The Cummings-Stell model of associative fluids: a general solution

J. F. Rojas*

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Abstract

In a series of publications the Cummings-Stell model (CSM), for a binary mixture of associative fluids with steric effects, has been solved analytically using the Percus-Yevick approximation (PYA). The solution consists in a square well potential of width $w$, whose center is placed into the hard sphere shell ($r < \sigma$): at $L = \sigma/n$ ($n = 1, \ldots, 4$). This paper presents a general solution, for any $n$, of the first order Difference Differential Equation (DDE), for the auxiliary Baxter’s function that appears in the CSM, using recursive properties of these auxiliary functions and a matrix composed by differential and shift operators (MDSO). This problem is common in some other models of associative fluids such as the CSM for homogeneous and inhomogeneous mixtures of sticky shielded hard spheres including solvent effects under PYA, and in that of mean-spherical approximation (MSA), for chemical ion association and dipolar dumbbells and polymers. The sticky potential implies a discontinuity step at $L$ in the solution of auxiliary Baxter’s functions so that, one side, $L$ now is arbitrary and, for some additional effects, it can be placed one or more sticky potentials at different positions into the hard shell.

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Contents

1 Introduction

2 The association model: hard spheres with shielded sticky interaction
   2.1 The model of binary mixture
   2.2 Solving for $n = 2$

3 The MDSO
   3.1 The case $n = 2$
   3.2 The more general case $n > 2$

4 The general MDSO
   4.1 The matrix
   4.2 The determinant inverse operator

*Email: frojas@fcfm.buap.mx;
1 Introduction

In 1984 Cummings and Stell [1] proposed a simplified hamiltonian model for a reactive system of two types of homogeneous fluids with the same density and diameter. In this model, type \( A \) and \( B \) molecules, can be associated by means of a selective square interaction that, in the appropriate limits, can be reduced to a sticky Baxter’s potential [2] located inside the hard core at a distance from the center of the particle \( L = \sigma/n \). The cases of \( n = 2, 3, 4 \) for the Baxter’s function have been solved in [1, 3, 4] using the same formalism and, at [5], they apply the results for a pair of reactive fluids and a solvent. Lee and Rasaiah solved the \( L = \sigma/4 \), \( L = \sigma/5 \) and proposed a solution for \( \sigma/n \) for chemical association and dipolar dumbbells [6].

The model of Lee and Rasaiah of association in electrolytes \( A^+ + B^- \rightleftharpoons AB \) is studied in [7]. In this case the authors add a selective coulombian part, \( \pm e^2/r \), out of core, to the associating original CSM.

The sticky site inside the hard core incorporates geometrical conditions of steric saturation in the molecule and this idea is shown, using computational simulations in different ensembles, in ref. [8]. For different bonding length parameters the system allows formation of dimers for small \( L \), chains for \( L \) slightly larger, and vulcanization of species for bonding length values close to the diameter \( \sigma \) of particles. Huerta and Naumis studied the connectivity of a binary mixture using a selectively hard sphere potential and a superposition as [9]:

\[
U_{ij}(r) = U_{ij}^{\text{hd}}(r) + (1 - \delta_{ij})U_{as}(r)
\]

where

\[
U_{ii}^{\text{hd}}(r) = \begin{cases} 
\infty, & r < 1 \\
0, & r > 1 
\end{cases}
\]

\[
U_{ij}^{\text{hd}}(r) = \begin{cases} 
\infty, & r < L - 0.5w \\
D, & L - 0.5w < r < 1 \\
0, & r > 1 
\end{cases}
\]

and

\[
U_{as}(r) = \begin{cases} 
0, & r < L - 0.5w \\
-\varepsilon_{as} - D, & L - 0.5w < r < l + 0.5w \\
0, & r > L + 0.5w, 
\end{cases}
\]

where \( L \) is the bonding distance, \( w \) the intracore square well width and \( i, j \) represents the species in the mixture. The final potential (see Figure 1) is equivalent to the original Cummings-Stell in the adequate limits for sticky approximation.

