University of Washington
Department of Chemistry
Chemistry 553
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Lecture 11: C-K Equation and the Fokker Planck Equation

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Text Reading: McQ 20.2, Chandra. Ch. 2.4

A. The Fokker-Planck Equation (FPE): Drift and Diffusion

- In lecture 10 we derived the FPE

$$\frac{\partial W(x,t)}{\partial t} = -\frac{\partial}{\partial x}\left\{\frac{\langle \Delta x\rangle}{\Delta t}W(x,t)\right\} + \frac{1}{2}\frac{\partial^2}{\partial x^2}\left\{\frac{\langle \Delta x^2\rangle}{\Delta t}W(x,t)\right\} \tag{11.1}$$

- Given a delta function initial condition $W(x,0) = \delta(x - x_0)$, the solution to the equation is the Green's function or conditional probability $P(x|x_0,t)$.
- The two stochastic average terms are evaluated in the limit $\Delta t \to 0$ and are often designated $D^{(1)} = \underset{\Delta t\to 0}{Lim}\frac{\langle \Delta x\rangle}{\Delta t}$ and $D^{(2)} = \underset{\Delta t\to 0}{Lim}\frac{\langle \Delta x^2\rangle}{2\Delta t}$ so that (11.1) is shown as

$$\frac{\partial P(x_1|x,t)}{\partial t} = -\frac{\partial}{\partial x}\left\{D^{(1)}P(x_1|x,t)\right\} + \frac{\partial^2}{\partial x^2}\left\{D^{(2)}P(x_1|x,t)\right\} \tag{11.2}$$

- $D^{(1)}$ is called the drift term and $D^{(2)}$ is called the diffusion term . These terms must be evaluated using a theory of stochastic variables, usually Langevin theory.
- 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

$$\frac{\partial P(x_1|x,t)}{\partial t} = -\sum_i \frac{\partial}{\partial x_i}\left\{\frac{\langle \Delta x_i\rangle}{\Delta t}P(x_1|x,t)\right\} + \frac{1}{2}\sum_i \frac{\partial^2}{\partial x_i^2}\left\{\frac{\langle \Delta x_i^2\rangle}{\Delta t}P(x_1|x,t)\right\} \tag{11.3}$$

  - To obtain (11.3) we assume the components of x average independently then $\langle \Delta x_i \Delta x_j\rangle = 0$ if $i \neq j$. Equation (11.3) can also be rendered as

$$\frac{\partial P(x_1|x,t)}{\partial t} = -\nabla_x \bullet \left\{D^{(1)}(x)P(x_1|x,t)\right\} + \nabla_x\nabla_x : \left\{D^{(2)}(x)P(x_1|x,t)\right\} \tag{11.4}$$

- The FPE is shown as a differential equation in the conditional probability. As shown in the homework, the FPE can also be expressed in terms of the absolute probability $W_1(x,t)$ accompanied by an initial condition;

$$\frac{\partial W_1(x,t)}{\partial t} = -\nabla_x \bullet \left\{D^{(1)}(x)W_1(x,t)\right\} + \nabla_x\nabla_x : \left\{D^{(2)}(x)W_1(x,t)\right\} \tag{11.5}$$

where $W_1\left(x,0\right)=\delta\left(x-x_1\right)$. It is common practice to drop the subscript 1 for the absolute probability.

- A more general form for the FPE in phase space can be derived in a manner similar to the method shown in the last lecture and found in McQ 20.2. Assume:

$$
\begin{aligned}
&P\left(r_1,u_1\left|r,u,t+\Delta t\right.\right)=\iint P\left(r_1,u_1\left|r-\Delta r,u-\Delta u,t\right.\right)P\left(\left|r-\Delta r,u-\Delta u\right|r,u,\Delta t\right)d\left(\Delta r\right)d\left(\Delta u\right)\\
&=\iint P\left(r_1,u_1\left|r-\Delta r,u-\Delta u,t\right.\right)\Psi\left(\left|r-\Delta r,u-\Delta u\right|\Delta r,\Delta u,\Delta t\right)d\left(\Delta r\right)d\left(\Delta u\right)\\
&=\int P\left(r_1,u_1\left|r-u\Delta t,u-\Delta u,t\right.\right)\Psi\left(\left|r-u\Delta t,u-\Delta u\right|u\Delta t,\Delta u,\Delta t\right)d\left(\Delta u\right)
\end{aligned}
\tag{11.6}
$$

where the last line in (11.6) is obtained because Δr=uΔt.

