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CLASSICAL BINARY DISTRIBUTION FUNCTION FOR THE CHEMICAL MODEL OF AN ELECTROLYTE SOLUTION

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The aim of the present work is to derive an analytical expression for the binary distribution function for ions in the dilute electrolyte solution represented in a chemical model in which allowance is made for the existence of bound states between ions of various species.

Key Words: Binary Distribution Function; Chemical Model; Electrolyte; Debye-Hückel Theory; Bogoliubov-Green-Yvon and Kirkwood (BBGKY) Hierarchy

Introduction

Many attempts have been made to study the structure of electrolyte solutions. Debye-Hückel adopted the theory of ionic solutions which was studied in same details as in [1] and [2], where ions were assumed to be charged points (charged point model. Other theoretical treatments have extended the Debye-Hückel theory to more concentrated solutions. Debye-Hückel were among the first to adopt the point of view discussed in [2], [3], [4] and [5]. They suggested that ions are charged hard spheres and the solution is replaced by a dielectric continuum (primitive model). Wheaton introduced a series of studies[6-11] concerning electrolyte solutions and plasma. His technique was based on the so-called chemical model (CM) in which each j-ion in a solution is represented by a rigid charged sphere of characteristic radius a_j surrounded by a solvent shell of width $(b_j - a_j)$ and dielectric constant D. The central ion plus this solvent shell has an effective dynamical radius. b_j. The solvated ion is further surrounded by a cosphere of radious R_j which is referred to as the domain of the ion. Using Wheaton's model, an analytical expression for the distribution function analogous to Bogoliubov's density expansion for the molecular distribution function[12] could be derived.

Real Electrolyte Solution

For the real system, where ions are assumed to interact with each other and every i and j-ion have ionic domains $R_d = R_i = R_j$. $R = R_i + R_j = 2R_d$, $R = R_{ji}$ (average distance between ions of kind i and j). The present work reports such a study for a system contained in volume V with a total of N elementary ions. Let N_1, N_2, ..., N_s represent the number of ions of species a_1, a_2, ..., a_3 respectively. The concentrations of species a_1, a_2, ..., a_s are denoted by n_1, n_2, ..., n_s (ion cm^{-3}), respectively, and the corresponding valences Z_1, Z_2, ..., Z_s. These valences may be either positive or negative, since the total charge must be zero.

Then

$$\sum_{i}^{s} n_i z_i = 0 \qquad \ldots (1)$$

where $\sum_{i}^{s}$ denotes the sum over these ion species.

BBGKY Hierarchy

The hierarchy of equations, due to Bogoliubov-Green-Yvon and Kirkwood is discussed in detail eleswhere. For a solution containing a total of V ions, the probability density function $D_N(r, ..., r_N)$ is such that

$$\int_{v} \ldots \int_{v} D_N(r_1, ..., r_n)\, \mathrm{d}r_1, ..., \mathrm{d}r_N = 1\,, \qquad \ldots (2)$$

where

$$D_N(r_1, ..., r_N = \exp[-U(r_1, r_2, ..., r_N)\beta]/Q_N)(r_1, ..., r_N) \qquad \ldots (3)$$

and Q_N denotes the configurational integral:

$$Q_N = \int_{v} \ldots \int_{v} \mathrm{d}r_N \exp[-\beta U_N(r_1, ..., r_N)];\ \beta = 1/KT. \qquad \ldots (4)$$

Assume that the potential average force U_N can be represented by a sum of pairs of potentials ψ_{ji}. Then

$$U_N(r_1, r_2, ..., r_N) = \sum_{1 \le j < i < N} \psi_{ji}(r_{ik})\,. \qquad \ldots (5)$$

The pair of potentials ψ_{ji} may be written as

$$\psi_{ji} = e_1\, e_j/Dr_{ji} + V'_{ji}(r_{ji})\,, \qquad \ldots (6)$$

where $(e_i e_j/Dr_{ji})$ is the long range potential, D is the dielectric constant pure solvent and V'_{ji} is the short range potential. Let us now go back to eq. (4), from which the distribution function is defined by

$$F_{a_1, ..., a_\nu}(r_1, ..., r) = V^N / Q_N \exp[-\beta U_N]\mathrm{d}r_{\nu+1}, ..., \mathrm{d}r_N \qquad \ldots (7)$$

By differentiating (7) with respect to r_k and after some manipulations, the hierarchy of equations takes the form

$$\nabla_n F_{a_1, ..., a_\nu}(r_1, ..., r_n) + \beta F_{a_1, ..., a_\nu}(r_1, ..., r_n) \nabla_k \left(\sum_{1 \le j < i < \nu} \psi_{a_j a_i} \right)$$

$$+ \beta_a \sum_{\nu+1} n_{a_{\nu+1}} \int \nabla_k (\psi_{a_1 a_{\nu+1}}) F_{a_1, ..., a_{\nu+1}} = 0\,. \qquad \ldots (8)$$

Owing to the chemical model[6,7] the short range potential is

$$v'_{ji} \simeq 0 \text{ for } r > R_{ji};\ r = r_{ji}. \qquad \ldots (9)$$

Inside the region $r = R_{ji}$, the distribution function for free i and j ions becomes

$$F_{ji}(r) = 0 \text{ for } r \leq R_{ji} = R_j + R_i, \qquad \ldots (10)$$

and all functions are written as power series in plasma parameter ε; $\varepsilon = e^2/\text{TDK}$, where $1/X$ = Debye-radius and e is the absolute value of the charge of an ion. It is shown that the binary distribution function for ions in a solution[8-10] is

$$F_{ji}(x,\eta) = \exp[z_j z_i H(x, T)\varepsilon] + T_{(x,\eta,\varepsilon)},\ x = Xr, \qquad \ldots (11)$$

where

$$T^* = \sum_{n=2}^{\infty} L_{ji}^{(n)}(x, \eta)\, \varepsilon^n,\ \eta = XR \qquad \ldots (12)$$

and

$$L_{ji}^{(n)} = H_{ji}^{(n)} - (z_j z_i)^n H^{(n,1)};\ H^{(n,1)} = \frac{1}{n!}(H^{(1)})^n \qquad \ldots (13)$$

Some Statistical Considerations

The distribution function in the hierarchy[12] is

$$F_{\alpha_1,\ldots,\alpha_\nu}(x_1, \ldots, x_n) = \prod_{n=1}^{\nu-2} \left\{ \left[\prod_{a_1,\ldots,a_{\nu-n}}^{\nu} F_{a_1,\ldots,a_{\nu-n}}(x_1,\ldots,x_{\nu-n}) \right]^{(-1)^{n-1}} . C_{\alpha_1,\ldots,\alpha_\nu}(x_1,\ldots,x_\nu) \right\}, \qquad \ldots (14)$$

where $C_{\alpha_1,\ldots,\alpha_\nu}$ represents the deviation from a general superposition principle.