The same idea is implemented by Pizio and Blum [10] for a hard-sphere fluid with dimerization \( A + A \rightleftharpoons A_2 \). In the development most of the models maintain \( L \) as a parameter (bonding distance) and finally take the case \( L = \sigma/2 \), however some other possibilities are presents having the analytical solution for arbitrary \( L \). Kalyuzhnyi and Stell [11] present a recount of cases for different ranges of the location \( L \). As we show here, the sticky potential into the hard sphere shell produces a discontinuity step in the auxiliary functions of Baxter. This fact allows us to think of systems with more than one sticky site inside the shell or, even, a distribution of sticky wells.

\[\text{It will be detailed in next section.}\]
Figure 1: The image shows the basic form of the potential. Below, their structural effects for different $L$ according to [9].

The vertical dashed arrows show the sense of the Baxter’s sticky limit [1]. The molecular diameter is $\sigma$ and the dashed curves (with labels “AA” and “AB”) corresponds to the colulombian interaction for electrolyte [7].

In the following sections, we first develop the matrix of differential and shift operators MDSO, and its inverse, for the simplest case $n = 2$, followed for the inversion of the MDSO’s for a very general case that corresponds to the set of $n$ DDE’s, to $n$ subintervals of $[0, \sigma]$ and to a sticky location $L = m\sigma/n$. 
2 The association model: hard spheres with shielded sticky interaction

2.1 The model of binary mixture

The statistical mechanical model of chemical reactions of Cummings and Stell [1] represents the association of two species \( A + B \rightleftharpoons AB \), with the same density and diameter, which simplifies the mathematical problem. The potential proposed in the CSM consists of a hard sphere repulsion between like species (\( A-A \) or \( B-B \)) and a mound of width \( \sigma \) with a deep, narrow, and attractive square well, with width \( w \) centred on \( L \). Here \( L < \sigma/2 \) and \( L + w/2 \leq \sigma/2 \) for \( AB \) interactions:

\[
\phi_{AB}/k_B = \begin{cases} 
\epsilon_1 & \text{if } 0 < r < L - w/2 \\
-\epsilon_2 & \text{if } L - w/2 < r < L + w/2 \\
\epsilon_1 & \text{if } L + w/2 < r < \sigma \\
0 & \text{if } r > \sigma 
\end{cases} \tag{1}
\]

The geometric consideration of this model for the \( AB \) interactions ensures steric saturation in the system (there is no formation of \( n \)-mers for \( n \geq 3 \)) due to overlapping. In addition, this model has a solution in the PY approximation, mapping the square well onto an infinitely deep and stretch well like the sticky potential of Baxter [2]. The connection between the Baxter’s original and this model, is obtained equating the second virial coefficients: first it is considered the limit \( \epsilon_1 \to \infty \), \( \epsilon_2 \to \infty \), \( w \to 0 \). The limits of \( \epsilon_2 \to \infty \) and \( w \to 0 \) are taken to maintain tractable the problem in the PY approximation [2]. The limit \( \epsilon_1 \to \infty \) (in the repulsive part: see figure 1) doesn’t change very much the results, but simplifies the solution [3].

The total and direct correlation functions are related by the Ornstein-Zernike (OZ) equation that, for this binary mixture, can be written as [12]

\[
h_{ij}(r) = c_{ij}(r) + \sum_{k=A,B} \rho_{k,0} \int c_{ik}(s)h_{kj}(|r-s|)ds \tag{2}
\]

where the integral is evaluated in the whole space, \( s = ||s|| \), and \( \rho_{k,0} \) is the number density of species \( k \) particles. In the CSM the densities are considered equal.