- Then expand the lhs around Δt=0 and the rhs around Δr=0 (i.e. around Δt=0) and around Δu=0. This yields:

$$\frac{\partial W}{\partial t}+u\frac{\partial W}{\partial r}=-\frac{\partial}{\partial u}\left\{D^{(1)}W\right\}+\frac{\partial^2}{\partial u^2}\left\{D^{(2)}W\right\} \tag{11.7}$$

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B. Calculating the Averages $D^{(1)}$ and $D^{(2)}$ in Velocity Space

- (11.7) is a general form of the FPE. If the FPE is to render behavior characteristic of Brownian motion, the averages $\left\langle \Delta x_i\right\rangle$ and $\left\langle \Delta x_i^2\right\rangle$ must be evaluated by independent means…often assuming values predicted by Langevin theory or the Einstein-Smoluchowski theory of Brownian motion.
- Assume the Brownian variable x is velocity v. For simplicity assume one dimensional motion. Then the FPE has the form

$$\frac{\partial W}{\partial t}=-\frac{\partial}{\partial v}\left\{D^{(1)}W\right\}+\frac{\partial^2}{\partial v^2}\left\{D^{(2)}W\right\} \tag{11.8}$$

where $W\left(u,0\right)=\delta\left(u-u_0\right)$. Note that absolute probabilities are used in (11.6) with a delta function initial condition.

- We require first an expressions for $D^{(1)}=\lim\limits_{\Delta t\to 0}\frac{\left\langle \Delta v\right\rangle}{\Delta t}$ and for $D^{(2)}=\lim\limits_{\Delta t\to 0}\frac{\left\langle \Delta v^2\right\rangle}{2\Delta t}$. To do this we use the equations of Langevin theory:

$$v=\frac{dx}{dt};\quad \frac{dv}{dt}=-\frac{v}{\tau}+A\left(t\right);\quad K\left(s\right)=\left\langle A\left(0\right)A\left(s\right)\right\rangle=\frac{\left\langle F\left(0\right)F\left(s\right)\right\rangle}{M^2}=\frac{2k_BT}{M^2B}\delta\left(s\right) \tag{11.9}$$

we obtain $\left\langle u\right\rangle=u_0e^{-t/\tau}$ because $\left\langle A\left(t\right)\right\rangle=0$. Then it is clear that

$$\left\langle \Delta u\right\rangle=\left\langle u-u_0\right\rangle=u_0\left(e^{-\Delta t/\tau}-1\right) \tag{11.10}$$

for an interval Δt. Then the drag term is

$$D^{(1)} = \underset{\Delta t\to 0}{Lim}\frac{\langle \Delta u\rangle}{\Delta t} = \underset{\Delta t\to 0}{Lim}\frac{u_0\left(e^{-\Delta t/\tau}-1\right)}{\Delta t} \approx \frac{u_0\left(1-\frac{\Delta t}{\tau}-1\right)}{\Delta t} \approx -\frac{u_0}{\tau} \qquad (11.11)$$

- The bilinear average can be similarly shown to equal (for 1D)

$$\left\langle \Delta u^2\right\rangle = \left\langle \left(u-u_0\right)^2\right\rangle = \frac{2kT}{\tau M}\Delta t \qquad (11.12)$$

so that the diffusion term is

$$D^{(2)} = \underset{\Delta t\to 0}{Lim}\frac{\left\langle \Delta u^2\right\rangle}{2\Delta t} = \frac{k_B T}{\tau M} \qquad (11.13)$$