For $\nu = 3$, (14) becomes.

$$F_{jik}(x, x_{13}, x_{23}) = F_{ji}(x)\, F_{ik}(x_{13}) F_{ik}(x_{23}) C_{jik}(x, x_{13}, x_{23}) \qquad \ldots (15)$$

for $\nu = 4$, (14) is reduced to:

$$F_{jikl} = F_{ji} F_{jk} F_{jl} F_{ik} F_{il} F_{kl} \left\{ \prod_{n=1}^{2} \left(\prod_{a_1 \ldots > a_{5-n}}^{\nu=4} C_{a_1,\ldots,a_{5-n}}(x_1, \ldots, x_{5-n}) \right) \right\} \qquad \ldots (16)$$

where

$$C_{jik} C_{jil} C_{jkl} C_{ikl} C_{jikl} = \prod_{n=1}^{2} \left(\prod_{a_n \ldots \geq a_1}^{\nu=4} C_{a_1,\ldots,a_{5-n}}(x_1, \ldots, x_{5-n}) \right) \qquad \ldots (17)$$

Similar relations can be obtained for $\nu = 4, 5, \ldots$, etc.
In general, we can reformulate equation (14) to take the form

$$F_{\alpha_1,\ldots,\alpha_\nu}(x_1,\ldots,x_\nu)=\left(\prod_{1\le j<i<\nu}^{\nu} F_{\alpha_j\alpha_i}\right)\left(\prod_{n=1}^{\nu-2}\left[\prod_{\alpha_1\ldots\ge\alpha_{\nu-n+1}}^{\nu} C_{\alpha_1,\ldots,\alpha_{\nu-n+1}}(x_1,\ldots,x_{\nu-n+1})\right]\right). \quad \ldots(18)$$

We shall assume that

$$G_{\alpha_1,\ldots,\alpha_\nu}(x_1,\ldots,x_\nu)=\prod_{n=1}^{\nu-2}\prod_{\alpha_1\ldots\ge\alpha_{\nu-n+1}}^{\nu} C_{\alpha_1,\ldots,\alpha_{\nu-n+1}}.(x_1,\ldots,x_{\nu-n+1}), \quad \ldots(19)$$

provided that the new correlation function $G_{\alpha_1,\ldots,\alpha_\nu}(x_1,\ldots,x_\nu)$ satisfies the boundary conditions that will be discussed below. Since $G_{\alpha_1,\ldots,\alpha_\nu}(x_1,\ldots,x_\nu)$ can be written as a power series in plasma parameter, it follows from equation, (19) that

$$G_{\alpha_1,\ldots,\alpha_\nu}(x_1,\ldots,x_\nu)=\prod_{n=0}^{\infty} G^{(n)}_{\alpha_1,\ldots,\alpha_\nu}(x_1,\ldots,x_\nu)\varepsilon^n,\ G^{(0)}_{\alpha_1,\ldots,\alpha_\nu}=1 \quad \ldots(20)$$

Formation of the general equation that will be used to derive the new terms $G_{\alpha_1,\ldots,\alpha_\nu}(x_1,\ldots,x_\nu)$.

Using "BBGKY hierarchy" and substituting (19) into (18), we obtain

$$F_{\alpha_1,\ldots,\alpha_\nu}(x_1,\ldots,x_\nu)=\left(\prod_{1\le j<i\le\nu}^{\nu} F_{\alpha_j\alpha_i}\right)G_{\alpha_1,\ldots,\alpha_\nu}(x_1,\ldots,x_\nu) \quad \ldots(21)$$

Combining (11) and (21) yields

$$F_{\alpha_1,\ldots,\alpha_\nu}(x_1,\ldots,x_\nu)=\left(\prod_{1\le j<i\le\nu}[\exp(z_{\alpha_j}z_{\alpha_i}H(x,\eta)\varepsilon)+T_{\alpha_j\alpha_i}(x,\eta,\varepsilon)]\right)G_{\alpha_1,\ldots,\alpha_\nu} \quad \ldots(22)$$

which may be written as

$$F_{\alpha_1,\ldots,\alpha_\nu}(x_1,\ldots,x_\nu)=\left(\exp\sum_{1\le j<i\le\nu}H^{(1)}_{\alpha_j\alpha_i}\varepsilon\right)\left(\prod_{1\le j<i\le\nu}[1+T_{\alpha_j\alpha_i}\exp(H^{(1)}_{\alpha_j\alpha_i}\varepsilon)]\right)$$
$$G_{\alpha_1,\ldots,\alpha_\nu}(x_1,\ldots,x_\nu), \quad \ldots(23)$$

where

$$\exp\left(\sum_{1\le j<i\le\nu}H^{(1)}_{\alpha_j\alpha_i}\varepsilon\right)\left(\prod_{1\le j<i\le\nu}[1+T_{\alpha_j\alpha_i}\exp(-H^{(1)}_{\alpha_j\alpha_i}\varepsilon)]\right)$$
$$=\prod_{1\le j<i\le\nu}[\exp(z_{\alpha_i}z_{\alpha_i}H(x,\eta)\varepsilon)+T_{\alpha_j\alpha_i}(x,\eta,\varepsilon)], \quad \ldots(24)$$

and

$$H^{(1)}_{\alpha_j \alpha_i}(x, \eta) = z_{\alpha_j} z_{\alpha_i} H^{(1)}(x, \eta). \quad \ldots (25)$$

