Soltuions to Problem Set 3

Gwang-Soo Kim

Department of Chemical Engineering, MIT

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Problem 3

For generality, let's rederive diffusion equation from discrete equation. Let's consider the probability of walker being at (x,z) @ $t = t + \tau$. Providing that walker goes up one lattice, δ in the z direction and it can go either left or right with one lattice, δ in the x direction, there are only two possile sites (x-δ,z-δ) and (x+δ, z-$delta$) that can take up (x,z) at $t + \tau$. Then, the following relation holds:

$$P(x, z, t + \tau) = 1/2\, P(x - \delta, z - \delta, t) + 1/2\, P(x + \delta, z - \delta, t)$$

, where P is probability that the hole is located at (x,z) at time t.

Using Taylor expansion, LHS is expressed as follows:

$$P(x, z, t + \tau) = P(x, z, t) + \left(\frac{d}{dt}P(t)\right)\tau + O(\tau^2)$$

As for RHS,

$$P(x - \delta, z - \delta, t) = P(x, z, t) - \frac{\partial P}{\partial x}\delta - \frac{\partial P}{\partial z}\delta + \frac{1}{2}\frac{\partial^2 P}{\partial x^2}\delta^2 + \frac{1}{2}\frac{\partial^2 P}{\partial z^2}\delta^2 + \frac{\partial^2 P}{\partial x \partial z}\delta^2 + O(\delta^3)$$

$$P(x + \delta, z - \delta, t) = P(x, z, t) + \frac{\partial P}{\partial x}\delta - \frac{\partial P}{\partial z}\delta + \frac{1}{2}\frac{\partial^2 P}{\partial x^2}\delta^2 + \frac{1}{2}\frac{\partial^2 P}{\partial z^2}\delta^2 - \frac{\partial^2 P}{\partial x \partial z}\delta^2 + O(\delta^3)$$

Now, equating LHS and RHS gives,

$$P(x, z, t) + \frac{\partial}{\partial t}P\tau + O(\tau^2) = P(x, z, t) + \frac{\partial P}{\partial z}\delta + \frac{1}{2}\frac{\partial^2 P}{\partial x^2}\delta^2 + \frac{1}{2}\frac{\partial^2 P}{\partial z^2}\delta^2 + O(\delta^3)$$

Therefore,

$$\left(\frac{\partial P(x, z, t)}{\partial t}\right)\tau = -\left(\frac{\partial P(x, z, t)}{\partial z}\right)\delta + \frac{1}{2}\left(\frac{\partial^2 P(x, z, t)}{\partial x^2} + \frac{\partial^2 P(x, z, t)}{\partial z^2}\right)\delta^2$$

Or,

$$\frac{\partial P(x,z,t)}{\partial t} = -\left(\frac{\partial P(x,z,t)}{\partial z}\right) v + \left(\frac{\partial^2 P(x,z,t)}{\partial x^2} + \frac{\partial^2 P(x,z,t)}{\partial z^2}\right) D$$

$$= -\nabla \cdot \left(-D\left(\frac{\partial P(x,z,t)}{\partial x}\right) e_x + \left(Pv - D\frac{\partial P(x,z,t)}{\partial z}\right) e_z\right)$$

, where

$$v = \frac{\delta}{\tau}, D = \frac{\delta^2}{2\tau}$$

Note that the mass flux vector is defined as follows:

$$F_x = -D\frac{\partial P}{\partial x}, F_z = Pv - D\frac{\partial P}{\partial z}$$

Since in z direction, convection is dominant over diffusion, we can simplify the above equation as follows:

$$\frac{\partial P}{\partial \tau} = -\frac{\partial P}{\partial z} v + D\frac{\partial^2 P}{\partial x^2}$$

$$F_x = -D\frac{\partial P}{\partial x}, F_z = Pv$$

(a) Steady state mode:

$$0 = -\frac{\partial P}{\partial z} v + D\frac{\partial^2 P}{\partial x^2}$$

B.C.:

$$P(0,0) = \delta(x)\delta(z)$$

$$\int_{-\infty}^{\infty} P(x,z)dx = 1: \text{ normalization and conservation of mass}$$

