Yukawa Fluids in the Mean Scaling Approximation: III New Scales

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In recent work a general solution of the Ornstein Zernike equation for a general Yukawa closure for a single component fluid was found. Because of the complexity of the equations a simplifying assumption was made, namely that the main scaling matrix \( \Gamma \) had to be diagonal. While in principle this is mathematically correct, it is not physical because it will violate symmetry conditions when different Yukawas are assigned to different components. In this work we show that by using the symmetry conditions the off diagonal elements of \( \Gamma \) can be computed explicitly for the case of two Yukawas, and that although the solution is different than in the diagonal case, the excess entropy is formally the same as in the diagonal case. Analytical expressions for the Laplace transforms of the pair distribution functions are derived.

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I. INTRODUCTION

There are many problems of practical and academic interest that can be formulated as closures of some kind of either scalar or matrix Ornstein-Zernike (OZ) equation. These closures can always be expressed by a sum of exponentials, which do form a complete basis set if we allow for complex numbers \([1, 2]\).

While the initial motivation was to study simple approximations like the Mean Spherical (MSA) or Generalized Mean Spherical Approximation (GMSA), the availability of closed form solutions for the general closure of the hard core OZ equation makes it possible to write down analytical solutions for any given approximation that can be formulated by writing the direct correlation function \( c(r) \) outside the hard core as

\[
c(r) = \sum_{n=1}^{M} K^{(n)} e^{-\gamma_{n} (r-\sigma) / r} = \sum_{n=1}^{M} K^{(n)} e^{-\gamma_{n} r / r}
\]

In this equation \( K^{(n)} \) is the interaction/closure constant used in the general solution first found by Blum and Hoye (which we will call BH78) \([2]\), while \( \mathcal{K}^{(n)} \) is the definition used in the later general solution by Blum, Vericat and Herrera (BVH92 in what follows) \([3]\). In this work we will use the more common notation of BVH92. The case of factored interactions discussed by Blum, \([2]\) was simplified by Ginoza \([11, 12, 13]\) who found that as in the case of electrolytes \([14]\) the solution of the one exponent case could be expressed in terms of a single scaling parameter \( \Gamma \). In the factorizable case we have

\[
K^{(n)} = K^{(n)} \delta^{(n)}_{i} \delta^{(n)}_{j} \quad \mathcal{K}^{(n)} = K^{(n)} d^{(n)}_{i} d^{(n)}_{j}
\]

where we have defined

\[
\delta^{(n)}_{i} = d^{(n)}_{i} e^{-\gamma_{n} \sigma_{i} / 2}
\]

The general solution of this problem was formulated in by Blum, Vericat and Herrera \([3]\) in terms of a scaling matrix \( \Gamma \). The full solution was given recently by Blum et al. \([1, 15, 16]\). For only one component the matrix \( \Gamma \) was assumed to be diagonal diagonal and explicit expressions for the closure relations for any arbitrary number of Yukawa exponents \( M \) were obtained. The solution is then remarkably simple in the MSA since then explicit formulas for the thermodynamic properties are obtained.

The diagonal assumption is however not correct for mixtures, even if they are of the same hard core diameter. In this work we use the symmetry relations to calculate explicitly the off diagonal terms of \( \Gamma \) in the 1 component, 2 yukawa case.

II. SUMMARY OF PREVIOUS WORK

We study the Ornstein-Zernike (OZ) equation

\[
h_{ij}(12) = c_{ij}(12) + \sum_{k} \int d3h_{ik}(13) \rho_{k} c_{kj}(32)
\]

where \( h_{ij}(12) \) is the molecular total correlation function and \( c_{ij}(12) \) is the molecular direct correlation function, \( \rho_{i} \) is the number density of the molecules \( i \), and \( i = 1, 2 \)
is the position \( \vec{r}_i \), \( r_{12} = |\vec{r}_1 - \vec{r}_2| \) and \( \sigma_{ij} \) is the distance of closest approach of two particles \( i, j \). The direct correlation function is

\[
c_{ij}(r) = \sum_{n=1}^{M} R_{ij}^{(n)} e^{-z_n(r-\sigma_{ij})}/r, \quad r > \sigma_{ij} \tag{5}
\]

and the pair correlation function is

\[
h_{ij}(r) = g_{ij}(r) - 1 = -1, \quad r \leq \sigma_{ij} \tag{6}
\]