In terms of Deby-length X, plasma parameter (ε) and density $n_{\nu+1}$ BBGKY hierarchy of equation (8) becomes

$$\nabla_1 F_{\alpha_1, \ldots, \alpha_\nu}(x_1, \ldots, x_\nu) + \varepsilon F_{\alpha_1, \ldots, \alpha_\nu}(x_1, \ldots, x_\nu) \nabla_1 \left(\sum_{1 \le j < i \le \nu} \phi_{\alpha_j \alpha_i} \right)$$
$$+ \frac{1}{\chi^3} \sum_{\nu+1} n_{\nu+1} \varepsilon \int \nabla_1 \phi_{1, \nu+1} F_{\alpha_1, \ldots, \alpha_{\nu+1}}(x_1, \ldots, x_{\nu+1}) \mathrm{d}x_{\nu+1} = 0, \quad \ldots (26)$$

where

$$\beta \psi_{ji}(r) = \varepsilon \phi_{ji}(\mathrm{x}) = \varepsilon z_j z_i (1/x) \quad \ldots (27)$$

for a pair of ions i and j, .. eq. (24) reduces to

$$\nabla_1 F_{ji}(x) + \varepsilon F_{ji}(x) \nabla_i \phi_{ji} + \frac{\varepsilon}{\chi^3} \sum_K n_k \int \nabla_1 \phi_{ji}(x_{13}) F_{jik}(x, x_{13}, x_{23}) \mathrm{d}x_3 = 0 \quad \ldots (28)$$

Owing to wheaton's assumption[10], all functions are written as power series in plasma parameter (ε), where

$$F_{ji}(x) = \sum_{n=1}^{\infty} H^{(n)}_{ji}(x) \varepsilon^n \quad \ldots (29)$$

$$F_{jik}(x, x_{13}, x_{23}) = \sum_{n=1}^{\infty} H^{(n)}_{jik}(x, x_{13}, x_{23}) \varepsilon^n, \quad \ldots (30)$$

Substituting (29) and (30) into (28) we obtain

$$\sum_{n=0}^{\infty} \varepsilon^n \{ \nabla_1 H^{(n)}_{ji}(x) + H^{(n-1)}_{ji}(x) \nabla_i \phi_{ji}(x) \} + \frac{1}{\chi^3} \sum_k n_k \int \nabla_1 \phi_{ik}(x_{13}) H^{(n-1)}_{jik}$$
$$\times (x, x^{13}, x_{23}) \mathrm{d}x_3 \} = 0 \quad \ldots (31)$$

which may be written explicitly, as

$$\sum_{n=0}^{\infty} f^{(n)}_{ji}(x) \varepsilon^n = 0, \quad \ldots (32)$$

where

$$f_{ji}(\mathrm{x}) = \nabla_1 H^{(n-1)}_{ji}(x) + H^{(n-1)}_{ji}(x) \nabla_i \phi_{ji}(x) + \frac{1}{\chi^3} \sum_k n_k \int \nabla_1 \phi_{jk}(x_{13})$$
$$\times H^{(n-1)}_{jik}(x, x_{13}, x_{23}) \mathrm{d}x_3 = 0. \quad \ldots (33)$$

Using the assumption that

$$H_{ji}^{-1}(x) = H_{jik}^{-1}(x, x_{13}, x_{23}) = 0\,, \qquad \ldots (34)$$

eq. (33) reduces, when $n = 1$, to

$$\nabla_1 H_{ji}^{(1)}(x) + \nabla_1 \phi_{ji}(x) = 0\,, \qquad \ldots (35)$$

where

$$\frac{1}{\chi^3} \sum_k n_k \int \nabla_1 \phi_{jk}(x_{13})\, \mathrm{d}x_3 = 0\,, [see \text{ eq. } (27)]\,. \qquad \ldots (36)$$

Using the conditions that $H_{ji}^{(1)}(\infty) = 0$, the solution of the first order differential equation takes the form

$$H_{ji}^{(1)}(x) = -\phi_{ji}(x)\,,$$

and

$$\varepsilon H_{ji}^{(1)}(x) = -\varepsilon\phi_{ji}(x) = -\beta\psi_{ji}(r)\,[\text{see eq. } (27)]\,. \qquad \ldots (37)$$

Substituting the results of (24) and (37) into (26) we obtain the final form

$$\nabla_k \left\{ G_{\alpha_1, \ldots, \alpha_\nu}(x_1, \ldots, x_\nu) \left(\prod_{1 \le j < i \le \nu} [1 + T_{\alpha_i \alpha_i} \exp(-H_{\alpha_j \alpha_i}^{(1)} \varepsilon)] \right) \right\}$$
$$- \frac{1}{\chi^3} \sum_{\nu+1} n_{\nu+1} \int \nabla_k \left(\exp \sum_{1 \le j < i \le \nu} H_{\alpha_j \alpha_i}^{(1)} \varepsilon \right)$$
$$\times \left(\prod_{1 \le j < i \le \nu} [1 + T_{\alpha_i \alpha_i} \exp(-H_{\alpha_j \alpha_i}^{(1)} \varepsilon)] \right) . G_{\alpha_1, \ldots, \alpha_{\nu+1}}(x_1, \ldots, x_{\nu+1}) . \mathrm{d}x_{\nu+1} = 0. \qquad \ldots (38)$$

Eq. (38) is the principal equation from which $G_{\alpha_1, \ldots, \alpha_\nu}(x_1, \ldots, x_\nu)$ will be calculated.

1. *Condition satisfied by $L_{ji}^{(n)}$ and $H_{ji}^{(n)}$*

The boundary conditions satisfied by $L_{ji}^{(n)}$ are based on wheaton's assumption. From Equation (13), the following condition is defined.

$$H^{(0,1)} = \frac{1}{0!} [H^{(1)}(x)]^{(0)} = 1\,. \qquad \ldots (39)$$

Consequently,

$$L_{ji}^{(0)} = H_{ji}^{(0)} = (z_j z_i)\, H^{(0,1)} = 0 \,. \qquad \ldots (40)$$

The quantity $H_{ji}^{(1)}(x)$ is already investigated[8]. In terms of charge coefficient, it takes the form

$$H_{ji}^{(1)}(x) = z_j z_i H^{(1)}(x) \,, \qquad \ldots (41)$$

where

$$H^{(1)}(x) = \frac{e^{\eta}}{1+\eta}(e^{-x}/x) \,. \qquad \ldots (42)$$

For $n = 1$, (13) becomes

$$L_{ji}^{(1)} = H_{ji}^{(1)} - Z_j Z_i \; H_{ji}^{(1,1)} = 0 \,. \qquad \ldots (43)$$

