# Excluded volume effect and its mean field approximanion: comparison of continuum and discrete simulation on desorption/sorption phenomena of lattice gas

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## 1 Introduction

Diffusion equation derived from Bernoulli'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 exact 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 as well. This can be validated by comparing the concentration profile result with discrete random walk result, providing that the discrete random walk result is valid. This report contains following contents. First, continuum equations for desorption/sorption phenomena is posed and numerical method is described to solve resulting nonlinear equation. Then, discrete random walk simulation is described. Finally, the results from continuum and discrete simulations are compared and some feasible modification are suggested.

# 2 Continuum equation

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 $\xi$,

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

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

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

Combining above equations, one can show following equation holds:

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

I.C. and B.C. (1) For desorption,

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

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

(2) For sorption,

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

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

From the equation, one can show that there can be some $\xi_c$, where $\Phi$ is "exactly" unity, so similarity equation turns into

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

Solution of this equation is

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

$$\Phi' = \xi$$

The first solution corresponds to concentration outside of $\xi_c$. The second solution corresponds to the "moving" front. This condition can be used to locate the transition point, $\xi_c$.

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, $\xi_c$ should be found.

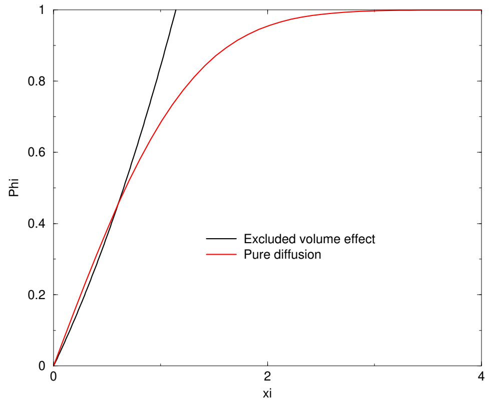


Figure 1: Comparison between pure diffusion and excluded volume effect in desorption phenomena. Note discontinuous slopes at the cusp.

# 3 Discrete simulation

For the discrete simulation, rectangular lattice is used. Blind walker sampling method is used. Starting with filled lattice, for each time, 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.

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

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

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

, where $t = \tau i$ and $x = \delta j$. Note here that the time increment, $\tau = \delta^2/(4D_0)$ is used to get the match with the continuum equation in the two dimensional simulation. The factor 4 in the denominator can be interpreted as maximum number of nearest neighbor.

# 4 Results

Concentration profiles of desorption and sorption from continuum simulation are shown in figures 1 and 2 respectively.

Figure 1 shows that there is sharp transition of concentration where slope is discontinuous. This transition point is $\xi_c = 1.1426924782$. For the discrete solution, the effect of domain

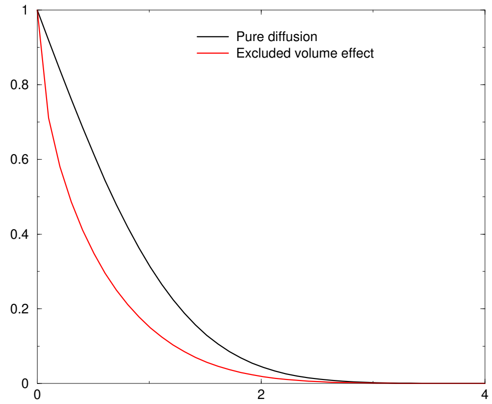


Figure 2: Comparison between pure diffusion and excluded volume effect in sorption phenomena.

size is checked. Figure 3 shows the result of desorption simulation in the different domain size. As can be seen, there are not much difference in the current sets of domain sizes. Figure 4 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.

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 6 [3, 5, 6]. 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 $\theta$ is an average angle walker changes in two subsequent moves.