We use the Baxter-Wertheim (BW) factorization of the OZ equation

\[
[I + \rho \tilde{H}(k)] [I - \rho \tilde{C}(k)] = I \tag{7}
\]

where \( I \) is the identity matrix, and we have used the notation

\[
\tilde{H}(k) = 2 \int_0^\infty dr \cos(kr)J(r) \tag{8}
\]

\[
\tilde{C}(k) = 2 \int_0^\infty dr \cos(kr)S(r) \tag{9}
\]

The matrices \( J \) and \( S \) have matrix elements

\[
J_{ij}(r) = 2\pi \int_r^\infty ds h_{ij}(s) \tag{10}
\]

\[
S_{ij}(r) = 2\pi \int_r^\infty ds c_{ij}(s) \tag{11}
\]

\[
[I - \rho \tilde{C}(k)] = [I - \rho \tilde{Q}(k)] [I - \rho \tilde{Q}^T(-k)] \tag{12}
\]

where \( \tilde{Q}^T(-k) \) is the complex conjugate and transpose of \( \tilde{Q}(k) \). The first matrix is non-singular in the upper half complex \( k \)-plane, while the second is non-singular in the lower half complex \( k \)-plane.

It can be shown that the factored correlation functions must be of the form

\[
\tilde{Q}(k) = I - \rho \int_{\lambda_{ji}}^{\infty} dr e^{ikr} \tilde{Q}(r) \tag{13}
\]

where we used the following definition

\[
\lambda_{ji} = \frac{1}{2} (\sigma - \sigma_i) \tag{14}
\]

Similarly, from Eq. (12) and Eq. (7) we get, using the analytical properties of \( Q \) and Cauchy’s theorem

\[
J(r) = Q(r) + \int dr_1 J(r-r_1)\rho Q(r_1) \tag{16}
\]

The general solution is discussed in [3, 11], and yields

\[
q_{ij}(r) = q_{ij}^0(r) + \sum_{n=1}^{M} D_{ij}^{(n)} e^{-z_n r} \lambda_{ji} < r \tag{17}
\]

\[
q_{ij}^0(r) = \frac{1}{2} A [(r - \sigma/2)^2 - (\sigma_i/2)^2] + \beta [r - \sigma/2] - (\sigma_i/2) + \sum_{n=1}^{M} C_{ij}^{(n)} e^{-z_n \sigma/2} r - e^{-z_n \sigma_i/2}], \lambda_{ji} < r < \sigma_{ij} \tag{18}
\]

From here

\[
X_i^{(n)} - \sigma_i \phi_0(z_n \sigma_i) \Pi_i^{(n)} = \delta_{i}^{(n)} - \frac{1}{2} \sigma_i \phi_0(z_n \sigma_i) \sum_{\ell} \rho_{\ell} \beta_{\ell} X_{\ell}^{(n)} - \sigma_i^2 z_n^2 \psi_1(z_n \sigma_i) \Delta^{(n)} \tag{19}
\]

or

\[
\sum_{\ell} \rho_{\ell} \left\{ -\tilde{J}_{i\ell}^{(n)} \Pi_{\ell}^{(n)} + \tilde{\phi}_{\ell i}^{(n)} X_{\ell}^{(n)} \right\} = \delta^{(n)} \tag{20}
\]

A. The Laplace Transforms

From Eq. (10) we obtain the Laplace transform of the pair correlation function

\[
2\pi \sum_{\ell} \tilde{g}_{\ell i}(s)[\delta_{ij} - \rho e \tilde{g}_{ij}(is)] = \tilde{q}_{ij}^0(is) \tag{21}
\]

where

\[
\tilde{q}_{ij}^0(is) = \int_{\sigma_{ij}}^{\infty} dr e^{-sr}[q_{ij}^0(r)]' \tag{22}
\]