Briefly reviewing the formulation of the CS model: we need the factorized form of the OZ [13] equations (2) with the PY closures

\[
\begin{align*}
h_{AA}(r) = h_{BB}(r) = -1, & \quad r < \sigma \\
c_{AA}(r) = c_{BB}(r) = 0, & \quad r > \sigma
\end{align*} \tag{3}
\]

and, in the considered limits

\[
\begin{align*}
h_{AB}(r) = -1 + \frac{N}{12} \delta(r - L), & \quad r < \sigma \\
c_{AB}(r) = 0, & \quad r > \sigma
\end{align*} \tag{4}
\]

Given the conditions of the problem, the factorized OZ equations are written [14, 11, 3, 4]

\[
\begin{align*}
rh_{11}(r) &= -q'_{11}(r) + 2\pi \rho \int_0^{\sigma} dt(r-t)[g_{11}(t)h_{11}(|r-t|) + q_{12}(t)h_{12}(|r-t|)] \\
rh_{12}(r) &= -q'_{12}(r) + 2\pi \rho \int_0^{\sigma} dt(r-t)[g_{12}(t)h_{12}(|r-t|) + q_{12}(t)h_{11}(|r-t|)].
\end{align*} \tag{5}
\]
where we changed the index of $h_{AA}$ or $h_{AB}$ to $h_{11}$ or $h_{12}$ respectively. The same for all functions.

Substituting the closure relations (3) and (4) in the set of OZ equations (5), the following system of difference-differential equations (DDE) for the auxiliary Baxter’s functions $q_{ij}(r)$ is obtained:

$$
q_1'(r) + p[q_2(r + L) - q_2(r - L)] = (a_{11} + Da_{12})r + b_{11} + Db_{12} \\
q_2'(r) + p[q_1(r + L) - q_1(r - L)] = (Da_{11} + a_{12})r + Db_{11} + b_{12} - \frac{\lambda L^2}{12} \delta(r - L),
$$

where $p = \pi \rho \lambda \frac{L^2}{6}$ and

$$
a_{ij} = \delta_{ij} - 2\pi \rho \int_0^\sigma q_{ij}(t)dt \\
b_{ij} = 2\pi \rho \int_0^\sigma t q_{ij}(t)dt
$$

and satisfies the boundary conditions

$$q_{11}(\sigma) = q_{12}(\sigma) = 0$$

$$q_{12}(L^-) = q_{12}(L^+) + \frac{\lambda L^2}{12}.$$  

After integration, a step appears in $r = L$ for the auxiliary function $q_{12}(r)$ due to the delta term associated with the well.

**2.2 Solving for $n = 2$**

In the first work of Cummings and Stell [1] a new pair of functions were used and defined as the sum and difference of the originals $q_{11}(r)$ and $q_{12}(r)$. The advantage of this trick is to obtain two uncoupled equations, one for $q_+(r)$ and another for $q_-(r)$ which can be solved in a separate way. If the functions $q_+(r) = q_{11}(r) + q_{12}(r)$ and $q_-(r) = q_{11}(r) - q_{12}(r)$ are defined then, adding and substracting Eqs. (6),

$$q_1'(r) + p[q_1(r + L) - q_1(r - L)] = a_+ r + b_+ - \frac{\lambda L^2}{12} \delta(r - L)$$

and

$$q_2'(r) - p[q_2(r + L) - q_2(r - L)] = a_- r + b_- + \frac{\lambda L^2}{12} \delta(r - L),$$

with the obvious definitions:

$$a_\pm = (1 \pm D) \left[ 1 - 2\pi \rho \int_0^\sigma dt q_\pm(t) \right]$$

and

$$b_\pm = (1 \pm D)2\pi \rho \int_0^\sigma dt t q_\pm(t).$$

The last term in (3) and (4) can be omitted since it is equal to zero in all subintervals except where $r = L = \sigma/n$. This condition is fixed in the boundary conditions (7). In the rest of subintervals, for the general case, must be true that

$$q(m\sigma/n^-) = q(m\sigma/n^+),$$

for $m = 2, 3, \ldots, n - 1$.  