- Using (1`.9) and (1`.11) the FPE in (13.6) becomes

$$\frac{\partial W}{\partial t} = -\frac{\partial}{\partial u}\left\{D^{(1)}W\right\} + \frac{\partial^2}{\partial u^2}\left\{D^{(2)}W\right\} = \frac{1}{\tau}\frac{\partial}{\partial u}\left\{uW\right\} + \frac{k_B T}{\tau M}\frac{\partial^2 W}{\partial u^2} \qquad (11.14)$$

- Equation (11.14) is the FPE for Brownian motion in velocity space. This equation is commonly used to treat the motion of molecules in dilute gases and to calculate transport properties for dilute gases.

B. Calculating the Averages $D^{(1)}$ and $D^{(2)}$ in Coordinate Space: the Smoluchowski Equation

- Consider the FPE in coordinate space. Assume one dimension x for simplicity:

$$\frac{\partial W}{\partial t} = -\frac{\partial}{\partial x}\left\{D^{(1)}W\right\} + \frac{\partial^2}{\partial x^2}\left\{D^{(2)}W\right\} \qquad (11.15)$$

- To evaluate the drift and diffusion terms we again require a set of Langevin equations:

$$\begin{aligned} &v = \frac{dx}{dt}; \quad \frac{dv}{dt} = -\frac{v}{\tau} + \frac{F(x)}{M} + A(t); \\ &K(s) = \left\langle A(0)A(s)\right\rangle = \frac{2k_B T}{\tau M}\delta(s)\ldots(1D\,\text{case}) \end{aligned} \qquad (11.16)$$

where F(x) is an external, deterministic force. To not confuse F(x) with the stochastic force F(t) we can express F(x) in terms of a potential $F(x) = -\frac{dU(x)}{dx}$ and the second Langevin equation is modified slightly:

$$\frac{dv}{dt} = -\frac{v}{\tau} + \frac{F(x)}{M} + A(t) = -\frac{v}{\tau} - \frac{1}{M}\frac{dU(x)}{dx} + A(t) \qquad (11.17)$$

- To evaluate $D^{(1)}$ and $D^{(2)}$ we need to make the following assumptions:
    - The friction is large so that τ<t. This being the case $\frac{dv}{dt} \approx 0$
    - The particle executes its rms displacement within a region small compared to the gradient of the potential.
- Using assumption 1 the Langevin equation becomes

$$0 = -\frac{v}{\tau} - \frac{1}{M}\frac{dU(x)}{dx} + A(t) \Rightarrow v = -B\frac{dU(x)}{dx} + \tau A(t)$$

$$\therefore \langle x - x_0 \rangle = \langle \Delta x \rangle = \int_0^t \left[-B\frac{dU(x)}{dx} + \tau \langle A(t) \rangle \right] ds = -B\frac{dU(x)}{dx}\Delta t \qquad (11.18)$$

$$\therefore D^{(1)} = -B\frac{dU(x)}{dx}$$

- Using assumption 2 the mean squared displacement occurs free of the external force. Therefore

$$D^{(2)} = \frac{\langle \Delta x^2 \rangle}{2\Delta t} = \frac{2D\Delta t}{2\Delta t} = Bk_B T \qquad (11.19)$$

- With (11.18) and (11.19) equation (11.15) becomes

$$\frac{\partial W}{\partial t} = B\frac{\partial}{\partial x}\left\{ W\frac{dU}{dx} \right\} + Bk_B T\frac{\partial^2 W}{\partial x^2} \qquad (11.20)$$

- Equation (11.20) is the Smoluchowski equation (SE), which quantifies diffusion in an external potential. Note that if the external force is zero the SE equation reduces to

$$\frac{\partial W}{\partial t} = Bk_B T\frac{\partial^2 W}{\partial x^2} \qquad (11.21)$$

which is the equation for free diffusion.