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LETTER TO THE EDITOR

Analytical solution of the Ornstein–Zernike equation for a multicomponent fluid with a screened Coulomb plus power series interaction

M Yasutomi

Department of Physics and Earth Sciences, College of Science, University of the Ryukyus, Nishihara-Cho, Okinawa 903-0213, Japan

E-mail: g800002@lab.u-ryukyu.ac.jp

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Abstract

The analytical solution of the Ornstein–Zernike equation with a Sogami–Ise type closure for a multicomponent fluid discussed in our previous work (Yasutomi and Ginoza 2000 *J. Phys.: Condens. Matter* **12** L605) is extended to a more general case that

$$c_{ij}(r) = \sum_{n=1}\sum_{\tau=-1}^{L} K_{ij}^{(n,\tau)} z_n^{\tau+1} r^{\tau} \mathrm{e}^{-z_n r} \qquad \sigma_{ij} < r$$

where $c_{ij}(r)$ is the direct correlation function, r is the interparticle separation, $K_{ij}^{(n,\tau)}$ and z_n are constants, σ_{ij} is the distance at contact of the pair (i, j) of particles. Almost all of the interaction potentials between particles (such as a potential due to diffuse electric double layer, van der Waals potential, steric potential and so on) can be well approximated by the above closure. In this sense the present analytical solution will be applicable to a large variety of colloidal fluids under the mean-spherical-approximation (MSA).

The field of colloid and interface science has experienced a marked expansion in the last two decades. It now covers a wide range of specialist areas such as applied biology, chemical and pharmaceutical industries and various medical disciplines. It is also applied in the synthesis and characterization of novel materials. In the area of physics, the structure and thermodynamical properties of colloidal dispersions have been studied by theoretical and experimental methods and computer-simulation techniques.

The physical properties of colloidal fluids can be obtained from the distribution (or correlation) functions. These functions can be calculated using a number of methods (such as perturbation theories, integral-equation methods and numerical-simulation techniques) when a suitable interaction potential is specified. One of the most popular methods is integral-equation methods based on the Ornstein–Zernike (OZ) equation for the correlation functions. Before the OZ equation can be solved, we need the closure relations which relate the correlation functions and the interparticle potentials.

So far, analytical solutions of the OZ equation have been obtained for the five types of pair-interaction potentials:

(1) Neutral hard-sphere interaction which describes the excluded-volume effects due to the finite size of the colloidal particles (Henderson *et al* 1976, Waisman *et al* 1976, Thompson *et al* 1980, Henderson *et al* 1980, Plischke and Henderson 1986).
(2) Sticky hard-sphere interaction which represents a combination of both a hard-sphere repulsion and a very sharp, short-range attraction (Baxter R J 1968, Perram and Smith 1975, Barboy and Tenne 1979, Ginoza and Yasutomi 1996).
(3) Screened Coulombic (Yukawa) potential which describes the long-range electrostatic repulsion between charged particles (Waisman 1973, Blum and Høye 1978, Blum 1980, Ginoza M 1985, 1986).
(4) Sticky hard-sphere Yukawa interaction which represents a combination of a hard-sphere repulsion, a very sharp, short-range attraction, and a Yukawa potential (Yasutomi and Ginoza 1996)
(5) Sogami–Ise interaction which represents a combination of a hard-sphere repulsion and a screened Coulomb plus constant potential (Yasutomi and Ginoza 2000 (YG)).

In the previous work (YG), on the basis of the mean-spherical-approximation (MSA) we found analytical solutions of the OZ equation for systems of hard spheres with a Sogami–Ise type closure (Sogami and Ise 1984) given by

$$c_{ij}(r) = -\frac{\phi_{ij}(r)}{k_B T} = \sum_{n=1} \sum_{\tau=-1}^{L} K_{ij}^{(n,\tau)} z_n^{\tau+1} r^{\tau} e^{-z_n r} \qquad \sigma_{ij} = (\sigma_i + \sigma_j)/2 < r \tag{1}$$

and

$$g_{ij}(r) \equiv h_{ij}(r) + 1 = 0 \qquad r < \sigma_{ij} \tag{2}$$

where $L = 0$, $c_{ij}(r)$ and $h_{ij}(r)$ are the direct and the total correlation functions for two spherical molecules of species i and j, r is the interparticle separation, σ_i is the diameter of spherical hardcore of species i, $K_{ij}^{(n,\tau)}$ and z_n are constants to be adjusted by physical arguments, $\phi_{ij}(r)$ is the pair-interaction potential, $k_B T$ is Boltzmann's constant, and T is a temperature. We used the Fourier transform method (Baxter 1968, 1970) to lead to relatively simple sets of algebraic equations, and obtained explicit formulas for relavant quantities. The work extended the work of Blum (1980) of the solution of the case with an arbitrary number of Yukawas which corresponds to the above closure when $L = -1$. In the present letter we extend our previous work (YG) to a more general case of arbitrary integer L.

