# Soltuions to Problem Set 1b

Shilong Yang

Department of Chemistry, MIT

February 27, 2001

## 1 Intermediate Asymptotic perturbation for Skewness

For a general random walk with *iid* steps, the concentration $c(x,t)$ is given by the equation

$$\frac{\partial c}{\partial t} - D_2\frac{\partial^2 c}{\partial x^2} = -\mathcal{D}_3\frac{\partial^3 c}{\partial x^3}\tau^{\frac{1}{2}} + (\mathcal{D}_4\frac{\partial^4 c}{\partial x^4} - \frac{1}{2}\frac{\partial^2 c}{\partial t^2})\tau - \mathcal{D}_5\frac{\partial^5 c}{\partial x^5}\tau^{\frac{3}{2}} + \cdots \tag{1.1}$$

where $\mathcal{D}_n \equiv M_n/(n!\tau) = O(\tau^{n/2-1})$ as $\tau \to 0$ and $\mathcal{D}_2 = D_2 = D$ is the diffusion coefficient. Assuming there is no drift, i.e., $D_1 = 0$, which can always be reached by a change of variables, the "skewness" $\mathcal{D}_3 \neq 0$, the intermediate asymptotic equation for the correction at the order of $\tau^{1/2}$ is

$$\frac{\partial c}{\partial t} - D_2\frac{\partial^2 c}{\partial x^2} = -\mathcal{D}_3\frac{\partial^3 c}{\partial x^3}\tau^{\frac{1}{2}}. \tag{1.2}$$

From the discussion in class, we have the zeroth order solution for the equation,

$$c_0(x,t) = \frac{M_0}{\sqrt{2Dt}}\phi_0(\zeta), \tag{1.3}$$

where $M_0 = \int c(x,0)dx$ is the total mass, $\zeta = x/\sqrt{2Dt}$, and $\phi_0(\zeta) = e^{-\zeta^2/2}/\sqrt{2\pi}$ is the normal distribution. Define $\xi = \tau/t$ as the quantitiy to measure the discreteness of time, so at $O(\xi^0)$,

$$[\frac{\partial}{\partial t} - D\frac{\partial^2}{\partial x^2}]c(x,t) = 0, \tag{1.4}$$

therefore, $c_0(x,t) = M_0\phi_0(\zeta)/\sqrt{2Dt}$. At $O(\xi^{1/2})$,

$$[\frac{\partial}{\partial t} - D\frac{\partial^2}{\partial x^2}]c_{\frac{1}{2}}(x,t) = -\mathcal{D}_3\frac{\partial^3}{\partial x^3}c_0(x,t)\tau^{\frac{1}{2}}. \tag{1.5}$$

The $O(\xi^{1/2})$ correction term $c_{\frac{1}{2}}(x,t)$ can be written in the form that

$$c_{\frac{1}{2}}(x,t) = \xi^{\frac{1}{2}}c_0(x,t)f_{\frac{1}{2}}(\xi), \tag{1.6}$$

thus we have the equation that $f_{\frac{1}{2}}(\xi)$ must satisfy

$$[\frac{\partial}{\partial t} - D\frac{\partial^2}{\partial x^2}](\frac{f_{\frac{1}{2}}(\xi)}{\sqrt{t}}\frac{\phi_0(\zeta)}{\sqrt{2Dt}}) = -\mathcal{D}_3\frac{\partial^3}{\partial x^3}(\frac{\phi_0(\zeta)}{\sqrt{2Dt}}). \tag{1.7}$$

Direct evaluation of both side of Eq. (1.7) gives

$$\begin{aligned} RHS &= -\mathcal{D}_3\frac{\partial^3}{\partial x^3}(\frac{\phi_0(\zeta)}{\sqrt{2Dt}}) = -\frac{\mathcal{D}_3\phi_0(\zeta)}{(2Dt)^2}(3\zeta - \zeta^3), && (1.8)\\ LHS &= [\frac{\partial}{\partial t} - D\frac{\partial^2}{\partial x^2}](\frac{f_{\frac{1}{2}}(\xi)}{\sqrt{t}}\frac{\phi_0(\zeta)}{\sqrt{2Dt}}) = -\frac{\sqrt{2}D^{\frac{3}{2}}\phi_0(\zeta)}{(2Dt0^2}[f_{\frac{1}{2}}(\zeta) + f''_{\frac{1}{2}}(\zeta) - \zeta f'_{\frac{1}{2}}(\zeta)], && (1.9) \end{aligned}$$

where

$$\phi_0'(\zeta) = -\zeta\phi_0(\zeta), \quad \phi_0''(\zeta) = (\zeta^2 - 1)\phi_0(\zeta), \quad \phi_0'''(\zeta) = (3\zeta - \zeta^3)\phi_0(\zeta) \tag{1.10}$$

have been used to simplify the expressions. $RHS = LHS$ leads to

$$f_{\frac{1}{2}}(\zeta) + f''_{\frac{1}{2}}(\zeta) - \zeta f'_{\frac{1}{2}}(\zeta) = \frac{\mathcal{D}_3}{\sqrt{2}D^{\frac{3}{2}}}(3\zeta - \zeta^3). \tag{1.11}$$