The Laplace transform of Eqs. (17) and (18) yields

\[
e^{s \lambda_{ji}} \tilde{g}_{ij}(is) = \sigma_i^2 \psi_1(s \sigma_i) A_j + \sigma_i^2 \phi_1(s \sigma_i) \beta_j + \sum_{m} \frac{1}{s + z_m} \left[ C_{ij}^{(m)} D_{ij}^{(m)} e^{-z_m \lambda_{ji}} - C_{ij}^{(m)} e^{-z_m \sigma_j} z_m \sigma_i \phi_0(s \sigma_i) C_{ij}^{(m)} e^{-z_m \sigma_j} \right] \tag{23}
\]
This result will be used below.
Another important relation deduced from Eq. [22] by setting
\[ s = z_n \]
is
\[ -\Pi_j^{(n)} = \sum_m \tilde{M}_{nm} a_j^{(n)} \]  \hspace{1cm} (24)
where
\[ \tilde{M}_{nm} = \frac{1}{z_n + z_m} \sum_\ell \rho_\ell \left[ X_\ell^{(m)} (z_m X_\ell^{(m)} - \Pi_\ell^{(m)}) + X_\ell^{(m)} \Pi_\ell^{(n)} \right] \]

\[ (25) \]

III. THE GENERAL CLOSURE

The closure relation (BVH92 [3]) is, for only one component
\[ 2\pi K \delta^{(n)} / z_n + a^{(n)} \mathcal{F}^{(n)} - \sum_m \frac{1}{z_n + z_m} \rho a^{(n)} a^{(m)} \]
\[ \left[ \mathcal{F}^{(m)} (z_m X^{(m)} - \mathcal{F}^{(m)} X^{(m)}) \right] = 0 \]  \hspace{1cm} (26)
For the one component case this simplifies to
\[ \sum_m \left\{ 2\pi K \delta_{nm} + z_n A^{(nm)} + \frac{z_n}{z_n + z_m} [\rho a^{(n)} a^{(m)}] \right\} X^{(m)} = 0 \]
\[ (27) \]
This can also be written as
\[ 2\pi K \rho [X^{(n)}]^2 + z_n \rho a^{(n)} X^{(n)} \]
\[ + \sum_m \frac{z_n}{z_n + z_m} [\rho a^{(n)} a^{(m)}] \left[ \rho X^{(m)} X^{(n)} \right] = 0 \]  \hspace{1cm} (28)
which is the desired expression. This equation simplifies to
\[ 2\pi \rho K_n \left[ X^{(n)} \right]^2 + z_n \beta^{(n)} \left[ 1 + \sum_m \frac{1}{z_n + z_m} \beta^{(m)} \right] = 0 \]
\[ (29) \]
where \( \beta^{(n)} \) is
\[ \beta^{(n)} = \rho X^{(n)} a^{(n)} \]  \hspace{1cm} (30)

IV. SYMMETRY

In this section we will summarize and extend our previous analysis of the most general scaling relation [5] for the multiyukawa closure of the Ornstein Zernike equation. We have
\[ \Pi_i^{(n)} = -\sum_m \Gamma_{nm} X_i^{(m)} \]  \hspace{1cm} (31)
where \( \Gamma_{nm} \) is the \( M \times M \) matrix of scaling parameters. This matrix is not uniquely defined by the MSA closure relations and must be supplemented by \( M(M-1) \) equations obtained from symmetry requirements for the correlations. From the symmetry of the direct correlation function at the origin, Eq. (13)
\[ q_{ij}(\lambda_{ji}) = q_{ji}(\lambda_{ij}) \]
we write
\[ a_i^{(n)} = \sum_m \Lambda_{nm} X_i^{(m)} \]  \hspace{1cm} (33)
where, as was shown in reference [5], \( \Lambda \) must be a symmetric matrix.