The procedure is a generalization of our previous work (YG). The OZ equation in the Baxter formalism is

$$2\pi r c_{ij}(r) = -\frac{d}{dr} Q_{ij}(r) + \sum_l \rho_l \int_{\lambda_{lj}}^{\infty} dt\ Q_{jl}(t) \frac{d}{dr} Q_{il}(r+t) \tag{3a}$$

$$2\pi r h_{ij}(r) = -\frac{d}{dr} Q_{ij}(r) + 2\pi \sum_l \rho_l \int_{\lambda_{jl}}^{\infty} dt\ Q_{lj}(t)(r-t) h_{il}(|r-t|) \tag{3b}$$

where ρ_l is the number density of species l and $\lambda_{lj} = (\sigma_l - \sigma_j)/2$. We shall obtain the Baxter function $Q_{ij}(r)$ by solving these equations with the closure of equations (1) and (2).

The function $Q_{ij}(r)$ is written as (Blum and Høye 1978, Blum 1980),

$$Q_{ij}(r) = Q_{ij}^0(r) + Q_{ij}^1(r) \tag{4a}$$

$$Q_{ij}^0(r) = 0 \qquad r > \sigma_{ij} \quad \text{or} \quad r < \lambda_{ji}. \tag{4b}$$

Substitution of equation (4a) into equation (3a) and the use of equations (1) and (4b) yield

$$2\pi \sum_{n=1} \sum_{\tau=-1}^{L} K_{ij}^{(n,\tau)} z_n^{\tau+1} r^{\tau+1} e^{-z_n r} = -\frac{d}{dr} Q_{ij}^1(r) + \sum_l \rho_l \int_{\lambda_{lj}}^{\infty} dt\ Q_{jl}(t) \frac{d}{dr} Q_{il}^1(r+t). \tag{5a}$$

Substitution of equation (4a) into (3b) and the use of equations (2) and (4b) yield

$$\frac{\mathrm{d}}{\mathrm{d}r}Q^0_{ij}(r) = A_j\, r + B_j - \frac{\mathrm{d}}{\mathrm{d}r}Q^1_{ij}(r) - 2\pi\sum_l \rho_l \int_{\sigma_{il}}^{\infty} \mathrm{d}t\; g_{il}(t)\; t\; Q^1_{lj}(t+r) \qquad \lambda_{ji} < r < \sigma_{ij} \tag{5b}$$

where

$$A_j = 2\pi\left(1 - \sum_l \rho_l T^{(0)}_{lj}\right) \tag{6a}$$

$$B_j = 2\pi\sum_l \rho_l T^{(1)}_{lj} \tag{6b}$$

with

$$T^{(n)}_{lj} = \int_{\lambda_{jl}}^{\infty} \mathrm{d}r\; r^n Q_{lj}(r). \tag{6c}$$

Equations (5a) and (5b) suggest the following functional form for $Q^1_{ij}(r)$:

$$Q^1_{ij}(r) \equiv \sum_{n=1}\sum_{\tau=-1}^{L} D^{(n,\tau)}_{ij} z_n^{\tau+1} r^{\tau+1} \mathrm{e}^{-z_n r}. \tag{7}$$

In fact, the direct substitution shows that equation (7) is the solution of equation (5a) if the following equation is satisfied:

$$\begin{aligned}2\pi K^{(n,m-1)}_{ij} = {} & z_n \sum_l D^{(n,m-1)}_{il}\left[\delta_{jl} - \rho_l \tilde{Q}^{(0)}_{jl}(\mathrm{i}z_n)\right] \\ & -z_n(m+1)\sum_l D^{(n,m)}_{il}\left[\delta_{jl} + z_n\rho_l\tilde{Q}^{(1)}_{jl}(\mathrm{i}z_n) - \rho_l\tilde{Q}^{(0)}_{jl}(\mathrm{i}z_n)\right] \\ & + \sum_{\tau=m+1}^{L}\sum_l D^{(n,\tau)}_{il}\frac{z_n^{\tau+1}}{z_n^m}\rho_l\Big[(\tau+1)C^{\tau}_{\tau-m}\tilde{Q}^{(\tau-m)}_{jl}(\mathrm{i}z_n) \\ & -C^{\tau+1}_{\tau+1-m} z_n \tilde{Q}^{(\tau+1-m)}_{jl}(\mathrm{i}z_n)\Big]\end{aligned} \tag{8}$$

for $m = 0, 1, 2, \ldots, L+1$ where $D^{(n,\tau)}_{il} = 0$ for $\tau \geqslant L+1$, $C^n_m = n!/m!(n-m)!$ and

$$\tilde{Q}^{(m)}_{jl}(s) \equiv \int_{\lambda_{lj}}^{\infty} \mathrm{d}t\; Q_{jl}(t)t^m\, \mathrm{e}^{\mathrm{i}st}, \qquad (m = 0, 1, 2, \ldots, L+1). \tag{9}$$

