Solution of Smoluchowski Equation for Two Particle with Square Well Interaction

Mohammad Montazeri

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Abstract

Two particles, in absence of hydrodynamics interactions, are considered such a way to have interaction by a hard-core potential plus an potential hole of depth $-V_0$ and width of $\delta$. The Smoluchowski equation has solved for such a system in the center of mass coordinate. Also, the self diffusion coefficient for $N$ particle system interacting among square well potential up to the first order of concentration is calculated.

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1 Smoluchowski Equation

In absence of hydrodynamics interaction, for a two particle system interacting via the potential of $U$ and in the center of mass coordinates ($\vec{r} \equiv \vec{r}_1 - \vec{r}_2$), the
Smoluchowski equation reads [1, 2]:

$$\partial_t \rho(\vec{r}, t|\vec{r}_0) = L_s \rho(\vec{r}, t|\vec{r}_0)$$  \hspace{1cm} (1.1)

where, $L_s$ is the Smoluchowski operator:

$$L_s(\ldots) = 2D_0 \vec{\nabla} \cdot [\vec{\nabla}(\ldots) + \beta(\vec{\nabla}U(\vec{r}))(\ldots)]$$  \hspace{1cm} (1.2)

The formal solution to the equation 1.1 is:

$$\rho(\vec{r}, t|\vec{r}_0) = e^{L_s t} \rho(\vec{r}, 0|\vec{r}_0)$$  \hspace{1cm} (1.3)

We assume that the interaction between particles depend only on their distances and also consists of a hard-core potential and an attraction (repulsive) potential well of the form:

$$U(\vec{r}) \equiv U(r) = U_H + U_0(r) = U_H - V_0 \theta(\sigma - r)$$

$$= \begin{cases} 
\infty & , \quad 0 < r < d \\
-V_0 & , \quad d < r < \sigma \\
0 & , \quad \sigma < r 
\end{cases}$$  \hspace{1cm} (1.4)

where $d$ is diameter of particles and $\delta = \sigma - d > 0$ is width of the potential well and $V_0$ is its depth (see figure 1). Note that $V_0$ could be positive (attraction) as well as negative (repulsion). The initial condition could be consider as:

$$\rho(\vec{r}, 0|\vec{r}_0) = \delta(r - r_0) \theta(r - d)$$

$$= \frac{1}{r_0} \delta(r - r_0) \delta(\Omega - \Omega_0) \theta(r - d)$$  \hspace{1cm} (1.5)

where, in the las line we turn on the spherical coordinates $(r, \Omega)$ and the step function has added because of the effect of hard-core potential. The effect of hard-core potential is that two particles would not penetrate in each other at any time. We may take this property into account by a step function:

$$\rho(\vec{r}, t|\vec{r}_0) = \theta(r - d) \tilde{\rho}(r, \Omega, t|\vec{r}_0)$$  \hspace{1cm} (1.6)

where $\Omega$ is the solid angle. The initial condition correspond to $\tilde{\rho}$ reads:

$$\tilde{\rho}(r, \Omega, t|\vec{r}_0) = \frac{1}{r_0} \delta(r - r_0) \delta(\Omega - \Omega_0)$$  \hspace{1cm} (1.7)
Figure 1: Interaction potential: A hard-core interaction plus a square well.

2 Boundary Conditions

Rewriting the equation 1.1 and 1.2 in the spherical coordinates yields:

\[
\partial_t \rho = 2D_0 [\nabla^2 \rho + \beta \nabla \rho \cdot \nabla U + \beta \rho \nabla^2 U]
\]

\[
= 2D_0 \left[ \frac{1}{r^2} \partial_r (r^2 \partial_r \rho) - \frac{1}{r^2} \hat{L}^2 \rho + \beta \partial_r \rho \partial_r U + \frac{1}{r^2} \beta \rho \partial_r (r^2 \partial_r U) \right]
\]

(2.8)

where \( \hat{L} \) is the angular momentum operator. Hence:

\[
\partial_t \rho = \frac{2D_0}{r^2} \left[ \partial_r (r^2 \partial_r \rho) - \hat{L}^2 \rho + \beta r^2 \partial_r \rho \partial_r U + \beta \rho \partial_r (r^2 \partial_r U) \right]
\]

(2.9)

Replacing \( \rho \) by \( \theta(r - d) \rho \) yields:

\[
\theta(r - d) \partial_t \rho = \frac{2D_0}{r^2} \left[ \partial_r [r^2 \partial_r (\theta(r - d) \rho)] - \theta(r - d) \hat{L}^2 \rho \right]
\]
integrating of both sides of above equation in around the point \( r \) respectively. We may use of the property of the hard-core potential as [1]:

\[
\epsilon \to -\theta(r - d) + \delta(r - d) = -\beta \partial_r U_H \theta(r - d)
\]  

(2.11)

Proper use of above expression in the equation 2.10 yields:

\[
\theta(r - d) \partial_r \tilde{\rho} = \frac{2D_0}{r^2} \left\{ \partial_r \left[ r^2 \theta(r - d) \tilde{\rho} \right] - \theta(r - d) \tilde{L}^2 \tilde{\rho} + \beta \partial_r \left[ r^2 \theta(r - d) \tilde{\rho} \partial_r U_H [\tilde{\rho} \partial_r U_0] \right] \right\}
\]  

(2.10)

where \( U_H \) and \( U_0 \) correspond to the hard-core and the square well potential respectively.

Using the equation 1.4 we have:

\[
\partial_r U_0 = V_0 \delta(r - \sigma)
\]  

(2.13)

Hence, the equation 2.12 takes the form of:

\[
\theta(r - d) \partial_r \tilde{\rho} = 2D_0 \left\{ \theta(r - d) \left[ \partial_r^2 \tilde{\rho} + \frac{2}{r} \partial_r \tilde{\rho} - \frac{\tilde{L}^2}{r^2} \tilde{\rho} + \frac{2\beta V_0}{r} \delta(r - \sigma) \right] + \partial_r \tilde{\rho} \delta(r - d) + \beta \partial_r \left[ \theta(r - d) \tilde{\rho} \partial_r U_0 \right] \right\}
\]  

(2.14)

Above expression, suggest on discontinuity of derivative of pdf \( (\rho) \) at both point \( r = d, \sigma \) because of discontinuity of derivative of the potential at these points. By integrating of both sides of above equation in around the point \( r = d \) \( (\int_{d-\epsilon}^{d+\epsilon} dr, \) with \( \epsilon \to 0 \) we get:

\[
0 = 2D_0 \left[ \partial_r \tilde{\rho} \bigg|_d^{d+\epsilon} + \partial_r \tilde{\rho} \bigg|_{r=d} \right] \bigg|_{\epsilon \to 0}
\]  

(2.15)
where, we used the continuity of $\tilde{\rho}$ at $r = d$. Hence, the boundary condition around the point $r = d$ becomes:

$$\frac{\partial \tilde{\rho}(r, \Omega, t|\vec{r}_0)}{\partial r} |_{r\rightarrow d^+} = 0 \quad (2.16)$$

Which assert that particles could not have penetration in each other. This boundary condition is just what has used in [1, 2].

Turn back to the equation 2.14, and now take an integration of the both sides around the point $r = \sigma$ ($\int_{\sigma-\epsilon}^{\sigma+\epsilon} \text{dr}$, with $\epsilon \rightarrow 0$) we get:

$$0 = 2D_0[\partial_r \tilde{\rho}|_{\sigma+\epsilon}^{\sigma-\epsilon} + \frac{2\beta V_0}{r} \tilde{\rho}|_{r=\sigma}]|_{\epsilon \rightarrow 0} \quad (2.17)$$

or equivalently:

$$\left( \lim_{r \rightarrow \sigma^+} - \lim_{r \rightarrow \sigma^-} \right) \frac{\partial \tilde{\rho}(r, \Omega, t|\vec{r}_0)}{\partial r} = -\frac{2\beta V_0}{\sigma} \tilde{\rho}(\sigma, \Omega, t|\vec{r}_0) \quad (2.18)$$

which shows a discontinuity in derivative of $\rho$ at the barrier of attractive potential. Note that the magnitude of this discontinuity is proportional to length and depth of the potential and the temperature, such a way that as $\beta V_0$ tend to zero (which is equivalent to high temperature or weak interaction) or $\sigma$ tends to infinity the discontinuity would vanish, as what was desired. Note that temperature and potential depth appear as a product form $\beta V_0$, which assert that strength of effect of the potential (temperature) in the system is controlled by strength of temperature (potential). Also, at low temperatures (large $\beta$) or for strong potentials, the derivative of pdf decrease dramatically at $r = \sigma^+$, which assert that the probability of finding of particles decrease rapidly when passing the barrier of potential outside way.

In equation 2.14, for $r \neq d$ and $r \neq \sigma$, the Dirac delta functions could be neglected. Hence, the governing equation of the system correspond to the boundary conditions 2.16 and 2.18 reads:

$$\theta(r-d)\partial_r \tilde{\rho} = 2D_0\theta(r-d)[\partial_r^2 \tilde{\rho} + \frac{2}{r} \partial_r \tilde{\rho} - \frac{\hat{L}^2}{r^2} \tilde{\rho}] \quad (2.19)$$

or equivalently:

$$\partial_t \tilde{\rho}(r, \Omega, t|\vec{r}_0) = 2D_0(\partial_r^2 + \frac{2}{r} \partial_r - \frac{\hat{L}^2}{r^2}) \tilde{\rho}(r, \Omega, t|\vec{r}_0) \quad (2.20)$$

This equation together with the boundary conditions 2.16 and 2.18 and the initial condition 1.7, completely describe the system.