Now, (13) can be rewritten as

$$T = \sum_{n=2}^{\infty} L_{ji}^{(n)}(x, \eta)\varepsilon^n = \sum_{n=0} L_{ji}^{(n)}(x, \eta)\varepsilon^n \qquad \ldots (44)$$

$$T(\infty, \eta) = H_{ji}^{(n)}(\infty, \eta) - (Z_j Z_i)^n \, H^{(n,1)}(\infty, \eta) = 0 \,. \qquad \ldots (45)$$

II. *Conditions satisfied by* $G_{\alpha_1, \ldots, \alpha_n}(x_1, \ldots, x_\nu)$

The boundary conditions satisfied[9] by G_{jik} can be generalized to take the general form which are discussed by Falkenhagen[2], where

$$G_{\alpha_1, \ldots, \alpha_\nu}(x_1, \ldots, x_\nu) \to 1 \text{ when } |x_j - x_i| \to \infty \qquad \ldots (46)$$

and

$$G_{\alpha_1, \ldots, \alpha_\nu}^{(n)}(x_1, \ldots, x_\nu) = 0 \text{ when } |x_j - x_i| \to \infty \text{ for } n \geq 1 \,,$$

where

$$C_{\alpha_1, \ldots, \alpha_\nu}^{(0)}(x_1, \ldots, x_\nu) = 1 \text{ when } |x_j - x_i| \to \infty \qquad \ldots (47)$$

The Method

The solution of equation (38) requires a knowledge of $G_{\alpha_1, \ldots, \alpha_{\nu+1}}(x_1, \ldots, x_{\nu+1})$ to derive an expression for $G_{\alpha_1, \ldots, \alpha_\nu}(x_1, \ldots, \alpha_\nu)$. This problem can be simplified by solving (38) for 2-ions j and i, 3-ions, j, i and k individually, and so with respect to 4-ions, j, i, k and l, ... etc.

I. *Two Ions Correlation Function* $G_{ji}(x)$

Substituting $\nu = 2$ into (38) and considering the gradient in (38) with respect to X_1, we obtain

$$\nabla_1 G_{ji}(x) + \nabla_1 (T'_{ji} G_{ji}(x) \exp(-H_{ji}^{(1)} \varepsilon)) - \frac{1}{\chi^3} \sum_k n_k \nabla_1 \left(\text{ex} \right) \sum_{1 \le i \le \nu} H_{i,\nu+1}^{(1)} \varepsilon \Bigg)$$

$$\times [(1 + T'_{ji} \exp(-H_{ji}^{(1)} \varepsilon).(1 + T'_{jk} \exp(-H_{ji}^{(1)}{}_{jk} \varepsilon))(1 + T'_{ik} \exp(-H_{ik}^{(1)} e))] G_{ijk}$$

$$\times (x, x_{13}, x_{23}) \mathrm{d}x_3 = 0 . \qquad \ldots (48)$$

In a manner analagous to Cauchy's method, we can write

$$\nabla_1 \left(\exp \sum_{1 < i < \nu} H_{a_i a_i}^{(1)} \varepsilon \right) G_{jik}(x, x_{13}, x_{23}) = \sum_{n=0}^{\infty} \sum_{y=0}^{n} \nabla_1 \left(\frac{\sum_{1 \le i \le \nu} H_{a_1 a_{\nu+1}}^{(1)}}{y!} \right) G_{jik}^{(n-y)} \varepsilon^n , \qquad \ldots (49)$$

where

$$G_{jik}(x, x_{13}, x_{23}) = \sum_{m=0}^{\infty} G_{jik}^{(m)} \varepsilon^m ; \; G_{jik}^{(0)} = 1 \qquad \ldots (50)$$

Similarly.

$$T_{ji} G_{ji}(x) \exp(-H_{ji}^{(1)} \varepsilon) = \sum_{n=0}^{\infty} \sum_{u=0}^{n} \sum_{y=0}^{u} \frac{(-H_{ji}^{(1)})^y}{y!} G_{ji}^{(y-y)} L_{ji}^{(u-u)} \varepsilon^n , \qquad \ldots (51)$$

$$\left[\nabla_1 \exp \sum_{1 \le i \le \nu} H_i^{(1)}, + 1\varepsilon \right] [T_{ji} \exp(-H_{ji}^{(1)} \varepsilon)] G_{jik} = \sum_{n=0}^{\infty} \sum_{\nu=0}^{n} \sum_{u=0}^{\nu} \sum_{y=0}^{u} \nabla_i$$

$$\times \frac{\left(\sum_{1 \le i \le \nu^*} H_{a_i a_{\nu-1}}^{(1)} \right)^y}{y!} \cdot G_{jik}^{(u-y)} L_{ji}^{(\nu-u)} \frac{(-H_{ji}^{(1)})^{(n-\nu)}}{(n-\nu)!} \qquad \ldots (52)$$

The combination of (49), (51), (52) and (48) gives

$$\sum_{n=0}^{\infty} \varepsilon^n \left\{ \nabla_1 F_{ji}^{(n)}(x) + \nabla_1 \left[\sum_{u=0}^{n} \sum_{y=0}^{u} \frac{(-H_{ji}^{(1)})^y}{y!} G_{ji}^{(u-y)} L_{ji}^{(n-u)} \right] - \frac{1}{\chi^3} \sum_k n_k \right.$$

$$\times \int \left(\sum_{\nu=0}^{n} \nabla_1 \frac{\left(\sum_{1 \le i \le \nu} H_{a_i a_{\nu-1}} \right)^y}{y!} G_{jik}^{(n-y)} + \sum_{\nu=0}^{n} \sum_{u=0}^{\nu} \sum_{y=0}^{u} \nabla_1 \frac{\left(\sum_{1 \le i \le \nu} H_{a_i a_{\nu-1}}^{(1)} \right)^{(y)}}{y!} \right.$$

$$\left. \left. G_{jik}^{(u-y)} \left(\sum_{1 \le j < i \ge \nu} L_{a_i a_i}^{(\nu-u)} \frac{(-H_{a_i a_i}^{(1)})}{(n-\nu)!} \right)^{n-\nu} + \ldots \right) \mathrm{d}x_3 \right\} = 0 , \qquad \ldots (53)$$