From the symmetry of the contact pair correlation function Eq. (10) we get
\[ \{ q_{ij}(\sigma_{ij}) = q_{ji}(\sigma_{ij}) \} \implies \{ q_{ij}(\sigma_{ij})' = q_{ji}(\sigma_{ij})' \} \]  \hspace{1cm} (34)
which are
\[ \sum_n (\Pi_i^{(n)} - z_n X_i^{(n)}) a^{(n)} = \sum_n (\Pi_i^{(n)} - z_n X_i^{(n)} a^{(n)} ) \]
\[ (35) \]
from which we get the scaling relation
\[ \Pi_i^{(n)} = z_n X_i^{(n)} = \sum_m \Upsilon_{nm} a_i^{(m)} \]  \hspace{1cm} (36)
and a new set of \( M(M-1)/2 \) symmetry relations
\[ \Upsilon_{mn} = \Upsilon_{nm} \]  \hspace{1cm} (37)
Furthermore, using the scaling relations we get
\[ \tilde{M} \cdot \Lambda = \Gamma \]  \hspace{1cm} (38)
where the matrix \( \tilde{M} \) (see Eq. [24]) has elements
\[ [\tilde{M}]_{nm} = \frac{1}{s_{nm}} \sum_\ell \rho_\ell \left[ X_\ell^{(n)} (z_m X_\ell^{(m)} - \Pi_\ell^{(m)}) + X_\ell^{(m)} \Pi_\ell^{(n)} \right] \]
\[ (39) \]
Solving these equations yields the relations
\[ \tilde{M}^{-1} \cdot \Gamma = \Lambda \]  \hspace{1cm} (40)
and
\[ -(I + z \cdot \Gamma^{-1}) \cdot \tilde{M} = \Upsilon \]  \hspace{1cm} (41)
Both \( \Upsilon \) and \( \Lambda \) must be symmetric matrices. We have therefore a total of \( M(M-1) \) symmetry relations, which together with the \( M \) closure equations give the required equations for the \( M^2 \) elements of the matrix \( \Gamma \).
The symmetry requirements are more explicitly
\[ \Gamma \cdot \tilde{M}^T = \tilde{M} \cdot \Gamma^T \]  \hspace{1cm} $S I$ (42)
and
\[ (I + z \cdot \Gamma^{-1}) \cdot \tilde{M} = \tilde{M}^T \cdot (I + [\Gamma^{-1}]^T \cdot z) \]  \hspace{1cm} $S I I$ (43)
the matrix \( \tilde{M} \) as
\[ \tilde{M} = \frac{1}{2} \tilde{D} + \frac{1}{2} \tilde{M}^A \]  \hspace{1cm} (44)
and
\[ \tilde{M} = \frac{1}{2} \tilde{D} + \frac{1}{2} \tilde{M}^A \]  \hspace{1cm} (44)
\[
[\tilde{M}^A]_{nm} = \frac{1}{s_{nm}} \sum_{\ell} \rho_{\ell} \left[ X_{\ell}^{(n)} (z_m X_{\ell}^{(m)} - 2 \Pi_{\ell}^{(m)}) - (z_n X_{\ell}^{(n)} - 2 \Pi_{\ell}^{(n)}) X_{\ell}^{(m)} \right]
= \frac{-1}{z_n + z_m} \sum_{p} \rho \left[ X_{(n)}^{(p)} (z_m \delta_{pm} + 2 \Gamma_{np}) - (z_n \delta_{pm} + 2 \Gamma_{np}) X_{(m)}^{(p)} \right]
\]

where
\[
\alpha_{nm} = \frac{2 \rho}{z_n + z_m} \sum_{p} \left[ \Gamma_{mp} X_{(p)}^{(m)} - \Gamma_{np} X_{(m)}^{(p)} \right]
\]
and
\[
\gamma_{nm} = \frac{2 \Gamma^{(nn)} + z_n - 2 \Gamma^{(mm)} - z_m}{z_m + z_n}
\]

The second symmetry condition Eq. (48) is
\[
\tilde{M}^A = \Gamma^{-1} \cdot \tilde{M} \cdot z \cdot \tilde{M}^T \cdot [\Gamma^T]^{-1}
\]

V. THE 2 YUKAWA CASE: SYMMETRIC MATRIX RESULTS

We write equation (44) in matrix form (16)
\[
-\tilde{\Pi}_i = \tilde{M} \cdot \tilde{a}_i
\]

where
\[
\tilde{X}_i = \begin{bmatrix} X_{i}^{(1)} \\ X_{i}^{(2)} \end{bmatrix}, \quad \tilde{\Pi}_i = \begin{bmatrix} \Pi_{i}^{(1)} \\ \Pi_{i}^{(2)} \end{bmatrix}, \quad \tilde{a}_i = \begin{bmatrix} a_{i}^{(1)} \\ a_{i}^{(2)} \end{bmatrix}
\]