Note that in our case (just like [2] and [1]) the singular behavior of the gradient of the potential, make it possible to rewrite the Smoluchowski equation in a standard form of differential equation, classified in Bessel differential equations because of radial nature of the potential, in which the potential have contribution in the boundary conditions.
3 Solution to the Equation

Discontinuity of the gradient of the pdf at the point \( r = \sigma \) suggests on division of the problem into two regions in space. Region I: for \( d < r < \sigma \), and Region II for \( \sigma < r \rightarrow \infty \) (see figure 2). In each region, the equation 2.20 could be solved separately in a general form. However, dealing with the initial condition (equation 1.5) should be with caution: it may cause difference whether the particle initially be in the potential well \( (d < r_0 < \sigma) \) or outside of it \( (\sigma < r_0) \). In fact, we expect that time evolution of the system initially at either region I or region II \( (d \leq r_0 < \sigma \text{ or } \sigma < r_0) \) would be quite different.

Furthermore, for attractive interaction \( (V_0 > 0) \) when the system is initially bounded, the system time evolution may has transient(!!!) dependence on the temperature and depth of the potential, because particles need strong enough

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1Here, by transient we mean that depending on the \( \beta V_0 \), the system may or may not make a transition between some different physical regimes. For example, if the temperature be small enough and the particles form a bounded regime, they would not be able to form an unbounded system. In contrary, for large temperature, the particles make transition between bounded and unbounded regimes as the time pass.
of thermal fluctuations (depend on the depth of the potential) to have a significant diffusion of the particles toward outside of the potential well. And when the system initially be in the unbounded, the governor parameters of the time evolution are the width of the potential hole for short times and the temperature and depth of the potential for long time evolutions. That is, in the short time, diffusion of the particle toward inside of the potential hole are more significant for wider potential well. Other hand, escape of the particle from the potential hole in long time depends directly on the temperature and depth of the potential hole.

3.1 Particular Solution

The equation to be solved is:

\[ \partial_t \tilde{\rho}(r, \Omega, t|\vec{r}_0) = 2D_0 (\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{\hat{L}^2}{r^2}) \tilde{\rho}(r, \Omega, t|\vec{r}_0) \]  

(3.1)

We also assume the general form of the initial condition as:

\[ \tilde{\rho}(r, \Omega, t=0, |\vec{r}_0) = \delta(\vec{r} - \vec{r}_0) \]  

(3.2)

where, \( r_0 \) could be either inside of the potential hole (\( d < r_0 < \sigma \)) or outside of it (\( \sigma < r_0 \)). The particular solution of the equation (correspond to zero initial condition) could be evaluated in each region without specifying the initial condition (\( r_0 \)). However, to evaluation an explicit form of the complementary (hence the complete solution) solutions we should specify the initial condition (\( r_0 \)). In both cases we attack to the problem by separation of variables method. Consider the general form of the pdf as:

\[ \tilde{\rho}(r, \Omega, t|\vec{r}_0) = T(t) R(r|\vec{r}_0) \Theta(\Omega|\Omega_0) \]  

(3.3)

replacing in the equation 3.1 yields:

\[ R(r|r_0) \Theta(\Omega|\Omega_0) \frac{dT}{dt}(t) = 2D_0 T(t) \Theta(\Omega|\Omega_0) \left[ \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right] R(r|r_0) \]

\[ - \frac{2D_0}{r^2} T(t) R(r|r_0) \hat{L}^2 \Theta(\Omega|\Omega_0) \]  

(3.4)

or equivalently:

\[ \frac{1}{2D_0 T(t)} \frac{dT(t)}{dt} = \frac{1}{R(r|r_0)} \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) R(r|r_0) - \frac{1}{r^2 \Theta(\Omega|\Omega_0)} \hat{L}^2 \Theta(\Omega|\Omega_0) \]  

(3.5)

both side should be equal to a dimensionless number, namely \( \lambda \). Hence:

\[ \frac{1}{2D_0 T(t)} \frac{dT(t)}{dt} = \lambda \]  

(3.6)
which could be integrated trivially:

\[ T(t) = e^{2D_0 \lambda} \quad (3.7) \]

as the pdf should be finite when \( t \to 0 \), \( \lambda \) should have negative value, say \( \lambda = -q^2 \).

Hence, the time dependent part of the pdf should behave like:

\[ T(t) \sim e^{-2D_0 q^2 t} \quad (3.8) \]

returning this expression in the equation 3.5 yields:

\[-q^2 = \frac{1}{\Gamma_r(r|\bar{r}_0)} \left( \frac{d^2}{dr^2} + 2 \frac{d}{r} \right) R(t|r_0) - \frac{1}{r^2 \Theta(\Omega|\bar{\Omega}_0)} \hat{L}^2 \Theta(\Omega|\bar{\Omega}_0) \quad (3.9)\]

or equivalently:

\[ \frac{r^2}{R(r|r_0)} \left( \frac{d^2}{dr^2} + 2 \frac{d}{r} \right) R(t|r_0) + q^2 r^2 - \frac{1}{\Theta(\Omega|\bar{\Omega}_0)} \hat{L}^2 \Theta(\Omega|\bar{\Omega}_0) = 0 \quad (3.10)\]

The angular part of the above equation, as well as radial part, should be equal to a dimensionless number. It has a so standard form:

\[ \frac{1}{\Theta(\Omega|\bar{\Omega}_0)} \hat{L}^2 \Theta(\Omega|\bar{\Omega}_0) = l(l + 1) \quad (3.11)\]

Hence, the angular part of the pdf consists of spherical harmonics:

\[ \Theta(\Omega|\bar{\Omega}_0) \sim Y_{lm}(\Omega) \quad (3.12)\]

Back to the equation 3.10, we get:

\[ \frac{r^2}{R_l(r|r_0)} \left( \frac{d^2}{dr^2} + 2 \frac{d}{r} \right) R_l(t|r_0) + q^2 r^2 - l(l + 1) = 0 \quad (3.13)\]

or equivalently:

\[ \left( \frac{d^2}{dr^2} + 2 \frac{d}{r} \right) R_l(t|r_0) + [q^2 - \frac{l(l + 1)}{r^2}] R_l(t|r_0) = 0 \quad (3.14)\]

This is just Bessel equation. Hence, the radial part of pdf contains Bessel’s functions:

\[ R_l(r|r_0) \sim j_l(qr), y_l(qr) \quad (3.15)\]

Collecting the equation 3.8, 3.12 and 3.14, we may write a general form to the solution of the equation 3.1:

\[ \tilde{\rho}(r, \Omega, t|\bar{r}_0) = \int_0^\infty dq \ e^{-2D_0 q^2 t} \sum_{l=0}^\infty \sum_{m=-l}^l \Gamma_{lm}(q|\bar{\Omega}_0) Y_{lm}(\Omega) \left[ A_l(q|r_0) j_l(qr) + B_l(q|r_0) y_l(qr) \right] \quad (3.16)\]
where, $A_l$, $B_l$ and $\Gamma_{lm}$’s are unknown constants could be evaluated by considering the initial condition described in 3.2. In fact, either if the particles be initially bounded or unbounded, the unknown coefficients $A_l$, $B_l$ and $\Gamma_{lm}$’s are the same and could be evaluated only by applying the initial condition 3.2.

Let us re-write the initial condition in the equation 3.2 in a proper form in spherical coordinates with respect to the general form of the particular solution (equation 3.16):

$$\tilde{\rho}(r, \Omega, 0|\vec{r}_0) = \delta(\vec{r} - \vec{r}_0) = \frac{1}{r_0} \delta(r - r_0) \delta(\Omega - \Omega_0) = \frac{2}{\pi} \int_0^\infty dq \, q^2 j_l^\prime(qr) j_l^\prime(qr_0) \sum_{m=-l}^{m=l} Y_{lm}^*(\Omega_0) Y_{lm}(\Omega)$$

where we used two identities:

$$\delta(\Omega - \Omega_0) = \sum_{l=0}^{\infty} \sum_{m=-l}^{m=l} Y_{lm}^*(\Omega_0) Y_{lm}(\Omega)$$

$$\frac{1}{r_0^3} \delta(r - r_0) = \frac{2}{\pi} \int_0^\infty dq \, q^2 j_l^\prime(qr) j_l^\prime(qr_0), \quad l' > -\frac{3}{2} \quad (3.18)$$

Note that in equation 3.17, we have a freedom to choose $l' > -\frac{3}{2}$. At the time $t = 0$ we must have:

$$\tilde{\rho}^P(r, \Omega, 0|\vec{r}_0) = \tilde{\rho}(r, \Omega, 0|\vec{r}_0) \quad (3.19)$$