which may be written as

$$\sum_{n=0}^{\infty} L_{ji}^{(n)}(x)\varepsilon^n = 0. \qquad \ldots(54)$$

where

$$L_{ji}^{(n)} = \nabla_1 G_{ji}^{(n)} + \nabla_1 \left[\sum_{u=0}^{n} \sum_{y=0}^{u} \frac{(-H_{ji}^{(1)})^{(y)}}{y!} G_{ji}^{(u-y)} L_{ji}^{(n-u)} \right] - \frac{1}{\chi^3} \sum_k n_k$$

$$\times \int \left(\sum_{n=0}^{n} \nabla_1 \frac{\left(\sum_{1 \le i \le \nu} H(1)_{a_i a_{\nu-1}} \right)^{(y)}}{y!} G_{jik}^{(n-y)} \right)$$

$$+ \sum_{\nu=0}^{n} \sum_{u=0}^{\nu} \sum_{y=0}^{u} \Delta_1 \frac{\left(\sum_{1 \le i \le \nu} H_{a_i a_{\nu-1}}^{(1)} \right)^{(y)}}{y!} G_{jik}^{(u-y)} \left(\sum_{1 \le j < i \ge \nu} L_{a_\nu a_i}^{(\nu-u)} \right.$$

$$\left. \times \frac{(-H_{a_i a_i}^{(1)})^{(n-\nu)}}{(n-\nu)!} + \ldots \right) \mathrm{d}x_3 = 0 \qquad \ldots(55)$$

Thus an infinite set of integro-differential is obtained

$$L_{ji}^{n}(x) = 0, \text{ where } n = 0 \to \infty \qquad \ldots(56)$$

Examining (55), for $n = 1,2,3$ and 4, gives the following equations

$$\nabla_1 G_{ji}^{(1)} - \frac{1}{\chi^3} \Sigma n_k \int \nabla_1 \left(\sum_{1 \le i \le \nu}^{\nu=2} H_{a_i a_{\nu-1}}^{(1)} \right) \mathrm{d}x_3 = 0 \qquad \ldots(57)$$

$$\nabla_1 G_{ji}^{(2)} + \nabla_1 L_{ji}^{(2)} - \frac{1}{\chi^3} \sum_k n_k \int \left[G_{jik}^{(1)} \nabla_1 \left(\sum_{1 \le j \le i\nu}^{\nu=2} H_{a_i a_{\nu-1}}^{(1)} \right) \right.$$

$$\left. + \frac{1}{2!} \nabla_1 \left(\sum_{1 \le i \le \nu} H_{a_i a_{\nu-1}}^{(1)} \right)^2 \right] \mathrm{d}x_3 = 0 \qquad \ldots(58)$$

$$\nabla_1 G_{ji}^{(3)} + \nabla_1 [L_{ji}^{(3)} - H_{ji}^{(1)} L_{ji}^{(2)} + G_{ji}^{(1)} L_{ji}^{(2)}] - \frac{1}{\chi^3} \sum_k n_k \int \left[G_{jik}^{(2)} \nabla_1 \left(\sum_{1 \le i \le \nu}^{\nu=2} H_{a_i a_{\nu-1}}^{(1)} \right) \right.$$

$$+ \frac{1}{2!} G_{jik}^{(1)} \nabla_1 \left(\sum_{1 \le i \le \nu}^{\nu=2} H_{a_i a_{\nu-1}}^{(1)} \right)^2 + \frac{1}{3!} \nabla_1 \left(\sum_{1 \le i \le \nu}^{\nu=2} H_{a_i a_{\nu-1}}^{(1)} \right)^3$$

$$\left. + \left(\sum_{1 \le j < i \le \nu+1} L_{a_i a_i}^{(2)} \right) \nabla_1 \left(\sum_{1 \le i \le \nu}^{\nu=2} H_{a_i a_{\nu-1}}^{(1)} \right) \right] \mathrm{d}x = 0 \qquad \ldots(59)$$

and

$$\nabla_1 G_{ji}^{(4)} + \nabla_1 [L_{ji}^{(4)} + G_{ji}^{(1)} L_{ji}^{(3)} - H_{ji}^{(1)} L_{ji}^{(3)} + G_{ji}^{(2)} L_{ji}^{(2)} - G_{ji}^{(1)} H_{ji}^{(1)} L_{ji}^{(2)}$$

$$+\frac{1}{2!}(H_{ji}^{(1)})^2] L_{ji}^{(2)} - \frac{1}{\chi^3}\sum_k n_k \iint\Bigg[G_{jik}^{(3)} \nabla_1 \left(\sum_{1\le i\le \nu}^{\nu=2} H_{a_i a_{\nu+1}}^{(1)} \right)$$

$$+\frac{1}{2!} G_{jik}^{(2)} \nabla_1 \left(\sum_{1\le i\le \nu}^{\nu=2} H_{a_i a_{\nu+1}}^{(1)} \right)^2 + \frac{1}{3!} G_{jik}^{(1)} \nabla_1 \left(\sum_{1\le i\le \nu}^{\nu=2} H_{a_i a_{\nu+1}}^{(1)} \right)^3$$

$$+\frac{1}{4!} \nabla_1 \left(\sum_{1\le i\le \nu}^{\nu=2} H_{a_i a_{\nu+1}}^{(1)} \right)^4 - \left(\sum_{1\le j<i\le \nu+1}^{\nu=2} L_{a_i a_i}^{(2)} H_{a_i a_i}^{(1)} \right) \left(\nabla_1 \sum_{1\le i\le \nu}^{\nu=2} H_{a_i a_{\nu+1}}^{(1)} \right)$$

$$+ G_{jik}^{(1)} \left(\sum_{1\le j<i\le \nu}^{\nu+2} L_{a_i a_i}^{(2)} \right) \nabla_i \left(\sum_{1\le i\le \nu}^{\nu=2} H_{a_i a_{\nu+1}}^{(1)} \right) + \left(\sum_{1\le j<i\le \nu}^{\nu+2} L_{a_j a_i}^{(3)} \right) \left(\nabla_1 \sum_{1\le i\le \nu}^{\nu=2} H_{a_i a_{\nu+1}}^{(1)} \right)$$

$$+\frac{1}{2!} \left(\sum_{1\le j<i\le \nu}^{\nu=2} L_{a_i a_i}^{(2)} \right) \nabla_1 \left(\sum_{1\le i\le \nu}^{\nu=2} H_{a_i a_{\nu+1}}^{(1)} \right)^2 \mathrm{d}x_3 = 0 \qquad \ldots (60)$$

