2] be careful with spell check!

Brownian Motion

The physics

Assume that the random motion is due to rapidly fluctuating forces acting on the particle and there is a frictional force that's proportional to the momentum of the particle.

$$F_{frict} = -\gamma p = -\gamma m v \tag{91}$$

The damping rate, γ, is related to properties of the liquid and the sizs of the particle viz

$$\gamma = 6\pi\eta a/m \tag{92}$$

η= viscosity of liquid; a is the diameter of the (spherical) grain.

Brownian Motion

The physics

Newton's equations of motion then give:

$$m\frac{d^2x}{dt^2} = F_{frict} + F_{fluct} = -\gamma p + g\xi(t) \tag{93}$$

where $\xi(t)$ is the "white noise" process,

$$\langle \xi(t)\xi(t+\tau)\rangle = \delta(\tau) \tag{94}$$

Writing the EOM in terms of (x, p)

$$\frac{d}{dt}\begin{pmatrix} x \\ p \end{pmatrix} = \begin{pmatrix} 0 & 1/m \\ 0 & -\gamma \end{pmatrix}\begin{pmatrix} x \\ p \end{pmatrix} + \begin{pmatrix} 0 \\ \xi(t) \end{pmatrix} \tag{95}$$

Brownian Motion

The white noise term can be written in term of the Wiener process and we have the equations of motion written in differential form

$$\begin{pmatrix} dx \\ dp \end{pmatrix} = \begin{pmatrix} 0 & 1/m \\ 0 & -\gamma \end{pmatrix} \begin{pmatrix} x \\ p \end{pmatrix} dt + \begin{pmatrix} 0 \\ g \end{pmatrix} dW \tag{96}$$

We recognize our good old friend, the OU equation:

$$dp = -\gamma p dt + g dW \tag{97}$$

and we immediately arrive at

$$p(t) = e^{-\gamma t} p(0) + g \int_0^t e^{-\gamma(t-s)} dW(s) \tag{98}$$

Brownian Motion

We've seen how to evaluate stochastic integrals, so we can immediately write the equation for the variance of the momentum

$$V(p(t)) = g^2 \int_0^t e^{-2\gamma(t-s)} ds = \frac{g^2}{2\gamma}(1 - e^{-\gamma t}) \tag{99}$$

At long time, we should come to thermal equilibrium and have a steady-state solution

$$V_{ss}(p) = \lim_{t\to\infty} V(p(t)) = \frac{g^2}{2\gamma} = \langle p^2 \rangle \tag{100}$$

Furthermore, from equilibrium statistical mechanics, we know

$$\langle E \rangle = \frac{\langle p^2 \rangle}{2m} = \frac{1}{2} k_B T \tag{101}$$

for motion in 1D.

Brownian Motion

Thus we have (1D)

$$\frac{g^2}{24\pi\eta a} = \frac{1}{2}k_B T \tag{102}$$

i.e.

$$g = \sqrt{12\pi\eta a k_B T} \tag{103}$$

For 3D motion: $g = \sqrt{4\pi\eta a k_B T}$
Now, let's calculate the actual displacement of the grain.

Brownian Motion

We know $dx = dp/m$,

$$x(t) = \int_0^t \frac{p(s)}{m} ds \tag{104}$$

$$= \frac{p(0)}{m} \int_0^t e^{-\gamma s} ds + \frac{g}{m} \int_0^t \left[\int_0^s e^{-\gamma(s-s')} dW(s') \right] ds \tag{105}$$

We can swap the integration order (ord. calculus)

$$x(t) = \frac{p(0)}{m\gamma}(1 - e^{-\gamma t}) + \frac{g}{m} \int_0^t e^{\gamma s'} \left[\int_{s'}^s e^{-\gamma s} ds \right] dW(s') \tag{106}$$

$$= \frac{p(0)}{m\gamma}(1 - e^{-\gamma t}) + \frac{g}{m\gamma} \int_0^t (1 - e^{-\gamma s}) dW(s) \tag{107}$$

Brownian Motion

expectation values

We have the solution for a single trajectory, now we need to calculate the average position and its variance

$$\mu(t) = \langle x(t) \rangle = \left\langle \frac{p(0)}{m\gamma}(1 - e^{-\gamma t}) \right\rangle \tag{108}$$

The average over the stochastic part is 0 since it's a Wiener process. Similarly, we can assume that $\langle p(0) \rangle = 0$.