Here, the superscript $P$ snads for Particular. Hence:

$$\int_0^\infty dq \sum_{l=0}^{\infty} \sum_{m=-l}^{m=l} \Gamma_{lm}(q|\Omega) Y_{lm}(\Omega) [A_l(q|r_0) j_l(qr) + B_l(q|r_0) y_l(qr)]$$

$$= \frac{2}{\pi} \int_0^\infty dq \, q^2 \sum_{l=0}^{\infty} \sum_{m=-l}^{m=l} Y_{lm}^*(\Omega_0) Y_{lm}(\Omega) j_l(qr) j_l(qr_0)$$

$$\left(3.20\right)$$

where, we fixed $l' = l$. Orthogonality of $Y_{lm}$’s yields:

$$\Gamma_{lm}(q|\Omega_0) = Y_{lm}^*(\Omega_0) \quad (3.21)$$

$$\int_0^\infty dq \, [A_l(q|r_0) j_l(qr) + B_l(q|r_0) y_l(qr)] = \frac{2}{\pi} \int_0^\infty dq \, q^2 j_l(qr) j_l(qr_0) \quad (3.22)$$

multiplying both side of the last equality by $r^2 j_l(rq')$ and integrating over $r$ yields:

$$\int_0^\infty dq \int_0^\infty dr \, r^2 j_l(rq') [A_l(q|r_0) j_l(qr) + B_l(q|r_0) y_l(qr)]$$

$$= \frac{2}{\pi} \int_0^\infty dq \, q^2 \int_0^\infty dr \, r^2 j_l(rq') j_l(qr) j_l(qr_0) \quad (3.23)$$
Using the orthogonality of the $j_l$’s and independency between $j_l$ and $y_l$’s, yields:

$$\int_0^{\infty} dq \frac{\pi}{2q^2} \delta(q-q') A_l(q|r_0) = \frac{2}{\pi} \int_0^{\infty} dq \frac{1}{2q^2} \delta(q-q') j_l(qr_0)$$  \hspace{1cm} (3.24)

or, equivalently:

$$A_l(q|r_0) = \frac{2q^2}{\pi} j_l(qr_0)$$  \hspace{1cm} (3.25)

returning to the equation 3.22 we have:

$$\int_0^{\infty} dq \ B_l(q|r_0) y_l(qr) = 0$$  \hspace{1cm} (3.26)

This equality should be valid for all $l$’s, hence:

$$B_l(q|r_0) = 0$$  \hspace{1cm} (3.27)

Finally, we have the explicit form of the particular solution:

$$\tilde{\rho}_P(r,\Omega,t|\vec{r}_0) = \frac{2}{\pi} \int_0^{\infty} dq \frac{q^2 e^{-2D_0 q^2 t}}{z+2D_0 q^2} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} Y_{lm}^*(\Omega_0) Y_{lm}(\Omega) j_l(qr) j_l(qr_0)$$  \hspace{1cm} (3.28)

The Laplace transform of the particular solution is:

$$\tilde{\rho}_P(r,\Omega,z|\vec{r}_0) = \frac{2}{\pi} \int_0^{\infty} dq \frac{q^2}{z+2D_0 q^2} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} Y_{lm}^*(\Omega_0) Y_{lm}(\Omega) j_l(qr) j_l(qr_0)$$  \hspace{1cm} (3.29)

where, the Laplace transform has defined as:

$$f(z) \equiv \int_0^{\infty} dt \ e^{-zt} f(t)$$  \hspace{1cm} (3.30)

The particular solution is just what has calculated in [1].

### 3.2 Complementary Solution

The complementary solution must satisfy in the equation 3.1 but with zero initial condition. Rather than particular solution, it is much convenient to use Laplace transform to evaluate the complementary solution. This is because of zero initial condition of the complementary answer. We define the Laplace transform of some function of $t$ as:

$$f(z) \equiv \int_0^{\infty} dt \ e^{-zt} f(t)$$  \hspace{1cm} (3.31)
If the function has an initial value of \( f(0) \), then the Laplace transform of the derivative of the function has the form:

\[
\int_0^\infty dt \ e^{-zt} f'(t) = zf(z) - f(0)
\]  
(3.32)

Hence, if we make a Laplace transform in equation 3.1 we will get:

\[
z\tilde{\rho}^C(r,\Omega,z|\vec{r}_0) - \tilde{\rho}^C(r,\Omega,0|\vec{r}_0) = 2D_0(\partial_r^2 + \frac{2}{r}\partial_r - \frac{\hat{L}^2}{r^2})\tilde{\rho}^C(r,\Omega,z|\vec{r}_0)
\]  
(3.33)

Here, the superscript \( C \) stands for Complementary. Equivalently we have:

\[
(\partial_r^2 + \frac{2}{r}\partial_r - \frac{\hat{L}^2}{r^2})\tilde{\rho}^C(r,\Omega,z|\vec{r}_0) = 0
\]  
(3.34)

Now, we may follow the separation of variables procedure again. Consider the general form of \( \tilde{\rho} \) as:

\[
\tilde{\rho}^C(r,\Omega,z|\vec{r}_0) = R(r, z|\vec{r}_0)\Theta(\Omega|\Omega_0)
\]  
(3.35)

hence, the equation reads:

\[
\Theta(\Omega|\Omega_0)[\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{z}{2D_0}]R(r, z|\vec{r}_0) - R(r, z|\vec{r}_0)\hat{L}^2\Theta(\Omega|\Omega_0) = 0
\]  
(3.36)

or equivalently:

\[
\frac{r^2}{R(r, z|\vec{r}_0)}[\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{z}{2D_0}]R(r, z|\vec{r}_0) = \frac{1}{\Theta(\Omega|\Omega_0)}\hat{L}^2\Theta(\Omega|\Omega_0)
\]  
(3.37)

both side of above equation should be equal to a dimensionless number. Again, \( \Theta \) consists of spherical harmonics:

\[
\Theta(\Omega|\Omega_0) \sim Y_{lm}(\Omega)
\]  
(3.38)

Hence, the equation reads:

\[
\frac{r^2}{R_l(r, z|\vec{r}_0)}[\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{z}{2D_0}]R_l(r, z|\vec{r}_0) = l(l+1)
\]  
(3.39)

or equivalently:

\[
[\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{l(l+1)}{r^2}]R_l(r, z|\vec{r}_0) = 0
\]  
(3.40)

This is modified Bessel equation with the answers of modified Bessel’s function of first kind \((i_l)\) and third kind \((k_l)\). Hence, the radial part has the form of:

\[
R_l(r, z|\vec{r}_0) \sim i_l(r\sqrt{\frac{z}{2D_0}}), \ k_l(r\sqrt{\frac{z}{2D_0}})
\]  
(3.41)
Hence, we may form of the solution as:

\[
\tilde{\rho}(r, \Omega, z|\vec{r}_0) = \sum_{l=0}^{\infty} \sum_{m=-l}^{m=l} \Gamma_{lm}(z|\Omega_0) Y_{lm}(\Omega) [C_{l}(z|\vec{r}_0)i_{l}(r\sqrt{\frac{z}{2D_0}}) + D_{l}(z|\vec{r}_0)k_{l}(r\sqrt{\frac{z}{2D_0}})]
\]

(3.42)

where, \(C_{l}\) and \(D_{l}\)'s are constants which could be evaluated when the boundary condition be applied for the complete solution (particular+complementary).

This form of complementary solution is valid for both regions I and II. Furthermore, in region II, as \(r \to \infty\), the solution must remain finite. Hence the coefficient \(C_{l}\) is zero for this region. So, in region I (\(d < r < \sigma\)) we have:

\[
\tilde{\rho}^{I,C}(r, \Omega, z|\vec{r}_0) = \sum_{l=0}^{\infty} \sum_{m=-l}^{m=l} \Gamma_{lm}^{I}(z|\Omega_0) Y_{lm}(\Omega) [C_{l}^{I}(z|\vec{r}_0)i_{l}(r\sqrt{\frac{z}{2D_0}}) + D_{l}^{I}(z|\vec{r}_0)k_{l}(r\sqrt{\frac{z}{2D_0}})]
\]

(3.43)

and in region II (\(\sigma < r\)) we have:

\[
\tilde{\rho}^{II,C}(r, \Omega, z|\vec{r}_0) = \sum_{l=0}^{\infty} \sum_{m=-l}^{m=l} \Gamma_{lm}^{II}(z|\Omega_0) Y_{lm}(\Omega) D_{l}^{II}(z|\vec{r}_0)k_{l}(r\sqrt{\frac{z}{2D_0}})
\]

(3.44)

These solutions are true, either the particle initially be bounded or not. The unknown coefficients could be evaluated by applying the boundary conditions described in equations 3.54 and 3.55. Note that the boundary condition must be applied to the complete solution (complementary + particular solutions).