Let's define similarity variable

$$\xi = \frac{x}{\sqrt{2zD/v}}$$

From normalization condition, characteristic concentration P_c is given as follows :

$$P_c[=]1/L = \frac{1}{\sqrt{2zD/v}}$$

So, similarity ansatz is,

$$P = \frac{1}{\sqrt{2zD/v}}\Phi(\xi)$$

Using this ansatz, the derivatives are reformulated with respect to ξ.

$$\frac{\partial P}{\partial z} = \frac{1}{\sqrt{2zD/v}}\left(\frac{1}{-2z}\right)\Phi + \frac{1}{\sqrt{2zD/v}}\Phi' \frac{x}{\sqrt{2zD/v}} \cdot \frac{1}{-2z}$$

$$= \frac{1}{\sqrt{2zD/v}} \cdot \frac{1}{-2z}(\Phi + \xi\Phi')$$

$$\frac{\partial P}{\partial x} = \frac{1}{\sqrt{2zD/v}} \cdot \Phi' \cdot \frac{1}{\sqrt{2zD/v}}$$

$$\frac{\partial^2 P}{\partial x^2} = \frac{1}{\sqrt{2zD/v}} \cdot \Phi' \cdot \frac{1}{2zD/v}$$

Therefore,

$$0 = \frac{1}{\sqrt{2zD/v}} \cdot \frac{1}{-2z}(\Phi + \xi\Phi') + D \cdot \frac{1}{\sqrt{2zD/v}} \cdot \Phi' \cdot \frac{1}{2zD/v}$$

After canceling out terms, the resulting similarity equation is given as follows:

$$0 = \Phi'' + \xi\Phi' + \Phi$$

B.C.:

$$\int_{-\infty}^{\infty} \Phi(\xi) d\xi = 1$$

Since both governing equation and boundary condition is formulated with new set of variable ξ, our similarity ansatz works. The general solution for the above differential equation is,

$$\Phi = e^{-\xi^2/2}\left(C_1 + C_2 erf\left(\frac{i\xi}{\sqrt{2}}\right)\right)$$

Among these, only one of them is meaningful, and using normalization,

$$\Phi(\xi) = \frac{e^{-\xi^2/2}}{\sqrt{2\pi}}$$

,which can be shown to be only solution. Therefore,

$$P(x,z) = \frac{1}{\sqrt{2zD/v}} \cdot \frac{e^{-\xi^2/2}}{\sqrt{2\pi}}$$

, where

$$\xi = \frac{x}{\sqrt{2zD/v}}$$

Using this, mass flux can be obtained.

$$F_x = -D\frac{\partial P}{\partial x} = D \cdot \frac{1}{\sqrt{2zD/v}} \cdot \frac{e^{-\xi^2/2}}{\sqrt{2\pi}} \cdot \xi \frac{1}{\sqrt{2zD/v}}$$

$$= P \cdot D \cdot \frac{x}{2zD/v}$$

$$= \frac{vx}{2z} \cdot P$$

$$Fz = Pv = v\frac{1}{\sqrt{2zD/v}} \cdot \frac{e^{-\xi^2/2}}{\sqrt{2\pi}}$$

One can show that the ratio of these vector components is simply:

$$\frac{F_z}{F_x} = \frac{2z}{x}$$

If we look for the region where there are total 95 percent of total mass, we can simply search the region where $-2 \leq \xi \leq 2$.

Therefore,

$$-2 \leq \frac{x}{\sqrt{2zD/v}} \leq 2$$

Or,

$$\frac{x^2}{8D/v} \leq z$$

This region is parabolar.

One main qualitative difference between flow is the fact that the flow of granular object does not have nonlinear convection term as fluid does. Thus, the nonlinear effects, such as recirculation do not occur in the flow of granular substances.

(b) Parabolar container
Only difference with (a) is the boundary continion,

$$\int_{-x_c}^{x_c} P(x,z)dx = 1$$

,where

$$x_c = \pm - \sqrt{\frac{z}{k}}$$

Also, P is symmetric at x = 0.