Similarly, eq. (55) can be extended up to $n=5, 6, \ldots$. The examination of equations (57), (59) and (60) shows that the terms $G_{jik}^{(1)}$, $G_{jik}^{(2)}$ and $G_{jik}^{(3)}$ are required to $G_{ji}^{(2)}$, $G_{ji}^{(3)}$ and $G_{ji}^{(4)}$, in (58)-(60). Substituting $\nu=3$ into (38). A similar treatment of (55) gives

$$\sum_{n=0}^{\infty} L_{jik}^{(n)}(x, x_{13}, x_{23})\, \varepsilon^n = 0\,, \qquad \ldots (61)$$

where

$$L_{jik}^{(n)}(x, x_{13}, x_{23}) = \nabla_1 G_{jik}^{(n)} + \nabla_1 \left[\sum_{u=0}^{n} \sum_{y=0}^{u} G_{jik}^{(n)} \left(\sum_{1\le j\le \nu} L_{a_j a_i}^{(u-y)} \frac{(-H_{a_j a_i}^{(1)})^{(n-u)}}{(n-u)!} \right) \right]$$

$$-\frac{1}{\chi^3}\sum_1 n_1 \iint\Bigg[\sum_{y=0}^{n} \nabla_1 \frac{\left(\sum_{1\le i\le \nu} H_{a_i a_{\nu+1}}^{(1)} \right)^{(y)}}{y!} G_{jikl}^{(n-y)} + \sum_{\nu=0}^{n} \sum_{u=0}^{\nu} \sum_{y=0}^{u} \nabla_1$$

$$\times \frac{\left(\sum_{1\le i\le n} H_{a_i a_{\nu+1}}^{(1)} \right)^{(y)}}{y!} G_{jik}^{(u-y)} \left(\sum_{1\le j<i\le \nu+1} L_{a_j a_i}^{(\nu-u)} \frac{(-H_{a_j a_i}^{(1)})^{(n-\nu)}}{(n-u)!} \right) + \ldots \Bigg] \mathrm{d}x_4 = 0$$

$$\ldots (62)$$

where $n=1$ to ∞.

Now, substituting $n = 1,2$ and 3 into (62) the following is obtained

$$\nabla_1 G^{(1)}_{jik} - \frac{1}{\chi^3} \sum_1 n_1 \int \nabla_1 \left(\sum_{1 \le i \le \nu} H^{(1)}_{a_i a_{\nu+1}} \right) \mathrm{d}x_4 = 0 \qquad \ldots (63)$$

$$\nabla_1 G^{(2)}_{jik} + \left(\sum_{1 \le j < i \ge \nu} L^{(2)}_{a_i a_i} \right) - \frac{1}{\chi^3} \sum_1 n_1 \int \left[G^{(1)}_{jikl} \nabla_1 \left(\sum_{1 \le i \le \nu} H^{(1)}_{a_i a_{\nu+1}} \right) + \frac{1}{2!} \nabla_1 \left(\sum_{1 \le i \le \nu} H^{(1)}_{a_i a_{\nu+1}} \right)^{(2)} \right] \mathrm{d}x_3 = 0 \qquad \ldots (64)$$

and

$$\nabla_1 G^{(3)}_{jik} + \nabla_1 \left[\sum_{1 \le j < i \ge \nu} L^{(3)}_{a_j a_i} + G^{(1)}_{jik} \left(\sum_{1 \le j < i \ge \nu} L^{(2)}_{a_j a_i} \right) - \sum_{1 \le j < i \ge \nu} L^{(2)}_{a_j a_i} H^{(1)}_{a_j a_i} \right] - \frac{1}{\chi^3} \sum_1 n_1 \int \left[F^{(2)}_{jikl} \nabla_1 \left(\sum_{1 \le i \le \nu} H^{(1)}_{a_i a_{\nu+1}} \right) + \frac{1}{2!} G^{(1)}_{jikl} \nabla_1 \left(\sum_{1 \le i \le \nu} H^{(1)}_{a_i a_{\nu+1}} \right)^{(2)} + \frac{1}{3!} \nabla_1 \left(\sum_{1 \le i \le \nu} H^{(1)}_{a_i a_{\nu+1}} \right)^{3} + \left(\sum_{1 \le j < i \le \nu+1} L^{(2)}_{a_i a_i} \right) \nabla_1 \left(\sum_{1 \le i \le \nu} H^{(1)}_{a_i a_{\nu+1}} \right) \right] \mathrm{d}x_4 = 0 \qquad \ldots (65)$$

Similarly $G^{(4)}_{jik}, G^{(5)}_{jik}$ etc. can be found by substituting $n = 4, 5, \ldots$, into (62). As mentioned above, the indirect correlation terms $G^{(2)}_{jik}$ and $G^{(3)}_{jik}$ can not be determined without the knowledge of $G^{(1)}_{jikl}$ and $G^{(2)}_{jikl}$. If we consider, in the usual mannar $\nu = 4$, it can be shown that (38) takes the form

$$\sum_{n=0}^{\infty} F^{(n)}_{jikl}(x, x_{13}, x_{14}, x_{23}, x_{24}, x_{34}) \, \varepsilon^{(n)} = 0 \,, \qquad \ldots (66)$$

where $n = 0$ to ∞.