### 3.3 Complete Solution

#### 3.3.1 Formal Development

As we have calculated in last two subsections:

\[
\tilde{\rho}^{P}(r, \Omega, z|\vec{r}_0) = \frac{2}{\pi} \int_{0}^{\infty} dq \frac{q^2}{z + 2D_0q^2} \sum_{l=0}^{\infty} \sum_{m=-l}^{m=l} Y_{lm}^{*}(\Omega_0) Y_{lm}(\Omega) j_{l}(qr)j_{l}(qr_0)
\]

\[
= \sum_{l=0}^{\infty} \sum_{m=-l}^{m=l} Y_{lm}^{*}(\Omega_0) Y_{lm}(\Omega) \tilde{\rho}_{l}^{P}(r, z|\vec{r}_0)
\]

(3.45)

\[
\tilde{\rho}^{I,C}(r, \Omega, z|\vec{r}_0) = \sum_{l=0}^{\infty} \sum_{m=-l}^{m=l} \Gamma_{lm}^{I}(z|\Omega_0) Y_{lm}(\Omega) [C_{l}^{I}(z|\vec{r}_0)i_{l}(r\sqrt{\frac{z}{2D_0}}) + D_{l}^{I}(z|\vec{r}_0)k_{l}(r\sqrt{\frac{z}{2D_0}})]
\]
\[ I_l(z|\Omega_0) = \sum_{m=0}^{\infty} \sum_{m=-l}^{l} \Gamma_{lm}^I(z|\Omega_0) Y_{lm}(\Omega) \rho_{l,C}^I(r, z|r_0) \]

\[ I_I(r, \Omega, z|\Omega_0) = \sum_{m=0}^{\infty} \sum_{m=-l}^{l} \Gamma_{lm}^I(z|\Omega_0) Y_{lm}(\Omega) D_{l}^I(z|r_0) k_l(r \sqrt{\frac{z}{2D_0}}) \]

\[ I_{II,C}^I(r, z|\Omega_0) = \sum_{m=0}^{\infty} \sum_{m=-l}^{l} \Gamma_{lm}^I(z|\Omega_0) Y_{lm}(\Omega) D_{l}^I(z|r_0) k_l(r \sqrt{\frac{z}{2D_0}}) \]

\[ \tilde{\rho}_{P}^l(r, z|r_0) = \frac{2}{\pi} \int_0^\infty dq \frac{q^2}{z + 2D_0 q^2} j_l(q r) j_l(q r_0) \]

\[ \tilde{\rho}_{l,C}^I(r, z|r_0) = C_{l} I_l(z|r_0) i_l(r \sqrt{\frac{z}{2D_0}}) + D_{l}^I(z|z_0) k_l(r \sqrt{\frac{z}{2D_0}}) \]

\[ \tilde{\rho}_{II,C}^I(r, z|r_0) = D_{l}^I(z|z_0) k_l(r \sqrt{\frac{z}{2D_0}}) \]

where, \( \tilde{\rho}_{P}^l \), \( \tilde{\rho}_{l,C}^I \) and \( \tilde{\rho}_{II,C}^I \) have introduced for later simplicity. Either if the particles be initially bounded \( \tilde{\rho}_{l} = \tilde{\rho}_{P} + \tilde{\rho}_{l,C} \) or be initially unbounded \( \tilde{\rho}_{l} = \tilde{\rho}_{l,C} + \tilde{\rho}_{II,C} \), the continuity of the pdf at \( r = \sigma \) force:

\[ \Gamma_{lm}^I(z|\Omega_0) = \Gamma_{lm}^I(z|\Omega_0) = Y_{lm}^*(\Omega_0) \]

Hence, for evaluating the other coefficients, it is enough to concentrate on \( \tilde{\rho}_{P}^l \), \( \tilde{\rho}_{l,C}^I \) and \( \tilde{\rho}_{II,C}^I \):

\[ \tilde{\rho}_{P}^l(r, z|z_0) = \frac{2}{\pi} \int_0^\infty dq \frac{q^2}{z + 2D_0 q^2} j_l(q r_0) j_l(q r) \]

\[ \tilde{\rho}_{l,C}^I(r, z|z_0) = C_{l} I_l(z|z_0) i_l(r \sqrt{\frac{z}{2D_0}}) + D_{l}^I(z|z_0) k_l(r \sqrt{\frac{z}{2D_0}}) \]

\[ \tilde{\rho}_{II,C}^I(r, z|z_0) = D_{l}^I(z|z_0) k_l(r \sqrt{\frac{z}{2D_0}}) \]

We will show that for evaluating the self diffusion coefficient, it is sufficient to evaluate \( \tilde{\rho}_{l} \) for \( l = 1 \) and \( z \to 0 \) with \( r, r_0 = \sigma \) (see equation 4.29). Hence, for simplicity we may take to account the effect of this condition just now. for \( x < < 1 \) we have:

\[ i_1(x) \approx \frac{1}{3} x \]

\[ k_1(x) \approx \frac{1}{x^2} \]
which yields:

\[
\rho_{I,C}^1(r, z | r_0) = \frac{r}{3} \sqrt{\frac{z}{2D_0}} C_1^l + \frac{2D_0}{z r^2} D_1^l
\]

\[
\rho_{II,C}^1(r, z | r_0) = \frac{2D_0}{z r^2} D_1^l
\]

(3.53)

To proceed, we rewrite the boundary conditions again in here:

\[
\frac{\partial \tilde{\rho}(r, \Omega, z | \vec{r}_0)}{\partial r} \bigg|_{r \to d^+} = 0
\]

(3.54)

\[
\left( \lim_{r \to \sigma^-} - \lim_{r \to \sigma^+} \right) \frac{\partial \tilde{\rho}(r, \Omega, z | \vec{r}_0)}{\partial r} = -\frac{2\beta V_0}{\sigma} \tilde{\rho}(\sigma, \Omega, z | \vec{r}_0)
\]

(3.55)

These conditions should be satisfied together with the continuity condition of pdf at \( r = \sigma \). The pdf has the general form of:

\[
\tilde{\rho}(r, \Omega, z | \vec{r}_0) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} Y_{lm}^* (\Omega_0) Y_{lm} (\Omega) \tilde{\rho}_l (r, z | r_0)
\]

(3.56)

the orthogonality of \( Y_{lm} \)'s yields that the continuity and the boundary conditions must be valid for each \( \tilde{\rho}_l \)'s. Hence, for \( l = 1 \) we have:

\[
\frac{\partial \tilde{\rho}_1(r, z | r_0)}{\partial r} \bigg|_{r \to d^+} = 0
\]

\[
\left( \lim_{r \to \sigma^-} - \lim_{r \to \sigma^+} \right) \frac{\partial \tilde{\rho}_1(r, z | r_0)}{\partial r} = -\frac{2\beta V_0}{\sigma} \tilde{\rho}_1(\sigma, z | r_0)
\]

\[
\tilde{\rho}_1 (r \to \sigma^+, z | r_0) = \tilde{\rho}_1 (r \to \sigma^-, z | r_0)
\]

(3.57)

Now, it is time to separate our problem into two cases in which the particle be initially bounded or unbounded.

### 3.3.2 Particle Initially Bounded

When the particle is initially bounded \( (d < r_0 < \sigma) \), the particular solution exists only in region I. The complementary solution (correspond to zero initial condition) should be considered in both regions. Hence, the solution has the form of:

\[
\tilde{\rho}_1^I(r, z | r_0) = \tilde{\rho}_1^P(r, z | r_0) + \tilde{\rho}_1^{IC}(r, z | r_0)
\]

\[
\tilde{\rho}_1^P(r, z | r_0) = \tilde{\rho}_1^P(r, z | r_0) + \frac{r}{3} \sqrt{\frac{z}{2D_0}} C_1^l + \frac{2D_0}{z r^2} D_1^l \quad , \text{ for } d < r < \sigma
\]

\[
\tilde{\rho}_1^{IC}(r, z | r_0) = \tilde{\rho}_1^{IC}(r, z | r_0)
\]

\[
= \frac{2D_0}{z r^2} D_1^l \quad , \text{ for } \sigma < r
\]

(3.58)
where, the subscribes \( I \) or \( II \) specifies the solutions correspond to region \( I \) or \( II \). Also, the letters \( C \) and \( P \) stand for Particular and Complementary solutions.

From equations 3.57, the continuity equation at \( r = \sigma \) reads:

\[
\hat{\rho}_1^P(\sigma, z|\sigma) + \frac{\sigma}{2D_0} \frac{z}{2\sigma^2} C_1^I + \frac{2D_0}{z\sigma^2} D_1^I = \frac{2D_0}{z\sigma^2} D_1^{II} \quad (3.59)
\]

which could be solved for \( D_1^{II} \):

\[
D_1^{II} = D_1^I + \frac{z\sigma^2}{2D_0} \hat{\rho}_1^P(\sigma, z|\sigma_0) + \frac{\sigma^3}{3} \left( \frac{z}{2D_0} \right)^{3/2} C_1^I \quad (3.60)
\]

The second boundary condition, namely discontinuity of derivatives at \( r = \sigma \), from equation 3.57 reads:

\[
-\frac{4D_0}{z\sigma^4} D_1^{II} - \partial_r \hat{\rho}_1^P(\sigma, z|\sigma_0) = \frac{1}{3} \sqrt{\frac{z}{2D_0}} C_1^I + \frac{4D_0}{z\sigma^3} D_1^I = -\frac{2\beta V_0}{\sigma} \frac{2D_0}{z\sigma^2} D_1^{II} \quad (3.61)
\]

or, equivalently:

\[
\frac{4D_0}{z\sigma^4}(\beta V_0 - 1) D_1^{II} = -\frac{4D_0}{z\sigma^4} D_1^I + \frac{1}{3} \sqrt{\frac{z}{2D_0}} C_1^I + \partial_r \hat{\rho}_1^P(\sigma, z|\sigma_0) \quad (3.62)
\]

this equation could be solved for \( D_1^{II} \):

\[
D_1^{II} = (\beta V_0 - 1)^{-1} \left[ -D_1^I + \frac{\sigma^3}{6} \left( \frac{z}{2D_0} \right)^{3/2} C_1^I + \frac{\sigma^3}{4D_0} \partial_r \hat{\rho}_1^P(\sigma, z|\sigma_0) \right] \quad (3.63)
\]

collecting equations 3.60 and 3.63 together yields:

\[
D_1^I + \frac{z\sigma^2}{2D_0} \hat{\rho}_1^P(\sigma, z|\sigma_0) + \frac{\sigma^3}{3} \left( \frac{z}{2D_0} \right)^{3/2} C_1^I = (\beta V_0 - 1)^{-1} \left[ -D_1^I + \frac{\sigma^3}{6} \left( \frac{z}{2D_0} \right)^{3/2} C_1^I + \frac{\sigma^3}{4D_0} \partial_r \hat{\rho}_1^P(\sigma, z|\sigma_0) \right] \quad (3.64)
\]

this equation could be solved for \( D_1^I \):

\[
D_1^I = \frac{z\sigma^2}{4D_0\beta V_0} \left[ \sigma \partial_r \hat{\rho}_1^P(\sigma, z|\sigma_0) - 2(\beta V_0 - 1) \hat{\rho}_1^P(\sigma, z|\sigma_0) \right] - \frac{\sigma^3}{6\beta V_0} \left( \frac{z}{2D_0} \right)^{3/2} (2\beta V_0 - 3) C_1^I \quad (3.65)
\]
The first boundary condition, vanishing of derivative at \( r = d \), from equation 3.57 reads:

\[
\partial_r \tilde{\rho}_1^P(d, z|r_0) + \frac{1}{3} \sqrt{\frac{z}{2D_0}} C_1^I - \frac{4D_0}{zd^3} D_1^I = 0
\]