Using this formula, the continuum solution of desorption is recalculated. Results are shown in figure 7 with different $\alpha$ 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 $\alpha$ values. Main

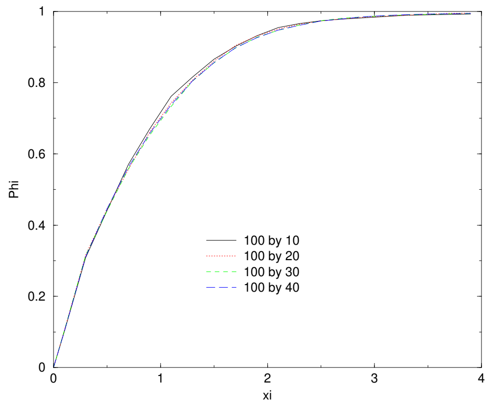


Figure 3: Effect of domain size in discrete simulation of desorption. There is no distinct dependency in vertical domain size

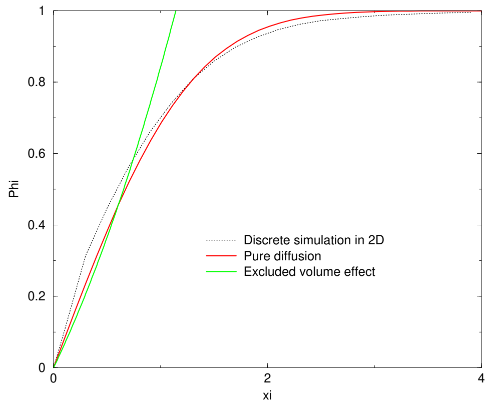


Figure 4: Comparison between discrete and continuum simulations for desorption.

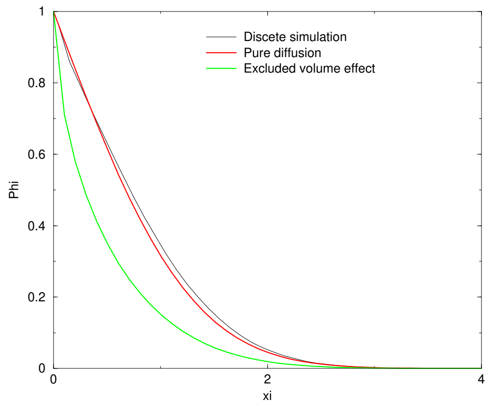


Figure 5: Comparison between discrete and continuum simulations for sorption.

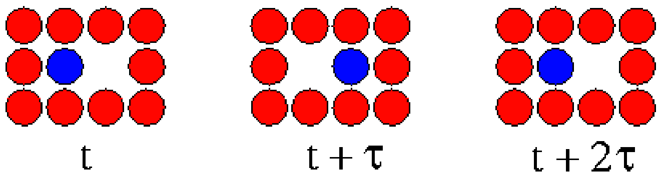


Figure 6: Schematic of back diffusion in dense concentration limit at subsequent time intervals.

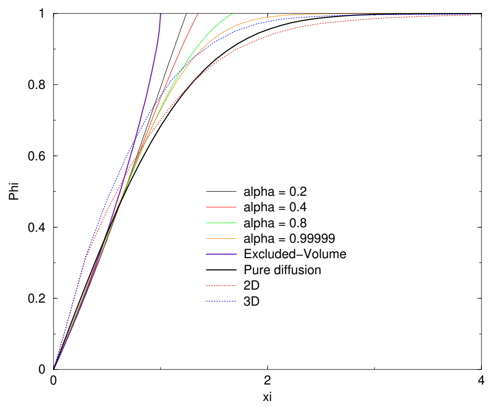


Figure 7: Effect of correlation factor in the concentration profile of desorption. As $\alpha$ value increases, the concentration profile approaches to pure diffusion case.

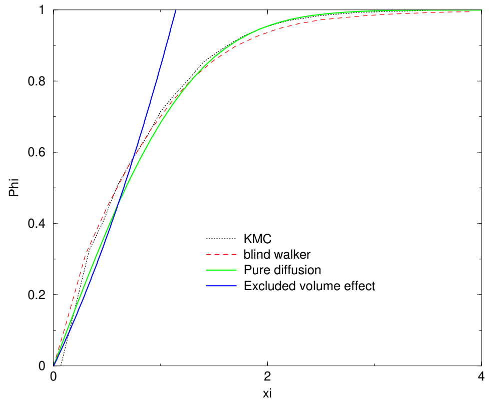


Figure 8: Comparison between KMC scheme and blind random walk.

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, 7]. 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 between 0 and 1. In our case when no short or long range interaction is included, $r_i$ 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 8.