\(^2\text{From [1] D = 1, so that } a_- = b_- = 0. \text{ This not implies changes in the results. We asume this fact in the rest of paper.}\)
We use here $q(r) \equiv q_{11}(r) + q_{12}(r)$. The aim of this proposal is to find an analytical form for the function $q(r)$ assuming that: i) the solution must be made in subintervals, ii) this implies that $q(r)$ will be defined also in subintervals, and iii) the original functions $q_{ij}(r)$ can be recovered: $q_{11}(r) = \frac{q_+(r) + q_-(r)}{2}$ and $q_{12}(r) = \frac{q_+(r) - q_-(r)}{2}$. Identical procedure shows that is sufficient to replace $\lambda \rightarrow -\lambda, p \rightarrow -p, \nu \rightarrow -\nu$ to obtain $q_-(r)$.

3 The MDSO

The cases shown in [1, 3, 4, 6] are solved here using MDSO. For convenience we show the case $L = \sigma/2$ of the CS model in detail, and the cases $L = \sigma/3$ and $L = \sigma/4$ summarized.

3.1 The case $n = 2$

The first case yields the system of coupled differential equations

$$\frac{dq_1(r)}{dr} + pq_2(r + \sigma/2) = ar + b, \quad \text{for } 0 < r < \sigma/2 \tag{11}$$

and

$$\frac{dq_2(r)}{dr} - pq_1(r - \sigma/2) = ar + b, \quad \text{for } \sigma/2 < r < \sigma. \tag{12}$$

where, evidently, $q_1$ corresponds to the first half of the interval and $q_2$ to the second. We define here the differential operator $\mathcal{D}$ as $\mathcal{D}f(x) \equiv \frac{df(x)}{dx}$ and the shift operator $\mathcal{E}^s$ by $\mathcal{E}^s f(x) \equiv f(x \pm s)$. With this operators defined, the set of (11) and (12) can be rewritten as

$$\mathcal{D}q_1(r) + p\mathcal{E}^{\sigma/2}q_2(r) = ar + b$$

and

$$\mathcal{D}q_2(r) - p\mathcal{E}^{-\sigma/2}q_1(r) = ar + b$$

or, in matricial form, as

$$\begin{pmatrix} \mathcal{D} & p\mathcal{E}^{\sigma/2} \\ -p\mathcal{E}^{-\sigma/2} & \mathcal{D} \end{pmatrix} \begin{pmatrix} q_1(r) \\ q_2(r) \end{pmatrix} = \begin{pmatrix} f_1(r) \\ f_2(r) \end{pmatrix}. \tag{13}$$

These equations can be reduced to a symbolic form

$$\mathcal{M}_2 q(r) = f(r) \tag{14}$$

where $\mathcal{M}_2$ is the matrix of differential and shift operators, or MDSO, that appears in (13), applied to the vector $q$ of functions $q_i(r)$. The right side is the vector $f$ of functions $f_i(r)$ that, in this case, are linear functions of $r$. The index in $\mathcal{M}$, corresponds to the number of equations (or partitions in the interval of solution).

The main idea of this paper is to find a solution for the system represented in (14) as

$$q(r) = \mathcal{M}_2^{-1} f(r).$$

This implies the knowledge of an explicit analytical form of the inverse of $\mathcal{M}_2$, and how it operates on $f(r)$. One way of defining the inverse of the differential operator $\mathcal{D}$ is by using the equation

$$y'(x) \pm ay(x) = f(x) \tag{15}$$
or
\[(D \pm a)y(x) = f(x)\]
whose solution leads us to define the inverse operator \((D \pm a)^{-1}\) as
\[(D \pm a)^{-1}f(x) \equiv Ce^{\pm ax} + e^{\pm ax} \int e^{\pm ax'} f(x')dx'.\] (16)

In the previous expression, the case \(a = 0\) implies that the inverse MDSO is reduced to the trivial definition of inverse differential operator as an integral operator. The case where \(a\) is a complex number (or a pure imaginary one) implies harmonic solutions \([16]\) and Fourier transform of the right hand side of differential equation.