(3.66)

which could be solved for \( D_1^I \):

\[
D_1^I = \frac{zd^3}{4D_0} \partial_r \tilde{\rho}_1^P(d, z|r_0) + \frac{d^3}{6} \left( \frac{z}{2D_0} \right)^{3/2} C_1^I
\]

(3.67)

dividing this equation, together with 3.65 yields:

\[
\frac{zd^3}{4D_0} \left[ \sigma \partial_r \tilde{\rho}_1^P(\sigma, z|r_0) - 2(\beta V_0 - 1) \tilde{\rho}_1^P(\sigma, z|r_0) \right] - \frac{\sigma^3}{6\beta V_0} \left( \frac{z}{2D_0} \right)^{3/2} (2\beta V_0 - 3) C_1^I = \frac{zd^3}{4D_0} \partial_r \tilde{\rho}_1^P(d, z|r_0) + \frac{d^3}{6} \left( \frac{z}{2D_0} \right)^{3/2} C_1^I
\]

(3.68)

or equivalently:

\[
\frac{zd^3}{4D_0} \left[ \sigma \partial_r \tilde{\rho}_1^P(\sigma, z|r_0) - 2(\beta V_0 - 1) \tilde{\rho}_1^P(\sigma, z|r_0) - d^3 \beta V_0 \partial_r \tilde{\rho}_1^P(d, z|r_0) - d^3 \beta V_0 \partial_r \tilde{\rho}_1^P(d, z|r_0) \right]
\]

(3.69)

Hence, we have:

\[
C_1^I = \frac{3}{2} \sqrt{\frac{d^3 \beta V_0 + 2\sigma^3 \beta V_0 - 3\sigma^3}{z}} \left[ \sigma \partial_r \tilde{\rho}_1^P(\sigma, z|r_0) - 2(\beta V_0 - 1) \tilde{\rho}_1^P(\sigma, z|r_0) - d^3 \beta V_0 \partial_r \tilde{\rho}_1^P(d, z|r_0) \right]
\]

(3.70)

From equation 3.67, \( D_1^I \) could be evaluated:

\[
D_1^I = \left( \frac{zd^3}{4D_0} \right) \left[ \sigma \partial_r \tilde{\rho}_1^P(\sigma, z|r_0) + 2 \left( 1 - \beta V_0 \right) \tilde{\rho}_1^P(\sigma, z|r_0) \right] - \frac{1}{\beta V_0(d^3 + 2\sigma^3)} \left[ \frac{2(\beta V_0 - 3)\sigma \partial_r \tilde{\rho}_1^P(d, z|r_0)}{\beta V_0(d^3 + 2\sigma^3) - 3\sigma^3} \right]
\]

(3.71)

Finally, the pdf in the region \( I \) reads:

\[
\tilde{\rho}_1^I(r, z|r_0) = \frac{2D_0}{zr^2} D_1^I + \frac{r}{3} \sqrt{\frac{z}{2D_0}} C_1^I + \tilde{\rho}_1^I(r, z|r_0)
\]
\[
\begin{align*}
&\rho_1^P (r, z | r_0) \\
&= \rho_1^P (r, z | r_0) \\
&\quad + \left( \frac{\sigma^3 \partial_r \rho_1^P (\sigma, z | r_0) - 2\sigma^2 (\beta V_0 - 1) \rho_1^P (\sigma, z | r_0)}{\beta V_0 (d^3 + 2\sigma^3) - 3\sigma^4} \right) (r + \frac{d^3}{2r^2}) \\
&\quad + \left( \frac{d^3 \partial_r \rho_1^P (d, z | r_0)}{\beta V_0 (d^3 + 2\sigma^3) - 3\sigma^4} \right) \left[ -\beta V_0 r + \frac{\sigma^3}{2r^2} (2\beta V_0 - 3) \right] \\
&\quad \beta V_0 \left( d^3 + 2\sigma^3 \right) - 3\sigma^4 \\
&\quad \left( r + \frac{d^3}{2r^2} \right) \\
&\quad \beta V_0 \left( d^3 + 2\sigma^3 \right) - 3\sigma^4 \\
&\quad \left( r + \frac{d^3}{2r^2} \right)
\end{align*}
\]

(3.72)

Now, let us evaluate an explicit form for \( \tilde{\rho}_1^P (r, z = 0 | r_0) \) and its derivatives. We have:

\[
\tilde{\rho}_1^P (r, z = 0 | r_0) = \frac{1}{D_0} \int_0^\infty dq \, j_1(qr) j_1(qr_0)
\]

(3.73)

in which:

\[
j_1(x) = \frac{\sin x}{x^2} - \frac{\cos x}{x}
\]

(3.74)

Hence:

\[
\tilde{\rho}_1^P (r, z = 0 | r_0) = \frac{1}{12r_0^2 D_0} \left[ r_0^3 [1 - \text{sgn}(r_0 - r)] + r^3 [1 + \text{sgn}(r_0 - r)] \right]
\]

(3.75)

and:

\[
\partial_r \tilde{\rho}_1^P (r, z = 0 | r_0) = \frac{1}{12r^2 r_0^2 D_0} \left[ r^3 [1 - \text{sgn}(r - r_0)] - 2r_0^3 [1 + \text{sgn}(r - r_0)] \right]
\]

(3.76)

where:

\[
\text{sgn}(x) = \begin{cases} 
+1 & , \quad x > 0 \\
0 & , \quad x = 0 \\
-1 & , \quad x < 0 
\end{cases}
\]

(3.77)

in consistence with \( \theta(0) = 1/2 \). As we mentioned, to evaluate the self diffusion coefficient, we need to put \( r = d \) and \( r_0 = \sigma \). As we desired to evaluate the pdf at \( r, r_0 = d, \sigma \) and remembering that \( \theta(0) = 1/2 \), we have:

\[
\begin{align*}
\tilde{\rho}_1^P (d, z = 0 | d) &= \frac{1}{6d D_0} \\
\tilde{\rho}_1^P (d, z = 0 | \sigma) &= \frac{d}{6\sigma^2 D_0} \\
\tilde{\rho}_1^P (\sigma, z = 0 | d) &= \frac{d}{6\sigma^2 D_0} \\
\tilde{\rho}_1^P (\sigma, z = 0 | \sigma) &= \frac{1}{6\sigma D_0}
\end{align*}
\]

(3.78)
Similarly:

\[
\begin{align*}
\partial_r \tilde{\rho}_1^P (d, z = 0|d) &= - \frac{1}{12d^2 D_0} \\
\partial_r \tilde{\rho}_1^P (d, z = 0|\sigma) &= \frac{1}{6\sigma^2 D_0} \\
\partial_r \tilde{\rho}_1^P (\sigma, z = 0|d) &= - \frac{d}{3\sigma^3 D_0} \\
\partial_r \tilde{\rho}_1^P (\sigma, z = 0|\sigma) &= - \frac{1}{12\sigma^2 D_0}
\end{align*}
\] (3.79)

replacing these results into 3.72 yields:

\[
\begin{align*}
\tilde{\rho}_1^I (d, z = 0|d) &= \frac{2\beta V_0 (\sigma^3 - d^3) - 3\sigma^3}{8dD_0[\beta V_0 (d^3 + 2\sigma^3) - 3\sigma^3]} \\
\tilde{\rho}_1^I (d, z = 0|\sigma) &= - \frac{3d\sigma}{8D_0[\beta V_0 (d^3 + 2\sigma^3) - 3\sigma^3]} \\
\tilde{\rho}_1^I (\sigma, z = 0|d) &= - \frac{d^3 + 2\sigma^3}{8\sigma D_0[\beta V_0 (d^3 + 2\sigma^3) - 3\sigma^3]} \\
\tilde{\rho}_1^I (\sigma, z = 0|\sigma) &= - \frac{d^3}{8\sigma D_0[\beta V_0 (d^3 + 2\sigma^3) - 3\sigma^3]}
\end{align*}
\] (3.80)