Using the symmetry relation eq. (42) we get
\[
\left( \frac{\Gamma^{(12)} X_{(2)}^{(1)} - \Gamma^{(21)} X_{(1)}^{(2)}}{X_{(1)}^{(2)}} \right) = \frac{s_2 \chi_2}{2} (\chi_{12} - \gamma_{12})
\]

with
\[
\chi_{12} = \frac{z_1 - z_2}{z_1 + z_2 + 2 \Gamma^{(11)} + 2 \Gamma^{(22)}}
\]
\[
\gamma_{12} = \frac{z_1 - z_2 + 2 \Gamma^{(11)} - 2 \Gamma^{(22)}}{z_1 + z_2}
\]
in eq. (49) we can write
\[
\tilde{M} = \rho \begin{bmatrix} X_{(1)} & 0 \\ 0 & X_{(2)} \end{bmatrix} \begin{bmatrix} 1 & 1 - \chi_{12} \\ 1 + \chi_{12} & 1 \end{bmatrix} \begin{bmatrix} X_{(1)} & 0 \\ 0 & X_{(2)} \end{bmatrix} = \rho \left[ X_{1}^{(1)} - \frac{2 \chi_{12}}{s_2} + 2 \Gamma^{(22)} \right] + \Gamma^{(22)} (z_2 + \Gamma^{(22)}) = 0
\]

We rewrite eq. (55) as
\[
2 \begin{bmatrix} G^{(1)} \\ G^{(2)} \end{bmatrix} = \begin{bmatrix} 1 & 1 - \chi_{12} \\ 1 & 1 \end{bmatrix} \begin{bmatrix} \beta^{(1)} \\ \beta^{(2)} \end{bmatrix}
\]

Here we have defined
\[
G^{(1)} = \Gamma^{(11)} + \frac{X_{(2)}^{(1)} \Gamma^{(12)}}{X_{(1)}^{(2)}}, \quad G^{(2)} = \Gamma^{(22)} + \frac{X_{(1)}^{(1)} \Gamma^{(21)}}{X_{(2)}^{(1)}}
\]

If we also define
\[
2G^{(s)} = G^{(1)} + G^{(2)}; \quad 2G^{(12)} = G^{(1)} - G^{(2)}
\]
then we can solve eq. (55)
\[
2G^{(s)} = 2 \beta_s + \beta_{12}; \quad 2G^{(12)} = -\beta_s \chi_{12}
\]
or
\[
\beta_s = -\frac{2G^{(12)}}{\chi_{12}}; \quad \beta_{12} = \frac{2}{\chi_{12}} \left[ G^{(s)} + \frac{G^{(12)}}{\chi_{12}} \right]
\]

From the second symmetry condition Eq. (63) we get
\[
\frac{X_{(2)}^{(1)} z_1 \Gamma^{(12)} - X_{(1)}^{(1)} z_2 \Gamma^{(21)} - 2 \Gamma^{(12)} \Gamma^{(21)} \chi_{12} + 2 \tau_{12} = 0}
\]

where
\[
\tau_{12} = \frac{2 \Gamma^{(11)} (z_1 + \Gamma^{(11)}) - z_1 \Gamma^{(22)} (z_2 + \Gamma^{(22)})}{z_1 + z_2 + 2 \Gamma^{(11)} + 2 \Gamma^{(22)}}
\]

We remark also that
\[
\tau_{12} = \frac{1}{2} \left[ z_2 \Gamma^{(11)} (1 + \chi_{12}) - z_1 \Gamma^{(22)} (1 - \chi_{12}) \right] + \chi_{12} \Gamma^{(11)} \Gamma^{(22)}
\]

in Eq. (60) we get
\[
\frac{X_{(2)}^{(1)} z_1 \Gamma^{(12)} - X_{(1)}^{(1)} z_2 \Gamma^{(21)} + 2 \chi_{12} D_\Gamma}{z_1 + z_2 + 2 \Gamma^{(11)} + 2 \Gamma^{(22)}} + [z_2 \Gamma^{(11)} (1 + \chi_{12}) - z_1 \Gamma^{(22)} (1 - \chi_{12})] = 0
\]

Using now eq. (51) we can write
\[
\tilde{M} = \rho \begin{bmatrix} X_{(1)} & 0 \\ 0 & X_{(2)} \end{bmatrix} \begin{bmatrix} 1 & 1 - \chi_{12} \\ 1 + \chi_{12} & 1 \end{bmatrix} \begin{bmatrix} X_{(1)} & 0 \\ 0 & X_{(2)} \end{bmatrix} = \rho \left[ X_{1}^{(1)} - \frac{2 \chi_{12}}{s_2} + 2 \Gamma^{(22)} \right] + \Gamma^{(22)} (z_2 + \Gamma^{(22)}) = 0
\]
VI. THERMODYNAMICS BY PARAMETER INTEGRATION

We will use the notation and results of Blum and Hernando [1]. We recall that

\[ J^{(n)} \Pi^{(n)} = \mathcal{I}^{(n)} X^{(n)} - \delta^{(n)} \]  