To conserve the zeroth, first and second moments, $f_{\frac{1}{2}}(\zeta)$ has to satisfy

$$\begin{aligned} \int f_{\frac{1}{2}}(\zeta)\phi_0(\zeta)d\zeta &= 0 && (1.12)\\ \int \zeta f_{\frac{1}{2}}(\zeta)\phi_0(\zeta)d\zeta &= 0 && (1.13)\\ \int \zeta^2 f_{\frac{1}{2}}(\zeta)\phi_0(\zeta)d\zeta &= 0, && (1.14) \end{aligned}$$

therefore

$$f_{\frac{1}{2}}(\zeta) = \frac{\mathcal{D}_3}{\sqrt{2}D^{\frac{3}{2}}}\frac{\zeta^3 - 3\zeta}{2}. \tag{1.15}$$

If $\eta \equiv M_3/M_2^{3/2}$ represents the skewness,

$$\frac{\mathcal{D}_3}{\sqrt{2}D^{\frac{3}{2}}} = \frac{M_3/(3!\tau^{\frac{3}{2}})}{\sqrt{2}[M_2/(2!\tau)]^{\frac{3}{2}}} = \frac{\eta}{3} \tag{1.16}$$

The expression $f_{\frac{1}{2}}(\zeta)$can be written as

$$f_{\frac{1}{2}}(\zeta) = \frac{\eta}{3!}(\zeta^3 - 3\zeta). \tag{1.17}$$

The correction to the order of $\xi^{1/2}$ is

$$c(x,t) = \frac{M_0}{\sqrt{2Dt}}\phi_0(\zeta)[1 + \xi^{1/2}\frac{\eta}{3!}(\zeta^3 - 3\zeta)] \tag{1.18}$$

When both $\mathcal{D}_3$ and $\mathcal{D}_4$ are nonzero, the correction to the order of $\xi^1$ can be obtained in the same fashion. The equation to be solved is

$$\frac{\partial c}{\partial t} - D_2\frac{\partial^2 c}{\partial x^2} = -\mathcal{D}_3\frac{\partial^3 c}{\partial x^3}\tau^{\frac{1}{2}} + (\mathcal{D}_4\frac{\partial^4 c}{\partial x^4} - \frac{1}{2}\frac{\partial^2 c}{\partial t^2})\tau. \tag{1.19}$$

where $c(x,t)$ can be expanded as

$$\begin{aligned} c(x,t) &= c_0(x,t) + c_{\frac{1}{2}}(x,t) + c_1(x,t), && (1.20)\\ c_{\frac{1}{2}}(x,t) &= c_0(x,t)\xi^{\frac{1}{2}} f_{\frac{1}{2}}(\xi), && (1.21)\\ c_1(x,t) &= c_0(x,t)\xi f_1(\xi), && (1.22) \end{aligned}$$

which lead to

$$\begin{aligned} \text{at } O(\xi^0),\ [\frac{\partial}{\partial t} - D\frac{\partial^2}{\partial x^2}]c_0(x,t) &= 0, && (1.23)\\ \text{at } O(\xi^{\frac{1}{2}}),\ [\frac{\partial}{\partial t} - D\frac{\partial^2}{\partial x^2}]c_{\frac{1}{2}}(x,t) &= -\mathcal{D}_3\frac{\partial^3}{\partial x^3}c_0(x,t)\tau^{\frac{1}{2}}, && (1.24)\\ \text{at } O(\xi^1),\ [\frac{\partial}{\partial t} - D\frac{\partial^2}{\partial x^2}]c_1(x,t) &= -\mathcal{D}_3\frac{\partial^3}{\partial x^3}c_{\frac{1}{2}}(x,t)\tau^{\frac{1}{2}} \\ &\quad +(\mathcal{D}_4\frac{\partial^4 c}{\partial x^4} - \frac{1}{2}\frac{\partial^2}{\partial t^2})c_0(x,t)\tau. && (1.25) \end{aligned}$$