Substituting equation (7) into equation (5b) and solving the resulting differential equation under the boundary condition $Q^0_{ij}(\sigma_{ij}) = 0$, we obtain

$$Q^0_{ij}(r) = \frac{1}{2}A_j(r^2 - \sigma^2_{ij}) + B_j(r - \sigma_{ij}) + \sum_{n=1}\sum_{k=0}^{L+1}\sum_{\xi=0}^{k}\frac{z_n^{k-\xi}C^{(n,k)}_{ij}k!}{(k-\xi)!}\left[r^{k-\xi}\mathrm{e}^{-z_n r} - \sigma_{ij}^{k-\xi}\mathrm{e}^{-z_n\sigma_{ij}}\right] \tag{10}$$

where

$$C^{(n,k)}_{ij} = -D^{(n,k-1)}_{ij} + (k+1)D^{(n,k)}_{ij} + \sum_l \sum_{\tau=1}^{(L+2)-k} C^{\tau+k-1}_{\tau-1} D^{(n,\tau+k-2)}_{lj}\gamma^{(\tau)}_{il}(z_n) \tag{11}$$

with

$$z_n^{2-m}\gamma^{(m)}_{il}(z_n) \equiv 2\pi\rho_l \tilde{g}^{(m)}_{il}(z_n) \qquad (m = 1, 2, 3, \ldots, L+2) \tag{12}$$

$$\tilde{g}_{il}^{(m)}(z_n) \equiv \int_{\sigma_{il}}^{\infty} \mathrm{d}x \ \mathrm{e}^{-z_n x} \ x^m g_{il}(x). \tag{13}$$

From (13) and (3b), we get

$$2\pi \sum_l \sum_{\xi=0}^{m} \tilde{g}_{il}^{(\xi+1)}(s) \left[\delta_{jl}\delta_{m\xi} - C_\xi^m \rho_l \tilde{Q}_{lj}^{(m-\xi)}(\mathrm{i}s)\right] = A_j \chi^{(m+1)}(\sigma_{ij}, s) + B_j \chi^{(m)}(\sigma_{ij}, s)$$
$$- \sum_n \sum_{\tau=0}^{L+1} z_n^{\tau+1} C_{ij}^{(n,\tau)} \chi^{(m+\tau)}(\sigma_{ij}, z_n + s) \tag{14}$$

where

$$\chi^{(k)}(b, a) = \int_b^{\infty} \mathrm{d}r \ r^k \mathrm{e}^{-ar} = \sum_{\xi=0}^{k} \frac{1}{a^{\xi+1}} \frac{k!}{(k-\xi)!} b^{k-\xi} \mathrm{e}^{-ab}. \tag{15}$$

Using (7) and (10), integration of (9) yields

$$\mathrm{e}^{-s\lambda_{lj}} \tilde{Q}_{lj}^{(m)}(\mathrm{i}s) = \frac{1}{2} A_j \Phi_{lj}^{(m+2,m)}(s, 0)$$
$$+ B_j \Phi_{lj}^{(m+1,m)}(s, 0) + \sum_{n=1} \sum_{k=0}^{L+1} \sum_{\xi=0}^{k} \frac{z_n^{k-\xi} C_{lj}^{(n,k)} k!}{(k-\xi)!} \Phi_{lj}^{(m+k-\xi,m)}(s, z_n)$$
$$+ \sum_{n=1} \sum_{\tau=-1}^{L} D_{lj}^{(n,\tau)} z_n^{\tau+1} \mathrm{e}^{-s\lambda_{lj}} \chi^{(m+\tau+1)}(\lambda_{jl}, z_n + s) \tag{16}$$

where

$$\mathrm{e}^{-s\lambda_{jl}} \Phi_{lj}^{(n,m)}(s, z) = \chi^{(n)}(\lambda_{jl}, z + s) - \chi^{(n)}(\sigma_{jl}, z + s)$$
$$- \sigma_{lj}^{n-m} \mathrm{e}^{-z\sigma_{lj}} \left[\chi^{(m)}(\lambda_{jl}, s) - \chi^{(m)}(\sigma_{jl}, s)\right]. \tag{17}$$