Now

$$F^{(n)}_{jikl} = \nabla_1 H^{(n)}_{jikl} + \nabla_1 \left[\sum_{u=0}^{n} \sum_{y=0}^{u} G^{(y)}_{jikl} \left(\sum_{1 \le j < i \ge \nu} L^{(u-y)}_{a_i a_i} \frac{(-H^{(1)}_{a_i a_i})^{(n-u)}}{(n-u)!} \right) \right]$$

$$- \frac{1}{\chi^3} \sum_m^n n_m \int \left\{ \sum_{y=0} \nabla_1 \frac{\left(\sum_{1 \le i \le \nu} H^{(1)}_{a_i a_{\nu+1}} \right)^{(y)}}{y!} G^{(n-y)}_{jiklm} + \sum_{c=0}^{n} \sum_{u=0}^{\nu} \sum_{y=0}^{u} \nabla_1 \right.$$

$$\times \frac{\left(\sum_{1\le i\le v} H_{a_i a_{v+1}}\right)^{(y)}}{y!} G^{(u-y)}_{jiklm} \cdot \frac{\left(\sum_{1\le j<i\le v} (-H^{(1)}_{a_j a_i}\right)^{(v-u)} L^{(n-y)}_{a_j a_i}}{(v-u)!} + \ldots \Bigg\} \mathrm{d}x_5 = 0 \qquad \ldots (67)$$

In a manner analogous to that discussed above we can prove that, for $n=1$ and 2. (67) becomes

$$\nabla_1 G^{(1)}_{jikl} - \frac{1}{\chi^3} \sum_m n_m \quad 1 \left(\sum_{1\le i\le v} H^{(1)}_{a_i a_{v+1}}\right) \mathrm{d}x_5 = 0 , \qquad \ldots (68)$$

and

$$\nabla_1 G^{(2)}_{jikl} + \nabla_1 \left(\sum_{1\le j<i\ge v} L^{(2)}_{a_j a_i}\right) - \frac{1}{\chi^3} \sum_m n_m \int\Bigg[G^{(1)}_{jiklm} \nabla_1 \left(\sum_{1\le i\le v} H^{(1)}_{a_i a_{v+1}}\right) + \frac{1}{2!} \nabla_1 \left(\sum_{1\le i\le v} H^{(1)}_{a_i a_{v+1}}\right)^2 \Bigg] \mathrm{d}x_5 = 0 . \qquad \ldots (69)$$

And using the boundary conditions discussed above (57), (63) and (68) the following is obtained

$$G^{(1)}_{ji}(x) = G^{(1)}_{jik}(x, x_{13}, x_{23}) = G^{(1)}_{jikl}(x, x_{13}, x_{23}, x_{14}, x_{24}, x_{34}) = G^{(1)}_{jiklm} = 0 \qquad \ldots (70)$$

Integration (58) with respect to x_1, and making use of the boundary conditions (46) and (47), we have

$$G^{(2)}_{ji} + L^{(2)}_{ji} = \frac{1}{2!\chi^3} \sum_k n_k \int [(H^{(1)}_{jk} + H^{(1)}_{ik})^2 - (H^{(1)}_{ik})^2] \mathrm{d}x_3, \qquad \ldots (71)$$

where

$$G^{(2)}_{ji}(\infty) = H^{(3)}_{ji}(\infty) = L^{(3)}_{ji}(\infty) = 0 \qquad \ldots (72)$$

Similarly from (64) and (69)

$$G^{(2)}_{jik} + [L^{(2)}_{ji} + L^{(2)}_{jk}] = \frac{1}{2!\chi^3} \sum_L n_i \int [H_{jl}(H^{(1)}_{jl} + 2H^{(1)}_{il} + 2H^{(1)}_{kl})] \mathrm{d}x_4. \qquad \ldots (73)$$

and

$$G^{(2)}_{jikl} + [L^{(2)}_{jk} + L^{(2)}_{jk} + L^{(2)}_{jl}] = \frac{1}{2!\chi^3} \sum_m n_k \int [H^{(1)}_{jm}(H^{(1)}_{jm} + 2H^{(1)}_{im} + 2H^{(1)}_{km}) + 2H^{(1)}_{lm})] \mathrm{d}x_5 \qquad \ldots (74)$$

Substituting (73) into (59), integrating the result with respect to x_1, and making use of the boundary conditions given by (46) and (47) the following is obtained

$$G_{ji}^{(3)} + [L_{ji}^{(3)} - L_{ji}^{(2)} H_{ji}^{(1)}] = \frac{1}{\chi^3} \sum_k n_k \int (L_{ik}^{(2)} H_{ik}^{(1)} + \frac{1}{3!} [(H_{ik}^{(1)} + H_{ik}^{(1)})^3 - (H_{ik}^{(1)})^3]) \mathrm{d}x_3$$

$$+ \left(\frac{1}{\chi^3}\right)^2 \sum_k \sum_l n_k n_l \int [- H_{jk}^{(1)} (H_{il}^{(1)} + H_{kl}^{(1)})^2 + k_1 (H_{jk}^{(1)}, H_{il}^{(1)}, H_{jk}^{(1)}, H_{il}^{(1)})$$

$$- k_1 (0, 0, H_{ik}^{(1)}, H_{il}^{(1)})] \mathrm{d}x_3 \, \mathrm{d}x_4 , \qquad \ldots (75)$$

where

$$k_1 (H_{jk}^{(1)} + H_{jl}^{(1)} + H_{ji}^{(1)}, H_{il}^{(1)}) = \int (H_{jl} + H_{il} + H_{kl})^2 \, \mathrm{d}(H_{jk})^{(1)}, \qquad \ldots (76)$$

Similarly, an expression may be derived for $G_{jik}^{(3)}$ by using (65) and substituting the value of G_{jik}^{3}) in eq. (70) and (73) into eq. (60), the following is obtained:

$$G_{ji}^{(4)} + [L_{ji}^{(4)} - L_{ji}^{(3)} + L_{ji}^{(1)} + G_{ji}^{(2)} L_{ji}^{(2)} + \frac{1}{2!} (H_{ji}^{(12)} L_{ji}^{(2)})]$$

$$= \frac{1}{\chi^3} \sum_k n_k \int \left\{ \frac{1}{4!} [(H_{jk}^{(1)} + H_{ik}^{(1)})^4 - (H_{ik}^{(1)})^4] \right\} + \frac{1}{2!} L_{ik}^{(2)} (H_{jk}^{(1)} + H_{ik}^{(1)})^{(2)}$$

$$+ \frac{1}{2!} L_{ik}^{(2)} (H_{ik}^{(1)})^{(2)} - L_{ik}^{(2)} H_{ik}^{(1)} H_{ik}^{(1)} + L_{ik}^{(3)} H_{ik}^{(1)} > \mathrm{d}x_3$$

$$+ \left(\frac{1}{\chi^3}\right) \sum_k \sum_l n_k n_l \int \left\{ \left(\frac{1}{2!}\right) [(H_{ij} + H_{kl}^{(1)})^2 (H_{ik}^{(1)})^2 - (H_{il}^{(1)} + H_{kl}^{(1)})^2 (H_{jk}^{(1)} + H_{ik}^{(1)})^2 \right.$$