It is trivial that $c_0(x,t)$ and $c_{\frac{1}{2}}(x,t)$ are given by Eq. (1.3) and (1.18), respectively. Similarly from the equation of $c_1(x,t)$, we obtain

$$\begin{aligned} RHS &= \frac{\kappa}{12}\frac{2D^2\phi_0(\zeta)}{(2Dt)^{\frac{5}{2}}}(3-6\zeta^2+\zeta^4) - 2(\frac{\eta}{3!})^2\frac{2D^2\phi_0(\zeta)}{(2Dt)^{\frac{5}{2}}}(-\zeta^6+15\zeta^4-45\zeta^2+15) && (1.26)\\ LHS &= -\frac{2D^2\phi_0(\zeta)}{(2Dt)^{\frac{5}{2}}}(2f_1+f_1''-\zeta f_1'). && (1.27) \end{aligned}$$

Thus $f_1(\zeta)$ is given by

$$2f_1 + f_1'' - \zeta f_1' = -\frac{\kappa}{12}(3-6\zeta^2+\zeta^4) + 2(\frac{\eta}{3!})^2(-\zeta^6+15\zeta^4-45\zeta^2+15) \tag{1.28}$$

Similarly $f_1(\zeta)$ conserves the zeroth, first, second, and third moments, since the correction due to $\mathcal{D}_4$ only already conserves these moments, all the rest work is to find a correction term due to the skewness that conserves all these moments. Using the same argument and compare the coefficients of the polynomial, we get

$$f_1(\zeta) = \frac{\kappa}{4!}(\zeta^4-6\zeta^2+3) + \frac{1}{2}(\frac{\eta}{3!})^2(\zeta^6-15\zeta^4+45\zeta^2-15). \tag{1.29}$$

For a simple asymmetric walk, $p_\tau(y) = p\delta(y-a)+q\delta(y+a)$, where $q = 1-p$, and $0 < p < 1$. So the moments of the transition probability function are

$$\begin{aligned} M_1 &= \int y[p\delta(y-a)+q\delta(y+a)]dy = (p-q)a\\ M_2 &= \int y^2[p\delta(y-a)+q\delta(y+a)]dy = a^2\\ M_3 &= \int y^3[p\delta(y-a)+q\delta(y+a)]dy = (p-q)a^3\\ M_4 &= \int y^4[p\delta(y-a)+q\delta(y+a)]dy = a^4. && (1.30) \end{aligned}$$

In order to eliminate the drift term, we define a new reference frame moving along with the drift. Thus in this frame, $z = y - (p-q)a$, the new transition probability is also redefined as

$$p_\tau(z) = p\delta(z - 2qa) + q\delta(z + 2pa). \tag{1.31}$$

The corresponding moments are changed to

$$\begin{aligned} M_1 &= 0 \\ M_2 &= 4pqa^2 \\ M_3 &= -8pq(p-q)a^3 \\ M_4 &= 16pq(1-3pq)a^4 \end{aligned} \tag{1.32}$$

In the new frame, $D_1 = M_1/\tau = 0$, $D_2 = M_2/(2\tau) = 2pqa^2/\tau$, $D_3 = M_3/(3!\tau) = -4pq(p-q)a^3/(3\tau)$, and $D_4 = M_4/(4!\tau) = 2pq(1-3pq)a^4/(3\tau)$. The skewness parameter define in part (a) is given as

$$\eta = \frac{M_3}{M_2^{3/2}} = -\frac{p-q}{\sqrt{pq}}. \tag{1.33}$$

The intermediate asymptotic approximation to the order of $(\tau/t)^{1/2}$ gives the equation

$$\frac{\partial c(z,t)}{\partial t} - D\frac{\partial^2 c(z,t)}{\partial z^2} = -\mathcal{D}_3 \frac{\partial^3 c(z,t)}{\partial z^3}\tau^{1/2}, \tag{1.34}$$

where $\mathcal{D}_3 = D_3/\tau^{1/2} = -4pq(p-q)a^3/(3\tau^{1/2})$, and $D = D_2 = 2pqa^2/\tau$. From our conclusion in part (a), we know that the intermediate asymptotic PDF to the order $(\tau/t)^{1/2} = n^{-1/2}$ is

$$\begin{aligned} c(z,t) &= c_0(z,t)[1 + (\frac{\tau}{t})^{1/2}\frac{\eta}{3!}(\zeta^3 - 3\zeta)], \\ c_0(z,t) &= \frac{1}{\sqrt{2Dt}}\phi_0(\zeta) \\ \phi_0(\zeta) &= \frac{1}{\sqrt{2\pi}}e^{-\frac{\zeta^2}{2}}, \quad \zeta = \frac{z}{\sqrt{2Dt}}. \end{aligned} \tag{1.35}$$