Continuing with the case \(L = \sigma/2\), the inverse of \(M_2\) is
\[M_2^{-1} = \frac{1}{\Delta_2} \begin{pmatrix} D & -pE^{-\sigma/2} \\ pE^{\sigma/2} & D \end{pmatrix} \equiv \frac{1}{\Delta_2} \tilde{M}_2\] (17)
where the commutation properties of the operators \(D\) and \(E\) were used. Direct calculation gives the determinant-operator of \(M_2^{-1}\) as
\[\Delta_2 \equiv D^2 + p^2 = (D + ip)(D - ip),\] (18)
so that (17) and (18) define completely the inverse determinant-operator of \(M_2\) as the product of two inverse operators of the form of (16):
\[\frac{1}{\Delta_2} = \Delta_{-1} = \frac{1}{D + ip} \frac{1}{D - ip}.\] (19)

This is the formal inverse determinant of the MDSO, however we still need to find the appropriate coefficients to satisfy the boundary conditions. So that, the direct application of the inverse MDSO, (17), on (11) and (12) gives \([15, 16]\)
\[q_1(r) = A \cos pr + B \sin pr - \frac{\sigma}{p}r + \frac{\alpha}{p^2}(1 - \nu/2) - \frac{b}{p}\]
\[q_2(r) = C \cos pr + D \sin pr + \frac{\sigma}{p}r + \frac{\alpha}{p^2}(1 - \nu/2) + \frac{b}{p}\]
with \(\nu \equiv p\sigma\). Now, considering (17) and the fact of (12) must be satisfied we obtain \([4]\) explicitly,
\[q_1(r) = A \cos pr + B \sin pr - \frac{\sigma}{p}r + \frac{\alpha}{p^2}(1 - \nu/2) - \frac{b}{p}\]
\[q_2(r) = A \sin p(r - \sigma/2) + B \cos p(r - \sigma/2) + \frac{\sigma}{p}r + \frac{\alpha}{p^2}(1 - \nu/2) + \frac{b}{p}\] (20)
which agree exactly with the results in \([1]\). The second equation, now has the same set of constants that the first. The harmonic functions have been interchanged and their arguments are shifted by \(-\sigma/2\).

\[3\text{The application of inverse shifting operators is the identity: } E^sE^{-s}f(x) = E^sf(x + s) = f(x + s - s) = f(x).\]

\[4\text{This fact allows us to establish the same set of constants for the harmonic part of the solution.}\]
3.2 The more general case \( n > 2 \)

In the case \( L = \sigma/3 \) there are three equations:\(^5\)

\[
\begin{align*}
\frac{dq_1(r)}{dr} + pq_2(r + \sigma/3) &= ar + b, \text{ for } 0 < r < \sigma/3 \\
\frac{dq_2(r)}{dr} + pq_3(r + \sigma/3) - pq_1(r - \sigma/3) &= ar + b, \text{ for } \sigma/3 < r < 2\sigma/3 \\
\frac{dq_3(r)}{dr} - pq_2(r - \sigma/3) &= ar + b, \text{ for } 2\sigma/3 < r < \sigma
\end{align*}
\]  

(21)

with the MDSO given as

\[
M_3 = \begin{pmatrix}
\mathcal{D} & pE^{\sigma/3} & 0 \\
-pE^{-\sigma/3} & \mathcal{D} & pE^{\sigma/3} \\
0 & -pE^{-\sigma/3} & \mathcal{D}
\end{pmatrix}
\]

and the inverse operator of \( M_3 \)

\[
M_3^{-1} = \frac{1}{\mathcal{D}(\mathcal{D}^2 + 2p^2)} \begin{pmatrix}
\mathcal{D}^2 + p^2 & -pE^{\sigma/3} & p^2E^{2\sigma/3} \\
-pDE^{-\sigma/3} & \mathcal{D}^2 & -pDE^{\sigma/3} \\
p^2E^{-2\sigma/3} & pDE^{\sigma/3} & \mathcal{D}^2 + p^2
\end{pmatrix}
\]