Note that for \( V_0 = 0 \) and \( \sigma \to \infty \), which means the particles interacting among hard-core potential, we have:

\[
\tilde{\rho}_1^I (r, z|r_0) \to \frac{d^3}{2\pi^2} \partial_r \tilde{\rho}_1^P (d, z|r_0) + \tilde{\rho}_1^P (r, z|r_0)
\]

\[
= \frac{1}{\pi D_0} \int_0^\infty dq j_1(qr_0) [j_1(qr) + q \frac{d^3}{2\pi^2} j_1'(qd)]
\] (3.81)

now, recalling the fact that for small \( z \):

\[
\frac{d^3}{2r^2} = - \sqrt{\frac{2D_0}{z}} k_1(r \sqrt{z/2D_0})
\] (3.82)

hence:

\[
\tilde{\rho}_1^I (r, z|r_0) \to \frac{1}{\pi D_0} \int_0^\infty dq j_1(qr_0) [j_1(qr) - q j_1'(qd)] \sqrt{\frac{2D_0}{z}} k_1(r \sqrt{z/2D_0})
\] (3.83)

which is reproducing of the equation (2.35) of [1] when \( z \to 0 \) be applied.
3.3.3 Particles Initially Unbounded

When the particle be initially unbounded, the particular solution appear to be exist in region $H$ ($\sigma < r$):

$$
\tilde{\rho}_I(r, z|r_0) = \frac{r^3}{3\sqrt{2D_0}} C_1^I + \frac{2D_0}{z\sigma^2} D_1^I \\
\tilde{\rho}_I^{II}(r, z|r_0) = \tilde{\rho}_P^I(r, z|r_0) + \frac{2D_0}{z\sigma^2} D_1^{II}
$$

(3.84)

applying the continuity of pdf at $r = \sigma$ yields:

$$
\tilde{\rho}_I(r, z|z_0) = \tilde{\rho}_I^{II}(r, z|z_0) \\
\frac{\sigma}{3} \frac{z}{2D_0} C_1^I + \frac{2D_0}{z\sigma^2} D_1^I = \tilde{\rho}_P^I(\sigma, z|z_0) + \frac{2D_0}{z\sigma^2} D_1^{II}
$$

(3.85)

which could be solved for $D_1^{II}$:

$$
D_1^{II} = -\frac{z\sigma^2}{2D_0} \tilde{\rho}_P^I(\sigma, z|z_0) + \frac{\sigma^3}{3} \left( \frac{z}{2D_0} \right)^{3/2} C_1^I + D_1^I
$$

(3.86)

the discontinuity of pdf at $r = \sigma$ (see equation 3.57) yields:

$$
\partial_r \tilde{\rho}_I^{II}(\sigma, z|z_0) - \partial_r \tilde{\rho}_P^I(\sigma, z|z_0) = -\frac{2\beta V_0}{\sigma} \tilde{\rho}_P^I(\sigma, z|z_0) \\
\partial_r \tilde{\rho}_P^I(\sigma, z|z_0) - \frac{4D_0}{z\sigma^2} D_1^{II} - \frac{1}{3} \frac{z}{2D_0} C_1^I + \frac{4D_0}{z\sigma^2} D_1^I \\
= -\frac{2\beta V_0}{\sigma} \frac{\sigma}{3} \left( \frac{z}{2D_0} \right)^{3/2} C_1^I + \frac{2D_0}{z\sigma^2} D_1^{II}
$$

(3.87)

this equation, also, could be solved for $D_1^{II}$:

$$
D_1^{II} = \frac{z\sigma^3}{4D_0} \partial_r \tilde{\rho}_P^I(\sigma, z|z_0) + \frac{\sigma^3}{6} \left( \frac{z}{2D_0} \right)^{3/2} (2\beta V_0 - 1) C_1^I + (1 + \beta V_0) D_1^I
$$

(3.88)

This equation together with equation 3.86 yields:

$$
-\frac{z\sigma^2}{2D_0} \tilde{\rho}_P^I(\sigma, z|z_0) + \frac{\sigma^3}{3} \left( \frac{z}{2D_0} \right)^{3/2} C_1^I + D_1^I \\
= \frac{z\sigma^3}{4D_0} \partial_r \tilde{\rho}_P^I(\sigma, z|z_0) + \frac{\sigma^3}{6} \left( \frac{z}{2D_0} \right)^{3/2} (2\beta V_0 - 1) C_1^I + (1 + \beta V_0) D_1^I
$$

(3.89)
or equivalently:

\[ D_1^I = -\frac{z\sigma^2}{4D_0\beta V_0} [2\tilde{\rho}_1^P (\sigma, z|\rho_0) + \sigma \partial_r \tilde{\rho}_1^P (\sigma, z|\rho_0)] + \frac{\sigma^3}{6\beta V_0} \left( \frac{z}{2D_0} \right)^{3/2} (3 - 2\beta V_0) C_1^I \]  

(3.90)

The boundary condition at \( r = d \) from equation 3.57 has a simple form:

\[ \partial_r \tilde{\rho}_1^I (d, z|\rho_0) = 0 \]

\[ \frac{1}{3} \sqrt{\frac{z}{2D_0}} C_1^I - \frac{4D_0}{z\rho_1^I} = 0 \]  

(3.91)

or equivalently:

\[ D_1^I = \frac{d^3}{6} \left( \frac{z}{2D_0} \right)^{3/2} C_1^I \]  

(3.92)

This equation together with the equation 3.90 yields:

\[ \frac{d^3}{6} \left( \frac{z}{2D_0} \right)^{3/2} C_1^I = -\frac{z\sigma^2}{4D_0\beta V_0} [2\tilde{\rho}_1^P (\sigma, z|\rho_0) + \sigma \partial_r \tilde{\rho}_1^P (\sigma, z|\rho_0)] + \frac{\sigma^3}{6\beta V_0} \left( \frac{z}{2D_0} \right)^{3/2} (3 - 2\beta V_0) C_1^I \]  

(3.93)

which could be solved for \( C_1^I \). Hence, finally we have:

\[ C_1^I = -\left( 3\sigma^2 \right) \sqrt{\frac{2D_0}{z}} \left[ \frac{2\tilde{\rho}_1^P (\sigma, z|\rho_0) + \sigma \partial_r \tilde{\rho}_1^P (\sigma, z|\rho_0)}{\beta V_0 (d^3 + \sigma^3) - 3\sigma^3} \right] \]  

(3.94)

Turning back to the equation 3.92 yields:

\[ D_1^I = -\left( \frac{zd^3\sigma^2}{4D_0} \right) \left[ \frac{2\tilde{\rho}_1^P (\sigma, z|\rho_0) + \sigma \partial_r \tilde{\rho}_1^P (\sigma, z|\rho_0)}{\beta V_0 (d^3 + \sigma^3) - 3\sigma^3} \right] \]  

(3.95)

Now, by replacing equation 3.94 and 3.95 into 3.84 we will have the pdf at region \( I \):

\[ \tilde{\rho}_1^I (r, z|\rho_0) = -\sigma^2 (r + \frac{d^3}{2r^2}) \left[ \frac{2\tilde{\rho}_1^P (\sigma, z|\rho_0) + \sigma \partial_r \tilde{\rho}_1^P (\sigma, z|\rho_0)}{\beta V_0 (d^3 + \sigma^3) - 3\sigma^3} \right] \]  

(3.96)
Like initially unbounded case, we desire to evaluate the pdf with \( r, r_0 = d, \sigma \). For this, we may use of equations 3.78 and 3.79:

\[
\begin{align*}
\tilde{\rho}^f(d, z|d) &= 0 \\
\tilde{\rho}^f(d, z|\sigma) &= -\frac{3\sigma d}{8D_0} \left( \beta V_0(d^3 + 2\sigma^3) - 3\sigma^3 \right) \\
\tilde{\rho}^f(\sigma, z|d) &= 0 \\
\tilde{\rho}^f(\sigma, z|\sigma) &= -\frac{\sigma^2}{4D_0} \left( 1 + \frac{d^3}{2\sigma^3} \right) \left( \frac{1}{\beta V_0(d^3 + 2\sigma^3) - 3\sigma^3} \right)
\end{align*}
\]  

(3.97)

4 Self Diffusion Coefficient

4.1 General Aspects

For a system consists of \( N \) colloidal particle, either if the pair particles be initially bounded or unbounded, we may to use of equation (3.9) of [1] to evaluate the self diffusion coefficient:

\[
D_s = D_0 - (\beta D_0)^2 \lim_{z \to 0} \frac{1}{Z} \int d\vec{r}_1 \cdots d\vec{r}_N \left( \hat{k} \cdot \partial U \right) (z - \hat{\Omega})^{-1} \left( \hat{k} \cdot \partial U \right) >
\]  

(4.1)

The averaging process has defined by:

\[
\langle F(\vec{r}_i) \rangle = \frac{1}{Z} \int d\vec{r}_1 \cdots d\vec{r}_N F(\vec{r}_i) e^{-\beta U(\vec{r}_i)}
\]  

(4.2)

where:

\[
Z = \int d\vec{r}_1 \cdots d\vec{r}_N e^{-\beta U(\vec{r}_i)}
\]  

(4.3)

Thus, up to the first order of concentration we have:

\[
D_s = D_0 - N \left( \frac{\beta D_0}{Z_{12}} \right)^2 \lim_{z \to 0} \int d\vec{r}_1 d\vec{r}_2 \left( \hat{k} \cdot \partial U_{12} \right) (z - \hat{\Omega}_{12})^{-1} \left( \hat{k} \cdot \partial U_{12} \right) e^{-\beta U_{12}}
\]  

(4.4)

where \( U_{12} \) is the two particle potential and the factor \( N \) is because of identical interactions between pair of particles. The normalization factor becomes:

\[
Z_{12} = \int d\vec{r}_1 d\vec{r}_2 e^{-\beta U_{12}}
\]  

(4.5)