$$+ k_2 (H_{jk}^{(1)}, H_{jl}^{(1)}, H_{jk}^{(1)}, H_{il}^{(1)}, H_{kl}^{(1)}) - k_2 (0, 0, H_{ik}^{(1)}, H_{il}^{(1)}, H_{kl}^{(1)})]$$

$$+ \frac{1}{3!} [- H_{jk}^{(1)} (H_{il}^{(1)} + H_{kl}^{(1)}) + k_3 (H_{jl}^{(1)}, H_{il}^{(1)}, H_{kl}^{(1)}, H_{jk}^{(1)}) - k_3 (0, H_{il}^{(1)}, H_{kl}^{(1)}, 0)$$

$$\left. + k_4 (L_{ik}^{(2)}, L_{il}^{(2)}, L_{kl}^{(2)}, H_{jl}^{(1)}, H_{jk}^{(1)}) - k_4 (L_{ik}^{(2)}, L_{il}^{(2)}, L_{kl}^{(2)}, 0, 0) \right\} \mathrm{d}x_3 \, \mathrm{d}x_4 + \ldots ,$$

$$\ldots (77)$$

where

$$k_2 (H_{jk}^{(1)}, H_{jl}^{(1)}, H_{ik}^{(1)}, H_{il}^{(1)}, H_{kl}^{(1)}) = (H_{jl}^{(1)} + H_{il}^{(1)} + H_{ki}^{(1)}) \, . \, \mathrm{d}(H_{jk}^{(1)} + H_{ik}^{(1)}) , \qquad \ldots (78)$$

$$k_3 (H_{jl}^{(1)}, H_{il}^{(1)}, H_{kl}^{(1)}, H_{jk}^{(1)}) = \int (H_{jl}^{(1)} + H_{il}^{(1)} + H_{kl}^{(1)})^3 \, \mathrm{d}(H_{jk}^{(1)}) , \qquad \ldots (79)$$

and

$$k_4(L_{ik}^{(2)}, L_{il}^{(2)}, L_{kl}^{(2)}, H_{ji}^{(1)}, H_{jk}) = (L_{ik}^{(2)} + L_{il}^{(2)} + L_{kl}^{(2)}) \int H_{ji}^{(1)} \mathrm{d}(H_{jk}^{(1)}), \quad \ldots (80)$$

If $\nu = 2$, (22) becomes

$$F_{jk}(x) = \exp[H_{ji}^{(1)}(x)\varepsilon][1 + T_{jk} \exp(-H_{ji}^{(1)}(x)\varepsilon] G_{ji}, \quad \ldots (81)$$

which may be written as

$$F_{ji}(x) = [\exp(H_{ji}^{(1)}(x)\varepsilon][1 + G_{ji}^{(1)} + L_{ji}^{(2)} + G_{ji}^{(2)})^2 + (G_{ji}^{(3)} + L_{ji}^{(3)} + H_{ji}^{(1)} L_{ji}^{(2)} + G_{ji}^{(1)} L_{ji}^{(2)} \varepsilon^3$$

$$+ (G_{ji}^{(4)} + L_{ji}^{(4)} - H_{ji}^{(1)} L_{ji}^{(3)} + G_{ji}^{(2)} L_{ji}^{(2)} + \frac{1}{2!}(H_{ji}^{(1)})^2 L_{ji}^{(2)} \varepsilon^4 + \ldots] \quad \ldots (82)$$

Substituting (70), (71), (76) and (77) into (82), the following is obtained

$$F_{ji}(x) = [\exp H_{ji}^{(1)}(x) e] \left\{ 1 + \frac{1}{\chi^3} \sum n_k \int ([\exp(H_{jk}^{(1)} + H_{ik}^{(1)}) - 1 - (H_{jk}^{(1)} + H_{ik}^{(1)})\varepsilon] \right.$$

$$- [\exp(H_{ik}^{(1)}\varepsilon) - 1 - H_{ik}^{(1)}] + \varepsilon^3 [L_{ik}^{(2)} H_{jk}^{(1)}] + \frac{\varepsilon^4}{2} [2L_{ik}^{(3)} H_{jk}^{(1)} + L_{ik}^{(2)} (H_{jk}^{(1)} + H_{ik}^{(1)})^2$$

$$\left. - L_{ik}^{(2)} (H_{ik}^{(1)})^2 - 2L_{ik}^{(2)} H_{jk}^{(1)} H_{ik}^{(1)}] + \ldots) + \left(\frac{1}{\chi^3}\right)^2 \sum_k \sum_l n_k n_l \int [\text{---}] \mathrm{d}x_3 \, \mathrm{d}x_4 \right\} \ldots$$

$$\ldots (83)$$

The last expression (83) can be written in the equivalent from

$$F_{ji}(x) = [\exp H_{ji}^{(1)}(x)] \left[1 + \frac{1}{\chi^3} \sum n_k \int (\phi_{jk} \phi_{ik} + \varepsilon H_{jk} \Phi_{ik} + \Phi_{ik} H_{ik} \varepsilon \right]$$

$$+ \frac{\varepsilon^2}{2!} [(H_{jk}^{(1)})^2 + 2H_{jk}^{(1)} H_{ik}^{(1)}] + \frac{\varepsilon^3}{3!} [3! L_{ik}^{(2)} H_{jk}^{(1)} + (H_{jk}^{(1)})^3]$$

$$+ \frac{\varepsilon^4}{2} [2L_{ik}^{(2)} H_{jk}^{(1)} + L_{ik}^{(2)} (H_{ik}^{(1)} + H_{ik}^{(1)})^2 - L_{ik}^{(2)} (H_{ik}^{(1)})^2 - 2L_{jk}^{(2)} H_{jk}^{(1)} H_{ik}^{(1)}$$

$$+ \frac{1}{12} (H_{jk}^{(1)})^4 + \ldots] \mathrm{d}x_3 + 0(n_j n_i), \quad \ldots (84)$$

where

$$\Phi'_{ji} = \exp(H_{ji}^{(1)} \varepsilon) - 1 - \varepsilon H_{ji}^{(1)} \quad \ldots (85)$$

The numerical calculations of the binary distribution function with chemical model will be discussed and compared to experimental data and other studies in part II.

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