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.

# 5 Discussion

Our result shows that discrete model does not show distinct effect of excluded volume effect. This fact is still unclear, but the main difference between the analysis in the literature and ours is that the other analysis is focused on tracking a single particle, whereas our analysis is on "averaging" partcile distribution. This can be interpreted that in the environment where the particles are indistinguishable, the effect of excluded volume does not manifest.

This means the mean field diffusivity model does not properly represent the diffusion process with the excluded voluem effect, at least in collective sense. Then, we could ask which phenomena can be explained by this formula. One thing author investigated is the effect of nearest neighbor interaction, which includes different diffusion barrier for different number of nearest neighbor. This is physically reasonable model when different number of nearest neighobor means different number of covalent bond or metallic bond to be broken. Assuming the diffusion probabilily is proportional to its diffusion rate, the following relation holds:

$$\text{Probabiliy} \propto exp\left(-\frac{nE_b}{RT}\right) \equiv \frac{1}{\alpha^n}$$

, where n is number of nearest neighbor and $E_b$ is a eneary for breaking a single bond. Figure 9 shows the disorption curves including this effect for different $\alpha$ values. As $\alpha$ increases, or equivalently bond energy increases, sharp transition between liquid and solid phases starts to form. But, still the narrow tail in high concentration regime is not removed even with very high $\alpha$ values. Though not tried in this study, if one want to have a discrete model which reproduces sharp transition interface, one could come up with a criteria to determine different phases and make movement of atoms significantly slower than liquid phase.

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. If one wishes to use a diffusivity relation in high concentration regime, and wants to include the effect of concentration, one could include the correlation factor discribed in the earlier section.

Then, what is the meaning of (1-c) factor in mean field approximation, if it does not shows any effect in discrete simulation and does not reproduce correct physics in continuum simulation? Though needed to be investigated further, the key to understand this factor would be understanding the moves in discrete particle. As mentioned in the earlier, the atom has always higher probability to move back to its previous location, mainly because holes are always there unless other atoms moves into it in between. On the contrary, the probability of atom move other sites are still proportional to the number of available sites, which can be represented as (1-c). Also, this chances are true only when other atoms occupies this sites before atom of our interests move in the sites. A reference illustrates this facts with their waiting time distribution analysis [4]. They showed the waiting time distribution at zero time limit for backward moves are the same regardless of the concentration of the

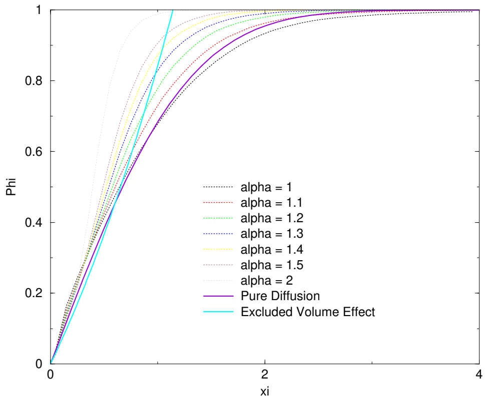


Figure 9: Effect of nearest neighbor interaction on the desorption concentration profile. Different $\alpha$ values indicate different interaction energy.

system, whereas waiting time distribution of other sites are scaled with (1-c) at zero time limit.

# 6 Conclusion

Continuum equation of desorption and sorption problems are solved with simple linearly varying diffusivity value with exact Newton-Rhapson method. Discrete random walker based on blind walkers produced result more closely to pure diffusion case and there is no sharp transition point of slope obtained. Correlation function multiplied to diffusivity relation relaxed sharp transition point and it produced concentration profile which looks more closely to discrete simulation result with one fudge factor $\alpha$.

Discrepancy of discrete simulation in the small concentration regime was fixed by implementing KMC scheme. However, now the concentration profile looks exactly the same as the pure diffusion result. This suggest that the discrete simulation scheme implemented in our simulation does not manifest excluded volume effect. This may be caused by the indistinguishable particle effect. Thus, tracking a trajectory of individual particle needs to be proceeded to observe manifesting excluded volume effect.

Still, the effect of computational domain size should be included and it would be interesting to extend this system to 1D or fractal dimension.

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