Brownian Motion

variance

The variance of the position is more interesting to evaluate

$$V(x(t)) = \frac{g^2}{(m\gamma)^2}\int_0^t (1-e^{-\gamma s})^2 ds \tag{109}$$

$$= \frac{g^2 t}{(m\gamma)^2} + \frac{g^2}{2m^2\gamma^3}\left(4e^{-\gamma t} - e^{-2\gamma t} - 3\right) \tag{110}$$

Langevin noted that the damping rate must be very fast, faster than any time-resolved experiment of his day. Thus, $\gamma t \gg 1$ and we can simplify this to read

$$V(x(t)) = \frac{g^2}{(m\gamma)^2}\int_0^t (1-e^{-\gamma s})^2 ds \tag{111}$$

$$= \frac{g^2 t}{(m\gamma)^2} - 3\frac{g^2}{2m^2\gamma^3} \approx \frac{g^2 t}{(m\gamma)^2} = \left(\frac{k_B T}{3\pi\eta a}\right) t \tag{112}$$

Brownian Motion

relation to the diffusion equation

we can write the diffusion equation for the particle density as

$$\frac{d}{dt}P(x,t) - D\nabla^2 P = 0 \tag{113}$$

which we can integrate subject to the condition that $P(x,0) = \delta(x)$. This is also known as the heat equation and the solution is the heat kernel

$$P(x,t) = \frac{1}{\sqrt{4\pi Dt}} \exp\left(\frac{-x^2}{4Dt}\right) \tag{114}$$

Upon taking the variance

$$V(x,t) = \int_{-\infty}^{+\infty} P(x,t)x^2 dx = 2Dt. \tag{115}$$

Brownian Motion

relation to the diffusion equation

Now we have an important connection:

$$D = \left(\frac{k_B T}{6 \pi \eta a} \right) \tag{116}$$

for 1D diffusion.

Stochastic theory of lineshape

In molecular spectroscopy, we generally are interested in the absorption or emission energies, since these tell us about the underlying Hamiltonian.
While we generally represent spectra in the frequency domain, we're really measuring is the polarization response of a sample.

$$P(t) = Tr[\mu\rho(t)] \tag{117}$$

where $\rho(t)$ is the density matrix and μ is the dipole operator. The details of this are elsewhere. [3]

[3] Everyone in the group should read either Mukamel's book or at least Peter Hamm's "Mukamel for Dummies" notes.

Stochastic theory of lineshapes

For linear spectra, we write the response as

$$S^{(1)}(t) = \frac{i}{\hbar}\langle \hat{\mu}(t)\hat{\mu}(0)\rho(-\infty)\rangle \tag{118}$$

where $\hat{\mu}(t)$ is the dipole operator written in the interaction representation

$$\hat{\mu}(t) = e^{+iH_o t}\hat{\mu}e^{-iH_o t} \tag{119}$$

Expanding this in terms of the eigenbasis

$$\mu_{01}(t) = \mu_-(t) = \mu e^{-i\omega_{10}t}|0\rangle\langle 1| \tag{120}$$

$$\mu_{10}(t) = \mu_+(t) = \mu e^{+i\omega_{10}t}|1\rangle\langle 0| \tag{121}$$

$$S(t) = \frac{i}{\hbar}\langle \mu_+(t)\mu_-(0)\rangle \tag{122}$$

$$= \frac{i}{\hbar}e^{-i\omega_{10}t}\mu^2 \tag{123}$$

Stochastic theory of lineshape

Generally, the transition frequency is not a static quantity. In reality, a molecule is in a condensed environment and the transition frequencies (and hence the energy gaps) are randomly modulated by external fluctuations.

$$\omega_{10}(t) = \bar{\omega} + \xi(t) \tag{124}$$

Consequently, we need to write the equations of motion for the dipole operators as

$$\mu_{\pm}(t) = e^{\pm i \int_0^t \omega_{10}(s) ds} \mu_{\pm}(0) \tag{125}$$

$$= e^{\pm i \bar{\omega}_{10} t} e^{\pm i \int_0^t \xi(s) ds} \tag{126}$$

So far, our only requirement is that $\langle \xi(t) \rangle = 0$

Stochastic theory of lineshape

The linear response is then given by

$$S(t) = \frac{i}{\hbar}\mu_{01}^2 e^{-i\omega_{10}t} \left\langle \exp\left(-i\int_0^t \xi(s)ds\right)\right\rangle \tag{127}$$

where we are left with a stochastic integral.

Relaxation time

Let $\xi(t)$ be a stochastic process with correlation

$$\langle \xi(t)\xi(t')\rangle = \Delta^2 e^{-\gamma_c|t-t'|} \tag{128}$$

Stochastic theory of lineshape

underlying OU process

Define $\xi(t)$ with an underlying Wiener process:

$$d\xi(t) = -\gamma_c \xi(t) dt + \sigma dW(t) \tag{129}$$

Autocorrelation:

$$\langle \xi(t)\xi(t')\rangle = \frac{\sigma^2}{2\gamma_c} e^{-\gamma_c |t-t'|} \tag{130}$$

Identify $\Delta^2 = \sigma^2 / 2\gamma_c$.
We see that the Kubo/Anderson model is based upon an OU equation for the energy gap fluctuations

Stochastic theory of lineshape

cumulant expansions

We now need to be able to do integrals of the form

$$I(t) = \left\langle \exp\left(-i\int_0^t \xi(s)ds\right)\right\rangle \quad (131)$$