Using the same similarity equation,

$$\Phi'' + \xi\Phi' + \Phi = 0$$

and similarity ansatz,

$$P(x,z) = \frac{1}{\sqrt{2zD/v}} \cdot \Phi(\xi),\ \xi = \frac{x}{\sqrt{2zD/v}}$$

Using this, B.C.'s tured into following forms:

$$\int_{-\xi_c}^{\xi_c} \Phi(\xi)d\xi = 1$$

and

$$\Phi'(0) = 0$$

Using general solution of the above differential equation introduced in (a), one can show that symmetry boundary condition makes C_2 zero. Also, C_1 can be obtained from normalization condition as follows:

$$\int_{-x_c}^{x_c} P(x,z)dx = 1$$

$$= C_1 \int_{-\xi_c}^{\xi_c} \exp(-\xi^2/2)d\xi = 1$$

Therefore,

$$C_1 = \frac{1}{\int_{-\xi_c}^{\xi_c} \exp(-\xi^2/2)d\xi}$$

Substituting C_1 and C_2, the resultant concentration profile is as follows:

$$P(x,z) = \frac{1}{\sqrt{2zD/v}} \cdot \frac{exp(-\xi^2/2)}{\int_{-\xi_c}^{\xi_c} \exp(-\xi^2/2)d\xi}$$

,where

$$\xi_c = \sqrt{\frac{v}{2kD}}$$

Velocity field is

$$F_x = -D\frac{\partial P}{\partial x} = \frac{vx}{2z} \cdot P$$

$$F_z = vP$$

,where P is given above.

For consistency, one can check whether no flux condition is satisfied at the parabolar wall. We can merely see whether $\vec{F} \cdot \vec{n}$ equals to zero. From above solution, flux vector is given as follows:

$$\vec{F} = vP\left(\frac{x}{2z}\vec{e}_x + \vec{e}_z\right)$$

Also, the normal vector at the boundary of container at arbitrary z is given follows:

$$\vec{n} = \nabla(z_c - kx_c^2) = -2kx_c\vec{e}_x + \vec{e}_z$$

$$= -\frac{2z_c}{x_c}\vec{e}_x + \vec{e}_z$$

Therefore, the inner product of these two vectors are as follows:

$$\vec{F} \cdot \vec{n} = vP\left(\frac{x_c}{2z_c}\vec{e}_x + \vec{e}_z\right) \cdot \left(-\frac{2z_c}{x_c}\vec{e}_x + \vec{e}_z\right)$$

$$= vP\left(\frac{x_c}{2z_c}\frac{-2z_c}{x_c} + 1\right) = vP\left(-1+1\right) = 0$$

As expected, there is no flux at the wall of container.

Problem 4

(a) Nonlinear Diffusion Approximation.

Why D_0 is replacedy by $D_0(1 - C/C_0)$?

Diffusion equation derived from Bernouilli's random walk assumes no interaction between different walkers. This is true in the dilute concentration limit, but in the higher concentration, the existance of other walkers affects the movement of walker of interest. Even though we may neglect any long range interaction or nearest neighbor interaction, at least excluded-volume interaction that specifies no single site can be occupied by different atoms should be included. Though the excluded volume scheme seems straightforward to implement in the context of discrete random walk simulation, continuum simulation is more tricky, since we need to devise "consitutive" equation to dictate the mobility of atoms as a function of bulk properties, such as concentration. Easiest and most intuitive idea is including heuristic term to the diffusion constant, so that diffusivity is decreasing as concentration increases and eventually go to zero when concentration becomes equal to bulk concentration. This can be formulated in the following way [1]:

$$D = D_0 \left(1 - \frac{C}{C_0}\right)$$

This relation is true in two extreme regime; when concentration is nearly zero, the diffusivity should be equal to single particle without any hinderance. In the extreme concentration regime, no particle can move, and thus the diffusivity vanishes. However, there is no guarantee that the behavior in the intermediate concentration regime should work also. This can be validated by comparing the concentration profile result with discrete random walk result, providing that the discrete random walk result is valid.