Transform back to the original coordinate system of $(x,t)$, we have

$$\begin{aligned} c(x,t) &= \frac{1}{\sqrt{8\pi pqna^2}}\phi_0(\frac{x-(p-q)na}{\sqrt{4pqna^2}}) \\ &\quad \{1 - \frac{1}{\sqrt{n}}\frac{p-q}{6\sqrt{pq}}[(\frac{x-(p-q)na}{\sqrt{4pqna^2}})^3 - 3(\frac{x-(p-q)na}{\sqrt{4pqna^2}})]\}. \end{aligned} \tag{1.36}$$

where $n = t/\tau$ is the number walk steps.

## 2 Self-Similar Solution to DLE

In the precious problem set 1a, we discussed the diffusion limited electrodeposition (DLE). In that problem, due to the lack of a natural length scale, a self-similar solution is possible.

Define the dimensionless group as

$$\theta = \frac{c - c_0}{c_0}, \quad \eta = \frac{Dt}{l^2}, \quad \phi = \frac{x}{l}, \tag{2.37}$$

where $l$ is a length scale to be defined. The original diffusion equation

$$\begin{aligned}
\frac{\partial c}{\partial t} &= D\frac{\partial^2 c}{\partial x^2}, \\
c(x,0) &= c_0, \\
-D\frac{\partial}{\partial x}c(0,t) &= J, \\
c(\infty,t) &= c_0
\end{aligned} \tag{2.38}$$

can be transformed to

$$\begin{aligned}
\frac{\partial \theta}{\partial \eta} &= \frac{\partial^2 \theta}{\partial \phi^2}, \\
c(\phi,0) &= 0, \\
-\frac{\partial}{\partial phi}c(0,\eta) &= \frac{Jl}{Dc_0}, \\
c(\infty,\eta) &= 0.
\end{aligned} \tag{2.39}$$

If we define

$$\zeta = \frac{\phi}{2\sqrt{\eta}}, \quad \theta = M_0 2\sqrt{\eta} f(\zeta), \tag{2.40}$$

where $M_0$ is a constant to be defined. The form we choose here is specific because we would like all the boundary conditions without any dependence on $\eta$.

$$\begin{aligned}
\frac{\partial \theta}{\partial \eta} &= M_0\frac{2\sqrt{\eta}}{2\eta}[f(\zeta) - \zeta f'(\zeta)], \\
\frac{\partial \theta}{\partial \phi} &= M_0 f'(\zeta) \\
\frac{\partial^2 \theta}{\partial \phi^2} &= M_0\frac{2\sqrt{\eta}}{4\eta} f''(\zeta).
\end{aligned} \tag{2.41}$$

So the ODE for the scaling function $f(\zeta)$ is

$$\begin{aligned}
f(\zeta) - \zeta f(\zeta) - \frac{1}{2}f''(\zeta) &= 0 \\
f(\infty) = 0, \quad M_0 f'(0) &= -\frac{Jl}{Dc_0}
\end{aligned} \tag{2.42}$$

It is easy to check that

$$f(\zeta) = \frac{1}{\sqrt{\pi}}e^{-\zeta^2} - \zeta \mathrm{Erfc}(\zeta) \tag{2.43}$$

is the right function satisfy the ODE, where $\mathrm{Erfc}(\zeta)$ is the complementary error function defined as

$$\mathrm{Erfc}(z) = 1 - \frac{2}{\sqrt{\pi}} \int_0^z e^{-t^2} dt. \tag{2.44}$$

Also from

$$f'(\zeta) = -\mathrm{Erfc}(\zeta), \tag{2.45}$$

we can get $M_0 = (Jl)/(Dc_0)$, the arbitrary length scale here can be taken as 1, thus

$$\theta(\phi, \eta) = \frac{J}{Dc_0} 2\sqrt{\eta} f(\frac{\phi}{2\sqrt{\eta}}). \tag{2.46}$$

Therefore the complete solution of the original PDE is

$$c(x,t) = c_0 + \frac{J}{D}[2\sqrt{\frac{Dt}{\pi}} e^{-\frac{x^2}{4Dt}} - x\mathrm{Erfc}(\frac{x}{2\sqrt{Dt}})], \tag{2.47}$$

exactly the same as the previous result obtained from direct Laplace transform.