University of Washington
Department of Chemistry
Chemistry 553
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Lecture 10: C-K Equation and the Fokker Planck Equation
04/18/11
Text Reading: McQ 20.2, Chandra. Ch. 2.4

A. The Fokker-Planck Equation (FPE)

- Master equations are extremely general differential equations for calculating time-dependent system probabilities.
- We can obtain a particular form of the master equation that can address all kinds of random processes, i.e. between momentum states, coordinates, or both. Brownian motion can be quantified in the presence of external fields.
- This modification of the master Equation is called the Fokker Planck Equation (FPE). The FPE is the fundamental equation used to derive probability distribution functions for Brownian motion problems.
- The FPE is a type of master equation and as such, can be obtained directly from the Chapman-Kolmogorov (CK) equation

$$P_2\left(x_2,t_2\middle|x_0,t_0\right)=\int P_3\left(x_2,t_2\middle|x_1,t_1;x_0,t_0\right)P\left(x_1,t_1\middle|x_0,t_0\right)dx_1 \tag{10.1}$$

- As we mentioned in the last lecture, for a markov process the C-K equation becomes

$$P_2\left(x_2,t_2\middle|x_0,t_0\right)=\int P_2\left(x_2,t_2\middle|x_1,t_1\right)P\left(x_1,t_1\middle|x_0,t_0\right)dx_1 \tag{10.2}$$

- In lecture 8 we showed how equation 10.2 yields the master equation

$$\frac{\partial P\left(l\middle|l_0;t\right)}{\partial t}=\int_{-\infty}^{+\infty}\left[w_{j\to l}P\left(j\middle|l_0;t\right)-w_{l\to j}P\left(l\middle|l_0;t\right)\right]dj \tag{10.3}$$

- Here we will use the simple case of a Brownian movement from a given physical condition (i.e. a given velocity or position) x_0 to x . This transition occurs in a short time Δt so we assume the change is by a small amount Δx . We assume that starting from x_0, the particle jumps in a time t to x-Δx. Then in a very short time Δt, the particle jumps from x-Δx to x.

$$P_2\left(x\middle|x_0,t+\Delta t\right)=\int P_2\left(x\middle|x-\Delta x,\Delta t\right)P_2\left(x-\Delta x\middle|x_0,t\right)d\left(\Delta x\right) \tag{10.4}$$

- Now we expand the lhs of (10.4) as a Taylor series around Δt=0…

$$P_2\left(x,t+\Delta t\middle|x_0\right)\approx P_2\left(x,t\middle|x_0\right)+\left(\frac{\partial P_2}{\partial t}\right)_{\Delta t=0}\left(t+\Delta t-t\right)+\ldots=P_2\left(x,t\middle|x_0\right)+\left(\frac{\partial P_2}{\partial t}\right)_{\Delta t=0}\Delta t+\ldots$$

(10.5)

- Note we can now write (10.4) as;

$$\Delta t \left.\frac{\partial P}{\partial t}\right|_{\Delta t=0} = -P_2\left(x|x_0,t\right) + \int P_2\left(x|x-\Delta x,\Delta t\right)P_2\left(x-\Delta x|x_0,t\right)d\left(\Delta x\right)$$

$$= -\int P_2\left(x|x_0,t\right)P_2\left(x-\Delta x|x,\Delta t\right)d\left(\Delta x\right) + \int P_2\left(x|x-\Delta x,\Delta t\right)P_2\left(x-\Delta x|x_0,t\right)d\left(\Delta x\right)$$

(10.6)

where the second line can be written because

- $$\int P_2\left(x|x-\Delta x,\Delta t\right)d\left(\Delta x\right) = 1 \qquad (10.7)$$

- Note (10.6) has the form of a master equation where $P_2\left(x-\Delta x|x,\Delta t\right) = \Delta t w_{x\to x-\Delta x}$ and $P_2\left(x|x-\Delta x,\Delta t\right) = \Delta t w_{x-\Delta x\to x}$
- Now to expand the integrand in the rhs of (10.6) around Δx=0 we change notation a little:

$$P_2\left(x|x-\Delta x,\Delta t\right)P_2\left(x-\Delta x|x_0,t\right) \xrightarrow{z=x-\Delta x} P_2\left(z+\Delta x|z,\Delta t\right)P_2\left(z|x_0,t\right) \qquad (10.8)$$

- Then we expand (10.8) around Δx=0

$$P_2\left(x|x-\Delta x,\Delta t\right)P_2\left(x-\Delta x|x_0,t\right) = P_2\left(z+\Delta x|z,\Delta t\right)P_2\left(z|x_0,t\right)$$

- $$= \sum_{n=0}^{\infty}\frac{\left(-\right)^n}{n!}\left(\Delta x\right)^n\frac{\partial^n}{\partial x^n}P_2\left(x+\Delta x|x,\Delta t\right)P_2\left(x|x_0,t\right) \qquad (10.9)$$