Existence of similarity solution

Using diffusivity of $D_0(1 - C/C_0)$, the time dependent mass balance equation is as follows.

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D_0\left(1 - \frac{C}{C_0}\right)\frac{\partial C}{\partial x}\right)$$

Let's define dimensionless variables

$$y = C/C_0$$

$$\xi = x/\sqrt{2D_0 t}$$

$$\Phi = y(\xi)$$

Then, equation can be normalized as follows:

$$\frac{\partial y}{\partial t} = \frac{\partial}{\partial x}\left(D_0\left(1 - y\right)\frac{\partial y}{\partial x}\right)$$

$$= D_0 \frac{\partial}{\partial x}\left(\frac{\partial y}{\partial x} - y\frac{\partial y}{\partial x}\right)$$

$$= D_0\left(\frac{\partial^2 y}{\partial x^2} - \left(\frac{\partial y}{\partial x}\right)^2 - y \cdot \frac{\partial y}{\partial x}\right)$$

$$= D_0\left((1 - y) \cdot \frac{\partial^2 y}{\partial x^2} - \left(\frac{\partial y}{\partial x}\right)^2\right)$$

Using ξ,

$$\frac{\partial y}{\partial t} = \Phi' \xi \left(-\frac{1}{2t} \right)$$

$$\frac{\partial y}{\partial x} = \Phi' \frac{1}{\sqrt{2D_0 t}}$$

$$\frac{\partial y}{\partial x} = \Phi' \frac{1}{2D_0 t}$$

Combining above equations, one can show following equation holds:

$$-\Phi' \xi = (1 - \Phi)\Phi'' - (\Phi')^2$$

I.C. and B.C.
(i) For desorption,

$$C(x, 0) = C_0 \rightarrow \Phi(\infty) = 1$$

$$C(0, t) = 0 \rightarrow \Phi(0) = 0$$

(ii) For sorption,

$$C(x, 0) = 0 \rightarrow \Phi(\infty) = 0$$

$$C(0, t) = C_0 \rightarrow \Phi(0) = 1$$

Since both governing equation and boundary/initial conditions can be formulated with our choice of similarity variable, the similarity ansatz works.

Sketch of concentration profile
The above sets of equation cannot be solved analytically, since the governing equation is nonlinear. But, we can guess the shape of the curve. For the desorption case, one can show that there can be some ξ_c, where Φ is "exactly" unity, so similarity equation turns into

$$\Phi'(\Phi' - \xi) = 0$$

Solution of this equation is

$$\Phi' = 0, \text{ or } \Phi \text{ is constant.}$$

$$\Phi' = \xi$$

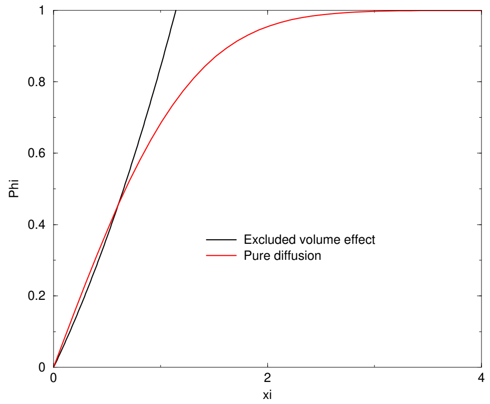

Figure 1: Comparison between pure diffusion and excluded volume effect in desorption phenomena. Note for discontinuous slope at the cusp.

The first solution corresponds to concentration outside of ξ_c. The second solution corresponds to the "moving" front. This condition can be used to locate the transition point, ξ_c. So, we can guess that the concentration increases and when it hits bulk concentration, it stays constant. For sorption case, we cannot apply the same logic, because there is no singlurity. We can just guess concentration would be just monotonically decreasing. For obtaining quantitative concentration profile, one could attemp to solve the above equation numerically. The above set of differential equation and boundary condition constitute of exactly determined systems of equation. The similarity equation is discretized using finite difference scheme. Newton-Rhapson method is used to solve resulting system of nonlinear equations. For sorption, only concentration need to be sought, whereas for desorption, not only the concentration at each node but also the location of transition point, ξ_c should be found. Concentration profiles of desorption and sorption from continuum simulation are shown in figures 1 and 2 respectively.