We may change the variables \( \vec{r}_1 \) and \( \vec{r}_2 \) to the center of mass coordinates:

\[
\vec{r} = \vec{r}_1 - \vec{r}_2 \\
\vec{R} = \frac{1}{2} (\vec{r}_1 + \vec{r}_2)
\]  

(4.6)

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Hence, for large \( N \) we have:

\[
D_s = D_0 - N \left( \frac{\beta D_0}{Z_{12}} \right)^2 \lim_{z \to 0} \int d\mathbf{\hat{r}} d\mathbf{\hat{R}} (\mathbf{\hat{k}} \cdot \frac{\partial U_{12}}{\partial \mathbf{r}})(z - \mathbf{\hat{\Omega}}_{12})^{-1}(\mathbf{\hat{k}} \cdot \frac{\partial U_{12}}{\partial \mathbf{r}}) e^{-\beta U_{12}}
\]

\[
= D_0 - NV \left( \frac{\beta D_0}{Z_{12}} \right)^2 \lim_{z \to 0} \int d\mathbf{\hat{r}} d\mathbf{\hat{R}} (\mathbf{\hat{k}} \cdot \frac{\partial U_{12}}{\partial \mathbf{r}})(z - \mathbf{\hat{\Omega}}_{12})^{-1}(\mathbf{\hat{k}} \cdot \frac{\partial U_{12}}{\partial \mathbf{r}}) e^{-\beta U_{12}}
\]

(4.7)

For our specific shape of potential (see 1.4), the normalization factor reads:

\[
Z_{12} = \int d\mathbf{\hat{r}} d\mathbf{\hat{R}} e^{-\beta U_{12}}
\]

\[
= V \int d\mathbf{r} e^{-\beta U_{12}}
\]

\[
= 4\pi V \int dr \ r^2 e^{-\beta U_{12}}
\]

\[
= 4\pi V \left[ \int_0^\sigma dr \ r^2 \theta(r - d) e^{\beta V_0} + \int_{r > \sigma} dr \ r^2 \right]
\]

\[
= V \left[ \frac{4\pi}{3} e^{\beta V_0} (\sigma^3 - d^3) + V - \frac{4\pi}{3} \sigma^3 \right]
\]

(4.8)

Let us define \( \gamma \) as:

\[
\gamma = 1 + \frac{4\pi}{3} V (e^{\beta V_0} - 1) - \frac{4\pi}{3} \sigma^3 e^{\beta V_0}
\]

\[
= 1 + v_i (e^{\beta V_0} - 1) - v_0 e^{\beta V_0}
\]

(4.9)

where, \( v_i \) is the ratio of the volume under interaction of one pair particle to the total volume and \( v_0 \) is the ratio of one particle volume to the total volume.

Hence:

\[
Z_{12} = V^2 \gamma
\]

(4.10)

Hence, the self diffusion coefficient reads:

\[
D_s = D_0 - \left( \frac{\beta D_0}{\gamma} \right)^2 c \lim_{z \to 0} \int d\mathbf{\hat{r}} d\mathbf{\hat{R}} (\mathbf{\hat{k}} \cdot \frac{\partial U_{12}}{\partial \mathbf{r}})(z - \mathbf{\hat{\Omega}}_{12})^{-1}(\mathbf{\hat{k}} \cdot \frac{\partial U_{12}}{\partial \mathbf{r}}) e^{-\beta U_{12}}
\]

(4.11)

where, \( c = N/V \) is the concentration of particles. Now, let us concentrate on the integral. The terms in front of the time evolution operator are:

\[
F = (\mathbf{\hat{k}} \cdot \frac{\partial U_{12}}{\partial \mathbf{r}}) e^{-\beta U_{12}}
\]

\[
= (\mathbf{\hat{k}} \cdot \mathbf{r}) \frac{\partial U_{12}}{\partial \mathbf{r}} e^{-\beta U_{12}}
\]

(4.12)
replacing the explicit form of the potential yields:

\[
F = (\hat{k} \cdot \hat{r})\left( \frac{\partial U_H}{\partial r} + \frac{\partial U_0}{\partial r} \right) e^{-\beta U_H - \beta U_0} = (\hat{k} \cdot \hat{r})\left( \frac{\partial U_H}{\partial r} + \frac{\partial U_0}{\partial r} \right) \theta(r - d)e^{-\beta U_H} - \beta U_0
\] (4.13)

As we mentioned before, considering \( \theta(r - d) = e^{-\beta U_H} \) will give:

\[
\delta(r - d) = -\beta \theta(r - d) \frac{\partial U_H}{\partial r}
\] (4.14)

Hence:

\[
F = (\hat{k} \cdot \hat{r})\left[ -\frac{1}{\beta} \theta(r - d) + V_0 \delta(r - \sigma) \right] e^{-\beta U_0}
\] (4.15)

where, we have used:

\[
U_0(r = \sigma) = -V_0 \theta(0) = -\frac{1}{2} V_0
\] (4.16)

The expression has non-vanishing terms at the points \( r = d \) or \( r = \sigma > d \), so it would be harmless if we multiply \( F \) by a step function:

\[
F = -\frac{e^{\beta V_0}}{\beta} (\hat{k} \cdot \hat{r}) \left[ 2\delta(r - d) - \beta V_0 \delta(r - \sigma)e^{-\beta V_0/2} \right]\theta(r - d)
\] (4.17)

the factor 2 on the first term is because of \( \theta(0) = 1/2 \). Now, we can turn back to the equation 4.11:

\[
D_s = D_0 + \frac{\beta D_0^2 e^{\beta V_0}}{\gamma} c \lim_{z \to 0} \int d\vec{r} (\hat{k} \cdot \hat{r}) (\frac{\partial U_{12}}{\partial r}) (z - \hat{\Omega}_{12})^{-1} (\hat{k} \cdot \hat{r}) \left[ 2\delta(r - d) - \beta V_0 \delta(r - \sigma)e^{-\beta V_0/2} \right]\theta(r - d)
\] (4.18)

Now, we can introduce an integration of a delta function over \( \vec{r}_0 \) in front of the time evolution operator:

\[
D_s = D_0 + \frac{\beta D_0^2 e^{\beta V_0}}{\gamma} c \lim_{z \to 0} \int d\vec{r} d\vec{r}_0 (\hat{k} \cdot \hat{r}) (\frac{\partial U_{12}}{\partial r}) (z - \hat{\Omega}_{12})^{-1} \delta(\vec{r} - \vec{r}_0) \left[ 2\delta(r_0 - d) - \beta V_0 \delta(r_0 - \sigma)e^{-\beta V_0/2} \right]\theta(r - d)
\] (4.19)
the last terms is just the Laplace transform of two particle pdf:

\[ \rho(\vec{r}, z|\vec{r}_0) = (z - \Omega_{12})^{-1}\delta(\vec{r} - \vec{r}_0)\theta(r - d) \]  

(4.20)

Hence:

\[ D_s = D_0 + \frac{\beta D_0^2 e^{\beta V_0}}{\gamma} \sum_{l=-\infty}^{\infty} \sum_{m=-l}^{l} \int dr dr_0 \hat{k} \cdot \hat{r}_0 \left( \frac{\partial U_{12}}{\partial r} \right) [2\delta(r_0 - d) - \beta V_0\delta(r_0 - \sigma)e^{-\beta V_0/2}] \rho(\vec{r}, z|\vec{r}_0) \]

Using the fact that:

\[ \hat{k} \cdot \hat{r} = \cos \theta = \sqrt{\frac{4\pi}{3}} Y_{10}(\Omega) = \sqrt{\frac{4\pi}{3}} Y_{10}^*(\Omega) \]

(4.21)

yields:

\[ D_s = D_0 + \frac{4\pi \beta D_0^2 e^{\beta V_0}}{\gamma} \sum_{l=-\infty}^{\infty} \sum_{m=-l}^{l} \int dr dr_0 d\Omega d\Omega_0 \ r^2 r_0^2 Y_{10}(\Omega) Y_{10}^*(\Omega) \left( \frac{\partial U_{12}}{\partial r} \right) [2\delta(r_0 - d) - \beta V_0\delta(r_0 - \sigma)e^{-\beta V_0/2}] \rho(\vec{r}, z|\vec{r}_0) \]

(4.22)

The pdf has a general form of:

\[ \rho(\vec{r}, z|\vec{r}_0) = \theta(r - d) \sum_{l=0}^{\infty} \sum_{m=-l}^{l} Y_{lm}(\Omega) Y_{lm}^*(\Omega_0) \tilde{\rho}_l(r, z|r_0) \]

\[ = \theta(r - d) \sum_{l=0}^{\infty} \sum_{m=-l}^{l} Y_{lm}(\Omega) Y_{lm}^*(\Omega_0) \left[ \tilde{\rho}_l^T(r, z|r_0) + \tilde{\rho}_l^{II}(r, z|r_0) \right] \]

(4.23)

where, \( \tilde{\rho}_l^T \) and \( \tilde{\rho}_l^{II} \) are valid for \( d < r < \sigma \) and \( \sigma < r \) respectively. Thus:

\[ D_s = D_0 + \frac{4\pi \beta D_0^2 e^{\beta V_0}}{\gamma} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \int dr dr_0 d\Omega d\Omega_0 \ r^2 r_0^2 \tilde{\theta}(r - d) \]

\[ Y_{lm}(\Omega) Y_{lm}^*(\Omega_0) \left( \frac{\partial U_{12}}{\partial r} \right) [2\delta(r_0 - d) - \beta V_0\delta(r_0 - \sigma)e^{-\beta V_0/2}] \rho(\vec{r}, z|\vec{r}_0) \]