- Substitute this expansion into (10.6)…

$$\Delta t \left.\frac{\partial P}{\partial t}\right|_{\Delta t=0} = -P_2\left(x|x_0,t\right) + \int P_2\left(x|x-\Delta x,\Delta t\right)P_2\left(x-\Delta x|x_0,t\right)d\left(\Delta x\right)$$

$$= -P_2\left(x|x_0,t\right) + \int\sum_{n=0}^{\infty}\frac{\left(-\right)^n}{n!}\left(\Delta x\right)^n\frac{\partial^n}{\partial x^n}P_2\left(x+\Delta x|x,\Delta t\right)P_2\left(x|x_0,t\right)d\left(\Delta x\right)$$

(10.10)

$$= -P_2\left(x|x_0,t\right) + \sum_{n=0}^{\infty}\frac{\left(-\right)^n}{n!}\frac{\partial^n}{\partial x^n}\left[\int\left(\Delta x\right)^n P_2\left(x+\Delta x|x,\Delta t\right)d\left(\Delta x\right)\right]P_2\left(x|x_0,t\right)$$

$$= -P_2\left(x|x_0,t\right) + \sum_{n=0}^{\infty}\frac{\left(-\right)^n}{n!}\frac{\partial^n}{\partial x^n}\left[\left\langle\left(\Delta x\right)^n\right\rangle P_2\left(x|x_0,t\right)\right]$$

where $\left\langle\left(\Delta x\right)^n\right\rangle = \int\left(\Delta x\right)^n P_2\left(x+\Delta x|x,\Delta t\right)d\left(\Delta x\right)$ (10.11)

- We can write out the first three terms from the Taylor expansion:

- $$\Delta t \left.\frac{\partial P_2\left(x|x_0,t\right)}{\partial t}\right|_{\Delta t=0} = -P_2\left(x|x_0,t\right) + \sum_{n=0}^{\infty}\frac{(-)^n}{n!}\frac{\partial^n}{\partial x^n}\left[\left\langle(\Delta x)^n\right\rangle P_2\left(x|x_0,t\right)\right]$$

$$= -P_2\left(x|x_0,t\right) + P_2\left(x|x_0,t\right) - \frac{\partial}{\partial x}\left[\left\langle(\Delta x)\right\rangle P_2\left(x|x_0,t\right)\right] + \frac{1}{2}\frac{\partial^2}{\partial x^2}\left[\left\langle(\Delta x)^2\right\rangle P_2\left(x|x_0,t\right)\right]$$

$$\therefore \frac{\partial P_2\left(x|x_0,t\right)}{\partial t} = -\frac{\partial}{\partial x}\left[\frac{\langle\Delta x\rangle}{\Delta t}P_2\left(x|x_0,t\right)\right] + \frac{1}{2}\frac{\partial^2}{\partial x^2}\left[\frac{\left\langle\Delta x^2\right\rangle}{\Delta t}P_2\left(x|x_0,t\right)\right]$$

(10.12)

- Equation (10.12) is the Fokker-Planck equation (FPE) , and can also be validly written in terms of absolute probabilities . with initial condition $W(x,0)=\delta(x)$

$$\frac{\partial W(x,t)}{\partial t} = -\frac{\partial}{\partial x}\left\{\frac{\langle\Delta x\rangle}{\Delta t}W(x,t)\right\} + \frac{1}{2}\frac{\partial^2}{\partial x^2}\left\{\frac{\left\langle\Delta x^2\right\rangle}{\Delta t}W(x,t)\right\} \qquad (10.13)$$

- The variable x can refer to coordinates or momenta. But whether it is a coordinate or a momentum, x is in fact a vector. So if we expand the derivatives wrt x to include this fact we get

$$\frac{\partial W(x,t)}{\partial t} = -\sum_i\frac{\partial}{\partial x_i}\left\{\frac{\langle\Delta x_i\rangle}{\Delta t}W(x,t)\right\} + \frac{1}{2}\sum_{i,j}\frac{\partial^2}{\partial x_i\partial x_j}\left\{\frac{\left\langle\Delta x_i\Delta x_j\right\rangle}{\Delta t}W(x,t)\right\} \qquad (10.14)$$

- If we assume the components of x average independently then $\left\langle\Delta x_i\Delta x_j\right\rangle=0$ if $i\neq j$. Then (10.14) becomes:
- $$\frac{\partial W(x,t)}{\partial t} = -\sum_i\frac{\partial}{\partial x_i}\left\{\frac{\langle\Delta x_i\rangle}{\Delta t}W(x,t)\right\} + \frac{1}{2}\sum_i\frac{\partial^2}{\partial x_i^2}\left\{\frac{\left\langle\Delta x_i^2\right\rangle}{\Delta t}W(x,t)\right\} \qquad (10.15)$$
- It is also possible to write this FPE in terms of conditional probabilities:

$$\frac{\partial P\left(x_1|x,t\right)}{\partial t} = -\sum_i\frac{\partial}{\partial x_i}\left\{\frac{\langle\Delta x_i\rangle}{\Delta t}P\left(x_1|x,t\right)\right\} + \frac{1}{2}\sum_i\frac{\partial^2}{\partial x_i^2}\left\{\frac{\left\langle\Delta x_i^2\right\rangle}{\Delta t}P\left(x_1|x,t\right)\right\} \qquad (10.16)$$

- Equations (10.15) and (10.16) are alternative versions of the FPE.