where

\[
\Delta_3 = \frac{1}{\mathcal{D}(\mathcal{D}^2 + 2p^2)} = \frac{1}{(D - 0)} \frac{1}{(D + i\sqrt{2}p)} \frac{1}{(D - i\sqrt{2}p)}
\]

and\(^6\)

\[
\tilde{M}_3 = \begin{pmatrix}
\mathcal{D}^2 + p^2 & -pE^{\sigma/3} & p^2E^{2\sigma/3} \\
-pDE^{-\sigma/3} & \mathcal{D}^2 & -pDE^{\sigma/3} \\
p^2E^{-2\sigma/3} & pDE^{\sigma/3} & \mathcal{D}^2 + p^2
\end{pmatrix}
\]  

(22)

Obviously \( \frac{1}{\Delta_3} \) is a product of inverse operators in the form of (16). Applying these to the right hand side of (21) we obtain, directly

\[
q_1(r) = A_1 \cos \sqrt{2}pr + B_1 \sin \sqrt{2}pr + \frac{a}{2}r^2 - \frac{a}{2p}(1 - 2\nu/3)r + br + F_1
\]

\[
q_2(r) = A_2 \cos \sqrt{2}pr + B_2 \sin \sqrt{2}pr + F_2
\]

\[
q_3(r) = A_3 \cos \sqrt{2}pr + B_3 \sin \sqrt{2}pr + \frac{a}{2}r^2 + \frac{a}{2p}(1 - 2\nu/3)r + br + F_3
\]

and, imposing bound conditions in the respective subintervals and the fact of (21) must be satisfied (as in (20) for \( n = 2 \)), we obtain \( A_2, A_3, B_2 \) and \( B_3 \) in terms of \( A_1 \) and \( B_1 \)

\[
q_1(r) = A_1 \cos \sqrt{2}pr + B_1 \sin \sqrt{2}pr + \frac{a}{2}r^2 - \frac{a}{2p}(1 - 2\nu/3)r + br
\]

\(^5\)The first and last equations always have one term less, due to the condition of PYA, \( q(r) = 0 \) out of \([0, \sigma]\).

\(^6\)With this we are defining \( M_n^{-1} = \frac{1}{\Delta_n}M_n \).
\begin{align*}
q_2(r) &= \sqrt{2}A_1 \sin \sqrt{2}p (r - \sigma/3) + \sqrt{2}B_1 \cos \sqrt{2}p (r - \sigma/3) \\
q_3(r) &= -A_1 \cos \sqrt{2}p (r - 2\sigma/3) - B_1 \sin \sqrt{2}p (r - 2\sigma/3) + \frac{a}{2}r^2 + \frac{a}{2p} (1 - 2\nu/3)r + br.
\end{align*}

The case \( L = \sigma/4 \) has a tridiagonal matrix \( \mathcal{M}_4 \), whose determinant \( \Delta_4 = D^4 + 3D^2p^2 + p^4 \) has roots \( \pm i\sqrt{\frac{5-1}{2}}p \) and \( \pm i\sqrt{\frac{5+1}{2}}p \) so that

\[
\Delta_4 = \left[ D + i\sqrt{\frac{5-1}{2}}p \right] \left[ D - i\sqrt{\frac{5-1}{2}}p \right] \left[ D + i\sqrt{\frac{5+1}{2}}p \right] \left[ D - i\sqrt{\frac{5+1}{2}}p \right].
\]

Lee and Rasaiah, in [6], called these roots \( x = \sqrt{\frac{5-1}{2}}p \) and \( y = \sqrt{\frac{5+1}{2}}p \), and correspond to the \( \alpha_k \)'s defined below in this paper.

The case \( n = 5 \) or \( L = \sigma/5 \) has a determinant \( \Delta_5 = D^5 + 4D^3p^2 + 3Dp^4 \) whose roots are \( 0, \pm ip, \pm i\sqrt{3}p \), and the solutions have the same structure as (20) and (23), and that showed in [1, 3, 4, 5].