As can be seen in figure 1, there is sharp transition of concentration where slope is discontinuous. This transition point is $\xi_c = 1.1426924782$.

(b) Simulations

For the discrete simulation, rectangular lattice is used. Blind walker sampling method is used. Starting with filled lattice, for each time, $t = i\tau$, chances are given to all the atoms to pick a direction. If the move are acceptable, make a move; otherwise the chance is wasted. The following time scale is used.

$$\tau = \frac{\delta^2}{D_0}$$

When compared with the continuum solution, the similarity variable is defined as follows:

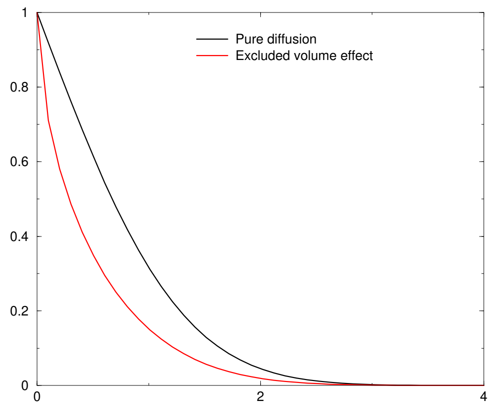

Figure 2: Comparison between pure diffusion and excluded volume effect in sorption phenomena.

$$\xi \equiv \frac{x}{\sqrt{2D_0 t}}$$

$$= \sqrt{2} \cdot \frac{j}{\sqrt{i}}$$

Figure 3 summarizes the comparison between discrete desorption simulation and continuum desorption simulation. It is evident in this simulation that the discrete solution is more close to pure diffusion case rather than excluded-volume case, and especially does not reproduce sharp transition point. Figure 4 is the comparison between dicrete sorption simulation and continuum desorption simulation.

A number of literatures suggested that $D = D_0(1 - C/C_0)$ relation should be really modified to $D = D_0(1 - C/C_0)f(C/C_0)$, where $f(C/C_0)$ accounts for strong tendency for a walker to go backward in high concentration regime which is illustrated in figure 5 [3, 4, 5]. According to this literature, the value of $f(C/C_0)$ is close to unity when concentration is very low, and is less than 1 when concentration approaches bulk concentration value. Another literature derived $f(C/C_0)$ and proposed following equation:

$$f(c) = \frac{1 + cos(\theta)}{1 + (2 - 3c)/(2 - c) \cdot cos(\theta)}$$

, where

$$\alpha \equiv cos(\theta)$$

and θ is average angle walker changes in two subsequent moves.

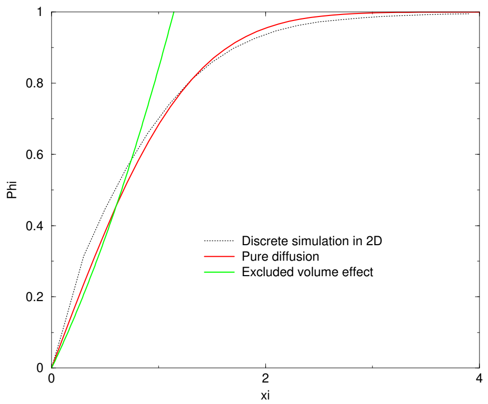

Figure 3: Comparison between discrete and continuum simulations for desorption.

