University of Washington
Department of Chemistry
Chemistry 553
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Lecture 12: Wiener Processes
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A. Solution of Smoluchowski Equations: Initial Value Green's Functions

- Last time we derived the Fokker-Planck equation:

$$\frac{\partial W}{\partial t} = L_{FP} W = \left[-\frac{\partial}{\partial x} D^{(1)} + \frac{\partial^2}{\partial x^2} D^{(2)} \right] W \tag{12.1}$$

  where L_{FP} is the Fokker-Planck operator, the drift coefficient $D^{(1)} = \frac{\langle \Delta x \rangle}{\Delta t}$ and the diffusion coefficient is $D^{(2)} = \frac{\langle \Delta x^2 \rangle}{2\Delta t}$.
- The drift and diffusion coefficients are obtained from Langevin theory. For a steady state Langevin equation

$$M\frac{dv}{dt} = 0 = -\zeta v + F(t) - \frac{dU}{dx} \tag{12.2}$$

  the solution is

$$\langle v \rangle = \frac{\langle \Delta x \rangle}{\Delta t} = -\frac{1}{\zeta}\frac{dU}{dx} = -BU'(x) \tag{12.3}$$

- Assuming the Brownian particle executes very small jumps relative to the scale of $U'(x)$ then $D^{(2)} = \frac{\langle \Delta x^2 \rangle}{2\Delta t} = D = Bk_B T$
- A process with a vanishing drift coefficient (i.e. U(x)=0), and a constant diffusion coefficient yields equation (12.4) and is called a Wiener Process

$$\frac{\partial W(x,t)}{\partial t} = BkT\frac{\partial^2 W(x,t)}{\partial x^2} \tag{12.4}$$

  with the initial condition: $P(x|x_0,0) = \delta(x - x_0)$.
- We had said that the solution to this problem is the conditional probability $P(x|x_0,t)$. Conditional probabilities belong to a class of functions called Green's functions. Green's functions appear in the field of ordinary and partial differential equations. A conditional probability which is the solution to the initial value problem in (12.1) is called an initial value Green's function.
- An initial value Green's function has the following property. Suppose we have a diffusion equation of the form (12.1) but with a more general initial condition $W(x,0) = f(x)$. If $P(x|x_0,t)$ solves (12.1) with the delta function initial condition, the solution to the more general initial condition is

$$W(x,t)=\int_{-\infty}^{+\infty}P\left(x\middle|x_0,t\right)f(x_0)\,dx_0 \tag{12.5}$$

B. Delta Function Initial Conditions.

- To solve (12.1) define the Fourier transform (FT) of W(x,t)

$$U(s,t)=FT\left(W(x,t)\right)=\int_{-\infty}^{+\infty}W(x,t)e^{isx}dx \tag{12.6}$$

- Recall the general relationship

$$FT\left(\frac{\partial^n W(x,t)}{\partial x^n}\right)=(-is)^n U(s,t) \tag{12.7}$$

- Next take the FT of equation (12.1), using (12.3) and (12.4) the result is

$$\frac{\partial U(s,t)}{\partial t}=-s^2 DU(s,t) \tag{12.8}$$

- The solution is:

$$U(s,t)=U(s,0)e^{-Ds^2t} \tag{12.9}$$

- We need to determine U(s,0). According to equation (14.6)

$$U(s,0)=\int_{-\infty}^{+\infty}P\left(x\middle|x_0,0\right)e^{isx}dx=\int_{-\infty}^{+\infty}\delta(x-x_0)e^{isx}dx=e^{isx_0}$$

(12.10)

- Now we take the inverse Fourier transform of the expression in (12.9):

$$P\left(x\middle|x_0,t\right)=\frac{1}{2\pi}\int_{-\infty}^{+\infty}U(s,t)e^{-isx}ds=\frac{1}{2\pi}\int_{-\infty}^{+\infty}e^{-s^2Dt}e^{isx_0}\,e^{-isx}ds$$

$$=\frac{1}{2\pi}\int_{-\infty}^{+\infty}e^{-s^2Dt}e^{is(x_0-x)}\,ds=\frac{1}{\pi}\int_{0}^{+\infty}e^{-s^2Dt}\cos\left[s(x_0-x)\right]ds=\frac{1}{\sqrt{4\pi Dt}}e^{-(x-x_0)^2/4Dt}$$

(12.11)

where we used the standard integral expression

$$\int_0^{\infty}dxe^{-ax^2}\cos bx\;=\frac{1}{2}\sqrt{\frac{\pi}{a}}e^{-b^2/4a} \tag{12.12}$$

- If we have t_0 nonzero but the process still stationary then…

$$P\left(x\middle|x_0,t-t_0\right)=\frac{1}{\sqrt{4\pi D(t-t_0)}}e^{-(x-x_0)^2/4D(t-t_0)} \tag{12.13}$$