4 The general MDSO

4.1 The matrix

Making the same construction for \( n \) divisions in the solution interval, one obtains \( n \) functions \( q_i \) that represent a continuous solution. Each of them must be such that

\[
q_i'(r) + p[q_{i+1}(r + \sigma/n) - q_{i-1}(r - \sigma/n)] = ar + b, \text{ for } \frac{i-1}{n}\sigma < r < \frac{i}{n}\sigma
\]

where \( i = 1, 2, 3, \ldots, n \) and \( q_0 = q_{n+1} = 0 \), in which

\[
q_i(r) = \begin{cases} 
  q(r), & \frac{i-1}{n}\sigma < r < \frac{i}{n}\sigma \\
  0, & \text{otherwise}.
\end{cases}
\]

The generalized MDSO for arbitrary \( n \) has the form tridiagonal

\[
(\mathcal{M}_n)_{ij} = \begin{cases} 
  D & \text{for } i = j \\
  pE^{\sigma/n} & \text{for } i = j-1 \\
  -pE^{-\sigma/n} & \text{for } i = j+1 \\
  0 & \text{otherwise}
\end{cases}
\]

or, in matrix form

\[
\mathcal{M}_n = \begin{pmatrix}
  D & pE^s & 0 & 0 & \ldots & 0 \\
  -pE^{-s} & D & pE^s & 0 & \ldots & 0 \\
  0 & -pE^{-s} & D & pE^s & \ldots & 0 \\
  \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\
  0 & 0 & \ldots & \ldots & -pE^{-s} & D \\
  0 & 0 & 0 & 0 & -pE^{-s} & D
\end{pmatrix}
\]

Due to symmetry of \( \mathcal{M}_n \) the shift operators are mutually canceled in the inverse of \( \Delta_n \). This fact enables us to put all solutions \( q_i(r) \) in terms of inverse differential operators of the form [16] and [19].
4.2 The determinant inverse operator

From the tridiagonal matrix obtained, (26), the determinants for different values of $n$ can be evaluated:

\[
\begin{align*}
\Delta_0 &= 1 \\
\Delta_1 &= D \\
\Delta_2 &= D^2 + p^2 \\
\Delta_3 &= D^3 + 2Dp^2 \\
\Delta_4 &= D^4 + 3D^2p^2 + p^4 \\
\Delta_5 &= D^5 + 4D^3p^2 + 3Dp^4 \\
\Delta_6 &= D^6 + 5D^4p^2 + 6D^2p^4 + p^6 \\
\cdot &\cdot \\
\Delta_{14} &= D^{14} + 13D^{12}p^2 + 66D^{10}p^4 + 165D^8p^6 + 210D^6p^8 + 126D^4p^{10} + \\
&\quad + 28D^2p^{12} + p^{14} \\
\Delta_{15} &= D^{15} + 14D^{13}p^2 + 78D^{11}p^4 + 220D^9p^6 + 330D^7p^8 + 252D^5p^{10} + \\
&\quad + 84D^3p^{12} + 8Dp^{14} \\
\cdot &\cdot \\
\end{align*}
\]

It is easy to prove that the recurrence relation between determinants of MDSO’s of different order is, for $n \geq 2$,

\[
\Delta_n = D\Delta_{n-1} + p^2\Delta_{n-2}
\]  (27)

where $\Delta_1 = D$ and $\Delta_0 = 1$. The index of $\Delta_n$ corresponds to the order of the MDSO. From this recurrence relation we obtain the general expression for $\Delta_n$:

\[
\Delta_n = D^n + \sum_{j=1}^{m} \frac{n-j}{{j!}^2} \prod_{k=j}^{j-1} (n-k)
\]

which, finally, can be reduced to

\[
\Delta_n = \sum_{j=0}^{m} \binom{n-j}{j} D^{n-2j}p^{2j}
\]  (28)

where, additionally

\[
\Delta_n = \prod_{k=1}^{n} (D - x_k).
\]  (29)

In these expressions $m = \lfloor n/2 \rfloor$ is the integral part of $n/2$. In (29) we have written $\Delta_n$ in factorized polynomial form. Here $x_k$ are all the $n$ roots of $\Delta_n$ which are all pure imaginary and proportional to $p$. When $n$ is even there are exactly $m = n/2$ pairs of complex conjugated roots $5 \pm i\alpha_k p$ and, if $n$ is odd, there is a further null root of $\Delta_n$, which requires an additional integration to obtain the $q_i$ functions.