(77)

Remember that

\[ X^{(n)} = \gamma^{(n)} + \hat{J}^{(n)} \hat{B}(z_n) \]  

(78)

Here

\[ \hat{J}^{(n)} = \delta \sigma \phi_0(z_n \sigma) - 2 \rho \beta^0 \sigma^3 \psi_1(z_n) \]  

(79)

and

\[ \gamma^{(n)} = \delta^{(n)} - \frac{2 \beta^0}{z_n} \sum \rho \delta^{(n)} (1 + \frac{z_n \sigma}{2}) \]  

(80)

The total excess internal energy is

\[ \frac{E(\beta)}{kT V} = \sum_n K_n \left\{ \rho \delta^{(n)} \hat{B}^{(n)} \right\} \]  

(81)

From eqs(31) we show that

\[ -\Pi^{(n)} = G^{(n)} X^{(n)} \]  

(82)

where \( G^{(n)} \) is a (generally algebraic) function of the coefficients \( \beta \equiv \{ \beta_1, \beta_2, \ldots \} \). In fact in eq(77)

\[ \delta^{(n)} = \sum_m |\mathcal{M}^{nm}| X^{(m)} \]  

\[ = \sum_m \{ \mathcal{I}^{(n)} \delta_{nm} + J^{(n)} \Gamma^{(nm)} \} X^{(m)} \]  

\[ = \mathcal{I}^{(n)} X^{(n)} + J^{(n)} \sum_m \Gamma^{(nm)} X^{(m)} \]  

\[ = \{ \mathcal{I}^{(n)} + J^{(n)} G^{(n)} \} X^{(n)} \]  

(83)

with

\[ G^{(n)} = \sum_m \Gamma^{(nm)} \frac{X^{(m)}}{X^{(m)}} \]  

(84)

For the 1 component case we get

\[ X^{(n)} = \frac{\hat{\delta}^{(n)}}{\mathcal{I}^{(n)} + G^{(n)} \hat{J}^{(n)}} \]  

(85)

Then, since the 'charge' parameters are constants at constant temperature, the derivative of \( \hat{B}^{(n)} \) with respect to the scaling parameter \( G^{(n)} \) is

\[ \left[ \frac{\partial \hat{B}^{(n)}}{\partial G^{(n)}} \right] = \left[ J^{(n)} \right]^{-1} \left\{ \partial \left( \frac{X^{(n)}}{G^{(n)}} \right) \right\} \]  

\[ = - \left[ J^{(n)} \right]^{-1} \left\{ \frac{G^{(n)} J^{(n)}}{\mathcal{I}^{(n)} + G^{(n)}} \right\} \]  

(86)
where we use the fact that $\mathcal{J}^{(n)}$ is independent of $G^{(n)}$. The desired energy derivative Eq. (81) are

$$\frac{\partial E}{\partial G^{(m)}} = -\rho[X^{(n)}]^2 \tag{87}$$

or

$$\frac{\partial E}{\partial G^{(nm)}} = -\sum_n \rho[X^{(n)}]^2; \tag{88}$$

The integrability condition is satisfied since

$$\frac{\partial^2 E}{\partial G^{(m)} \partial G^{(n)}} = \frac{\partial^2 E}{\partial G^{(n)} \partial G^{(m)}} = \delta_{nm} \left[ 2\rho[X^{(n)}]^2 \frac{\mathcal{J}^{(n)}}{\mathcal{F}^{(n)} + G^{(n)} \mathcal{J}^{(n)}} \right] \tag{89}$$

We use now Eq. (90) to obtain

$$\frac{\partial E}{\partial G^{(s)}} = \frac{1}{2} \left[ \beta_s^2 + s_{12} \beta_s + z_{12} \beta_{12} \right] = \tag{90}$$

and

$$\frac{\partial E}{\partial G^{(12)}} = \frac{1}{2} \left[ \beta_s (\beta_s + s_{12}) + z_{12} \beta_s + \frac{z_{12}}{s_{12}} \left( \beta_s^2 - \beta_{12}^2 \right) \right] = \tag{91}$$

Thermodynamic integration of these equations leads to

$$\Delta S = -\frac{k}{2\pi} ?? \tag{93}$$

different from that obtained using the diagonal $\Gamma$ assumption, the resulting entropy is identical to this case when proper reference states are used [4].

Although the derivation of this equation is completely