(4.24)

The orthogonality of \( Y_{lm} \) yields:

\[ D_s = D_0 + \frac{4\pi \beta D_0^2 e^{\beta V_0}}{\gamma} \sum_{l=0}^{\infty} \int dr dr_0 r^2 r_0^2 \tilde{\theta}(r - d) \left( \frac{\partial U_{12}}{\partial r} \right) [2\delta(r_0 - d) - \beta V_0\delta(r_0 - \sigma)e^{-\beta V_0/2}] \tilde{\rho}_l(r, z|r_0) \]

(4.25)

The orthogonality of \( Y_{lm} \) yields:

\[ D_s = D_0 + \frac{4\pi \beta D_0^2 e^{\beta V_0}}{\gamma} \sum_{l=0}^{\infty} \int dr dr_0 r^2 r_0^2 \tilde{\theta}(r - d) \left( \frac{\partial U_{12}}{\partial r} \right) [2\delta(r_0 - d) - \beta V_0\delta(r_0 - \sigma)e^{-\beta V_0/2}] \tilde{\rho}_l(r, z|r_0) \]

(4.26)
Again, the derivation of the potential reads:

\[
\theta(r - d)(\frac{\partial U_{12}}{\partial r}) = \theta(r - d)(\frac{\partial U_H}{\partial r} + \frac{\partial U_0}{\partial r}) \\
= -\frac{1}{\beta} \delta(r - d) + V_0 \theta(r - d) \delta(r - \sigma) \\
= -\frac{1}{\beta} [\delta(r - d) - \beta V_0 \delta(r - \sigma)] \tag{4.27}
\]
Hence:

\[
D_s = D_0 - \frac{4\pi D_0^2 e^{\beta V_0}}{3 \gamma} \lim_{z \to 0} \int dr_0 r_0^2 [2\delta(r_0 - d) - \beta V_0 \delta(r_0 - \sigma)e^{-\beta V_0/2}] \\
[\delta(r - d) - \beta V_0 \delta(r - \sigma)] \hat{\rho}_1(r, z) |_{r_0 = r_0} \\
\]

\[
= D_0 - \frac{4\pi D_0^2 e^{\beta V_0}}{3 \gamma} \lim_{z \to 0} \int dr_0 r_0^2 \\
[2\delta(r_0 - d) - \beta V_0 e^{-\beta V_0/2} \delta(r_0 - \sigma)] [d^2 \hat{\rho}_1(d, z) |_{r_0} - \sigma^2 \beta V_0 \hat{\rho}_1(\sigma, z) |_{r_0}] \\
\]

\[
= D_0 - \frac{4\pi D_0^2 e^{\beta V_0}}{3 \gamma} \lim_{z \to 0} \int [2d^2 \hat{\rho}_1(d, z) - 2d^2 \sigma^2 \beta V_0 \hat{\rho}_1(\sigma, z)] \\
- d^2 \sigma^2 \beta V_0 \hat{\rho}_1(\sigma, z) e^{-\beta V_0/2} + \sigma^4 \beta^2 V_0^2 \hat{\rho}_1(\sigma, z) e^{-\beta V_0/2} \tag{4.28}
\]

Finally, the self diffusion coefficient reads:

\[
D_s = D_0 - \frac{4\pi D_0^2 e^{\beta V_0}}{3 \gamma} \lim_{z \to 0} \int [2d^2 \hat{\rho}_1(d, z) - 2d^2 \sigma^2 \beta V_0 \hat{\rho}_1(\sigma, z = 0)] \\
- 2d^2 \sigma^2 \beta V_0 \hat{\rho}_1(\sigma, z = 0) + \sigma^4 \beta^2 V_0^2 \hat{\rho}_1(\sigma, z = 0) e^{-\beta V_0/2} \tag{4.29}
\]

Note that for \( \beta V_0 = 0 \), the result will reduce to the result which has derived in [1].

### 4.2 Particle Initially Bounded

To evaluate the self diffusion when the particles are initially bounded, it is sufficient to replace expressions 3.80 and 3.97 in the equation 4.29. Note that in equation 4.29, \( \tilde{\rho}_1(d, 0|d) \) and \( \hat{\rho}_1(\sigma, 0|\sigma) \) are correspond only to the particle be initially bounded, while \( \tilde{\rho}_1(d, 0|\sigma) \) and \( \hat{\rho}_1(\sigma, 0|\sigma) \) could be replaced either by solutions of particle initially bounded or unbounded. Furthermore, note that:

\[
\tilde{\rho}_1^{I, Bounded}(d, 0|\sigma) = \tilde{\rho}_1^{I, Unbounded}(d, 0|\sigma) \\
\tilde{\rho}_1^{I, Bounded}(\sigma, 0|\sigma) = \tilde{\rho}_1^{I, Unbounded}(\sigma, 0|\sigma) \tag{4.30}
\]
Finally, the self diffusion coefficient reads:

\[ D_s = D_0 + \frac{\pi}{6} D_0 e^{\beta V_0} c \gamma \left\{ 2d^3 \left( \frac{\beta V_0 (2d^3 - 5\sigma^3)}{\beta V_0 (d^3 + 2\sigma^3) - 3\sigma^3} \right) + \beta V_0 \sigma^3 e^{-\beta V_0 / 2} \left( \frac{\beta V_0 (d^3 + 2\sigma^3) - 3d^3}{\beta V_0 (d^3 + 2\sigma^3) - 3\sigma^3} \right) \right\} \]

where:

\[ \gamma = 1 + \frac{4\pi \sigma^3}{3V} (e^{\beta V_0} - 1) - \frac{4\pi d^3}{3V} e^{\beta V_0} \]

\[ = 1 + v_i (e^{\beta V_0} - 1) - v_0 e^{\beta V_0} \]  

where, \( v_i \) is the ratio of the volume under interaction of one pair particle to the total volume and \( v_0 \) is the ratio of one particle volume to the total volume.

Note that for \( \beta V_0 \to 0 \) as \( \gamma \to 1 \) we have:

\[ D_s = D_0 + \frac{\pi}{6} D_0 c \left( \frac{6d^3 \sigma^3}{3\sigma^3} \right) \]

\[ = D_0 (1 - \frac{\pi d^3}{3} c) \]

which is the self diffusion coefficient of a system with hard-core interaction as was desired. This expression has evaluated in [1]. However, the limit of \( \beta \to 0 \) or equivalently \( T \to \infty \) (here \( T \) is the temperature) for finite potentials (\( V_0 \) being finite, \( \beta V_0 \to 0 \) is valid) could be interpreted that at high temperature the potential hole could not be seen by particles and only the effect of hard-core interaction remains on the particles. This is an expected behavior.

4.3 Particle Initially Unbounded

To evaluate the self diffusion when the particles are initially unbounded, it is sufficient to replace expressions 3.97 in the equation 4.29 which yields:

\[ D_s = D_0 + \frac{\pi}{6} D_0 e^{\beta V_0 / 2} c \gamma \left( \frac{\beta V_0 (d^3 + 2\sigma^3) - 3d^3}{\beta V_0 (d^3 + 2\sigma^3) - 3\sigma^3} \right) \]

where:

\[ \gamma = 1 + \frac{4\pi \sigma^3}{3V} (e^{\beta V_0} - 1) - \frac{4\pi d^3}{3V} e^{\beta V_0} \]

\[ = 1 + v_i (e^{\beta V_0} - 1) - v_0 e^{\beta V_0} \]  

where, \( v_i \) is the ratio of the volume under interaction of one pair particle to the total volume and \( v_0 \) is the ratio of one particle volume to the total volume.
Taking $\beta V_0 \to 0$ and $\sigma \to d$, the result should approach to the case of hard core interaction. However, because in derivation of 4.34 we assumed $d < \sigma$ (and not equal to), this limit should be taken by some cautions. First of all, by putting $\beta V_0 = 0$ the equation 4.29 reads:

$$D_s = D_0 - \frac{4\pi}{3} D_0^2 \frac{c}{\gamma} 2d^4 \tilde{\rho}_1(d, z = 0|d)$$  (4.36)

in order to evaluate $\tilde{\rho}_1(d, z = 0|d)$, we must use expression 3.96 with $\beta V_0 = 0$ and $\sigma = d$:

$$\tilde{\rho}_1^P(d, z|d) = d^2(d + \frac{d^3}{2d^2}) \frac{2\tilde{\rho}_1^P(d, z|d)}{3d^3} + d \partial_r \tilde{\rho}_1^P(d, z|d)$$

$$= \tilde{\rho}_1^P(d, z|d) + \frac{1}{2} d \partial_r \tilde{\rho}_1^P(d, z|d)$$  (4.37)

Replacing from expressions 3.78 yields:

$$\tilde{\rho}_1^P(d, z|d) = \frac{1}{6dD_0} - \frac{d}{24d^2 D_0}$$

$$= \frac{1}{8dD_0}$$  (4.38)

Other hand, for $\beta V_0 = 0$ we have $\gamma = 0$. Hence, the self diffusion coefficient reads:

$$D_s = D_0 - \frac{4\pi}{3} D_0^2 c 2d^4 \frac{1}{8dD_0}$$

$$= D_0(1 - \frac{\pi d^3}{3} c)$$  (4.39)

Same as the self diffusion coefficient of hard core interaction.
References