\footnote{This was proved for $n = 1, 2, \ldots, 26.$}
We can write \( \Delta_n \), with \( m \) as defined above, as

\[
\Delta_n = \begin{cases} 
\prod_{k=1}^{m} D_k^2 & \text{for } n \text{ even} \\
D_0 \prod_{k=1}^{m} D_k^2 & \text{for } n \text{ odd}
\end{cases}
\]  

(30)

where we define \( D_k^2 \equiv (\mathcal{D} - x_k)(\mathcal{D} - \bar{x}_k) \) and \( x_k \equiv i\alpha_k p \). Also, \( \bar{x}_k \) is the complex conjugate of \( x_k \), \( \alpha_k \) is a real number, and \( D_0 \) is the operator associated with the root \( x_0 = 0 \) for \( n \) odd.

Direct application of individual inverse \( D_k^2 \) on a linear function gives

\[
D_k^{-2}(cr + d) = A_k \cos s_k r + B_k \sin s_k r + \frac{1}{s_k^2}(cr + d).
\]  

(31)

Same as before, \( s_k \) is defined by mean of \( x_k \equiv is_k \equiv i\alpha_k p \) and \( D_k^{-2} \equiv (D_k^2)^{-1} \). In the general case, a partition \( n \) even of the interval \([0, \sigma]\) results in

\[
D_1^{-2}D_2^{-2} \ldots D_m^{-2}(cr + d) = \sum_{k=1}^{m} A_k \cos s_k r + B_k \sin s_k r + \frac{1}{\prod_{k=1}^{m} s_k^2}(cr + d).
\]  

(32)

It is easy to see that if we define the vectorial function \( \mathbf{v}(r) \), using the definition in (17) or (22), as the application of \( \mathcal{M}_n \) to the vector \( \mathbf{f}(r) \),

\[
\mathbf{v}(r) = \mathcal{M}_n \mathbf{f}(r),
\]

we obtain a linear function \( \mathbf{v}(r) \). The general solution of the system of equations become

\[
\mathbf{q}(r) = \frac{1}{\Delta_n} \mathbf{v}(r)
\]

where

\[
\mathbf{q}(r) = \begin{pmatrix} 
q_1(r) \\
q_2(r) \\
\vdots \\
q_n(r)
\end{pmatrix},
\]

and \( q_i(r) \) is as defined in (23). The constants \( A_i \) and \( B_i \) that appears in (32) can be stablished from bound conditions at the frontiers of the subintervals given by (7) and (10) and the recurrence stablished in the original set of equations.

5 Discussion

A general solution of the set of DDE’s for the original CS model has been discussed here. It requires the roots of the polinomial expresion for the inverse determinant \( \Delta_{n-1} \) which always are of the form \( is_k p \) with \( s_k \) a real number. One of the advantages of this method is the fact that it allows to choose the site of the sticky potential, not only at \( L = \sigma/n \) for a few values of \( n \): the solution is valid for any \( n \). It allows to change the sticky potential site to positions more and more close to (or

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8The harmonic part comes from the inverse determinant.
away of) the center of the particle. For example in the case \( n = 3 \) the step of discontinuity \( \lambda L^2/12 \) can be defined at \( L = \sigma/3 \) or at \( L = 2\sigma/3 \).

This fact bring us the possibility to set the well at \( r = m\sigma/n \) to obtain different molecular structures \([9]\): by locating the step \( \lambda L^2/12 \) in the site of sticky and represent a step discontinuity in the solution at the position \( L = m\sigma/n \). With this in mind one can think, also, the possibility of two or more sticky square wells into the hard shell.

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