Expand:

$$I(t) = 1 - i\int_0^t \langle \xi(s)\rangle ds - \frac{1}{2}\int_0^t d\tau \int_0^t d\tau' \langle \xi(\tau)\xi(\tau')\rangle + \cdots \quad (132)$$

Cumulant expansion

$$\left\langle \exp\left(-i\int_0^t \xi(s)ds\right)\right\rangle \equiv e^{-g(t)} = 1 - g(t) + \frac{1}{2}g^2(t) + \cdots \quad (133)$$

Stochastic theory of lineshape

cumulant expansions

Expand $g(t)$ in powers of $\xi(t)$

$$g(t) = g_1(t) + g_2(t) + \cdots \tag{134}$$

Put this back into the exponent

$$e^{-g(t)} = 1 - (g_1(t) + g_2(t) + \cdots) + \frac{1}{2}(g_1(t) + g_2(t) + \cdots)^2 + \cdots \tag{135}$$

For stationary processes, the linear term vanishes $g_1 = 0$, so we define

Lineshape function

$$g(t) = g_2(t) = \frac{1}{2}\int_0^t d\tau \int_0^t d\tau' \langle \xi(\tau)\xi(\tau')\rangle \tag{136}$$

Stochastic theory of lineshape

summary

Spectral response

$$A(\omega) = 2\Re \int_0^\infty e^{i\omega t} \langle \mu_{01}(t)\mu_{10}(0)\rangle dt \tag{137}$$

$$= 2|\mu_{01}|^2 \Re \int_0^t dt e^{i(\omega-\omega_{10})t} e^{-g(t)} \tag{138}$$

For stationary process $\langle \xi(t) \rangle = 0$:

$$g(t) = \frac{1}{2} \int_0^t \int_0^t d\tau d\tau' \langle \xi(\tau - \tau')\xi(0)\rangle \tag{139}$$

$$= \int_0^t d\tau \int_0^\tau d\tau' \langle \xi(\tau')\xi(0)\rangle \tag{140}$$

Stochastic theory of lineshape

Kubo Lineshape

$$g(t) = \frac{\Delta^2}{\gamma_c^2}\left[e^{-\gamma_c t} + \gamma_c t - 1\right] \quad (141)$$

Fast modulation limit: $\Delta/\gamma_c \ll 1$

In this limit, the exponential terms vanish rapidly and we have $g(t) \to t/T_2$ with $T_2^{-1} = \Gamma = (\Delta^2/\gamma_c)$ is the *homogeneous* line width.

Absorption spectrum (Lorentzian)

$$A(\omega) = \Re \int_0^\infty e^{i(\omega-\omega_{01})t} e^{-t/T_2} dt \quad (142)$$

$$= \frac{\Gamma}{\Gamma^2 + (\omega - \omega_{01})^2} \quad (143)$$

Stochastic theory of lineshape

Kubo Lineshape

Slow modulation limit: $\Delta/\gamma_c \gg 1$

$$g(t) = \frac{\Delta^2}{2} t^2 \tag{144}$$

This is obtained by expanding out the exponential terms.

Absorption spectrum: Gaussian

$$A(\omega) = \Re \int_0^\infty e^{i(\omega-\omega_{01})t} e^{-\frac{\Delta^2}{2}t^2} dt \tag{145}$$

$$= \sqrt{\frac{\pi}{2\Delta^2}} e^{-(\omega-\omega_{01})^2/2\Delta^2} \tag{146}$$

Stochastic theory of lineshape

Kubo Lineshape: summary

- Lineshape gives indication of the underlying background dynamics for a system being probed using spectroscopy.
- Lorentzian vs Gaussian lineshapes imply very different time-scales for the system/bath couping.
- Lorentzian: Motional narrowing
- Gaussian: inhomogeneous sampling of different local environments.
- What if the underlying dynamics we not OU, or non-stationary? What happens to the lineshape?

Financial option pricing

The Black-Scholes Equation

Implementation in Mathematica

ItoProcess[]

Wiener Process

connection to Fokker-Planck eq.

Consider the Fokker-Planck Equation

$$\partial_t p(x,t) = \frac{1}{2}\nabla^2 p(x,t) \tag{147}$$

where we set the diffusion coefficient to unity. We assume at time $t = 0$ that $p(x, 0) = \delta(x)$ localized at the origin.
To solve, we define a characteristic function

$$\phi(k,t) = \int dx e^{ikx} p(x,t) \tag{148}$$

and note that

$$\partial_t \phi = -\frac{k^2}{2}\phi \tag{149}$$

which we can integrate

$$\phi(k,t) = e^{-k^2 t/2} \tag{150}$$

Wiener Process

connection to Fokker-Planck eq.

inverting the FT:

$$p(x,t) = \frac{1}{\sqrt{2\pi t}} e^{-x^2/2t} \tag{151}$$

which is a Gaussian $W(x)$ with

$$\langle W \rangle = 0 \tag{152}$$

$$\langle W^2 \rangle = t \tag{153}$$