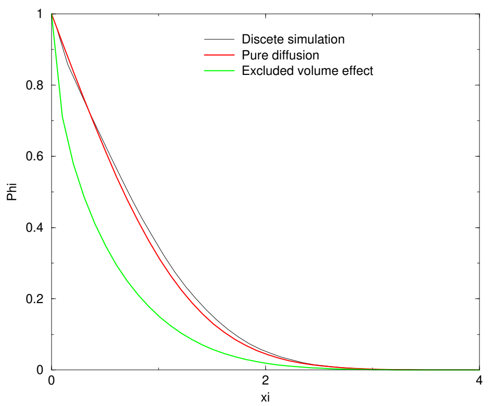

Figure 4: Comparison between discrete and continuum simulations for sorption.

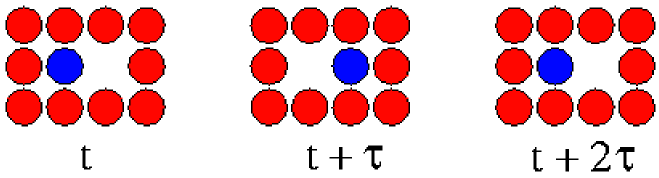

Figure 5: Schematic of back diffusion in dense concentration limit at subsequent time intervals.

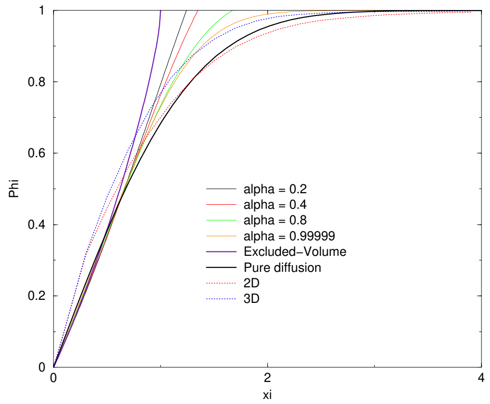

Figure 6: Effect of correlation factor in the concentration profile of desorption. As α value increases, the concentration profile approaches to pure diffusion case.

Using this formula, the continuum solution of desorption is recalculated. Results are shown in figure 6 with different α values. As can be seen, though there is a transition point, its value increases and in $\alpha \to 1$ regime, it approaches pure diffusion solution.

Though the addition of a correlation function $f(c)$ produces similar continuum solution to the atomistic solution, two results are not exactly the same with any α values. Main difference is higher concentration of discrete simulation at small concentration. Considering there is actually no difference between excluded volume and pure diffusion cases, it would be reasonable to argue that it is discerete simulation that is incorrect. This could be because the implementation of "blind walker" as a sampling scheme. Most rigorous way to handle this is using CTRW analysis, or equivalently using Kinetic Monte Carlo (KMC) scheme [2, 6]. In this scheme, only one feasible event are selected out of list of possible moves and time increment are calculated with following formula:

$$\tau_i = \frac{-ln(U)}{\Sigma n_i r_i}$$

, where U is uniform random variable [0, 1]. In our case, r_i is the same for all the possible moves, since no nearest neighbor interactions are considered. Since r_i should have a unit of t^{-1}, using diffusivity, it is chosen as follows:

$$r_i = \Gamma = \frac{\delta^2}{D_0}$$

Desorption problem is done over with this scheme and the comparison with other simulations is given in figure 7.

First, there definitely is difference between discrete simulations with blind walkers and KMC scheme. KMC scheme removes the discrepancy at low concentration level. However, the concentration profile from KMC scheme looks practically the same as the pure diffusion case.

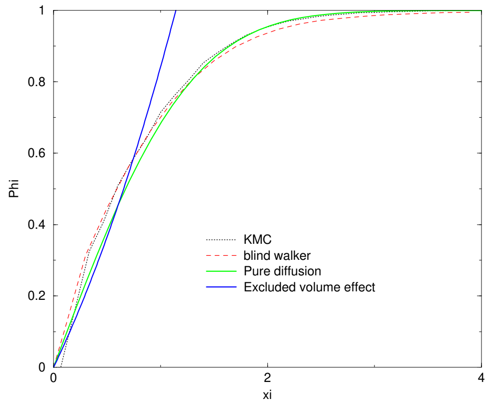

Figure 7: Comparison between KMC scheme and blind random walk.

References

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