As seen from (6c) and (9) we can write $T_{lj}^{(n)} = \tilde{Q}_{lj}^{(n)}(0)$. Using this relation and equations (16), (6a) and (6b) we get

$$A_j = \frac{2\pi}{\Delta}\left[1 + \frac{1}{2}\zeta_2\beta_j - \sum_{n=1} \sum_{\mu=-1}^{L} \sum_l \rho_l D_{lj}^{(n,\mu)} H_{lj}^{(\mu,0)}(z_n)\right] \tag{18}$$

$$\beta_j = \frac{\pi}{\Delta}\sigma_j + \frac{2\pi}{\Delta} \sum_{n=1} \sum_{\mu=-1}^{L} \sum_l \rho_l D_{lj}^{(n,\mu)} \left[H_{lj}^{(\mu,1)}(z_n) - \frac{1}{2}\sigma_j H_{lj}^{(\mu,0)}(z_n)\right] \tag{19}$$

where $\beta_j = B_j + \frac{1}{2}\sigma_j A_j$, $\zeta_k = \sum_l \rho_l \sigma_l^k$, $\Delta = 1 - \pi\zeta_3/6$ and

$$H_{lj}^{(\mu,m)}(z_n) = z_n^{\mu+1}\left[\chi^{(m+\mu+1)}(\lambda_{jl}, z_n) - \Phi_{lj}^{(m+\mu+1,m)}(0, z_n)\right]$$
$$+ \sum_{k=0}^{\mu+1} \sum_{\xi=0}^{k} \frac{z_n^{k-\xi} k!}{(k-\xi)!} \sum_\nu \Phi_{\nu j}^{(m+k-\xi,m)}(0, z_n) C_{\mu+1-k}^{\mu+1} \gamma_{l\nu}^{(\mu+2-k)}(z_n). \tag{20}$$

In the above derivations we used the relation $\rho_i \gamma_{il}^{(m)}(z_n) = \rho_l \gamma_{li}^{(m)}(z_n)$.

We have obtained the formal solution of the OZ equation with the closure of equations (1) and (2) on the basis of MSA. The solution $Q_{ij}(r)$ is given by equations (4a), (4b), (7) and (10) which are functions of two sets of parameters, $D_{ij}^{(n,\mu)}$ and $\gamma_{ij}^{(m)}(z_n)$. The set of parameters $D_{ij}^{(n,\mu)}$ can be obtained as a function of $\gamma_{ij}^{(m)}(z_n)$ from the linear equation (14) for $D_{ij}^{(n,\mu)}$ when

$s = z_n$, and substituted into (8), to get a set of nonlinear algebraic equations for $\gamma_{ij}^{(m)}(z_n)$. A physical branch of the solution has to be chosen from the manifold of solutions. In this stage, we can calculate all the coefficients in the function $Q_{ij}(r)$, and therefore, the pair correlation functions and structural and thermodynamic properties of a multicomponent fluid.

The pair interaction potential $\phi_{ij}(r)$ characterizes the structural and physical properties of colloidal fluids. Some of the well known potentials are the potential due to the diffuse electric double layer, the van der Waals potential, the Derjaguin–Landau–Verwey–Overbeek (DLVO) potential and the steric potential. All of them can be well approximated by the closure of equation (1).

As an example, we consider the case of the DLVO potential expressed as (Ginoza and Yasutomi 1997)

$$\phi_{\mathrm{DLVO}}(r) = \frac{(Z_{\mathrm{c}}^{*}e)^2}{\epsilon r}\mathrm{e}^{-\kappa(r-\sigma_{\mathrm{c}})} - \frac{A_{\mathrm{H}}}{12}\left[\frac{1}{x^2-1} + \frac{1}{x^2} + 2\ln\frac{x^2-1}{x^2}\right]_{x=r/\sigma_{\mathrm{c}}} \tag{21}$$

where

$$Z_{\mathrm{c}}^{*} = \frac{Z_{\mathrm{c}}}{1+\kappa\sigma_{\mathrm{c}}/2} \qquad \kappa^2 = 4\pi L_{\mathrm{B}}\sum_{i=1,2}\rho_i Z_i^2 \qquad L_{\mathrm{B}} = \frac{e^2}{k_{\mathrm{B}}T\epsilon}. \tag{22}$$

In the above equations, A_{H} is the Hamaker constant, Z_i is the valence of particle i and ϵ is the dielectric constant of the neutral solvent. The subscripts c, 1, and 2 represent the colloidal particles, counterions (microions) and coions (microions), respectively.

Using equation (1), we approximate the potential $\phi_{\mathrm{DLVO}}(r)$ as

$$-\frac{\phi_{\mathrm{DLVO}}(r)}{k_{\mathrm{B}}T} = \frac{K^{(1,-1)}}{r}\mathrm{e}^{-z_1 r} + \mathrm{e}^{-z_2 r}\sum_{\tau=-1}^{L} K^{(2,\tau)} z_2^{\tau+1} r^{\tau}. \tag{23}$$

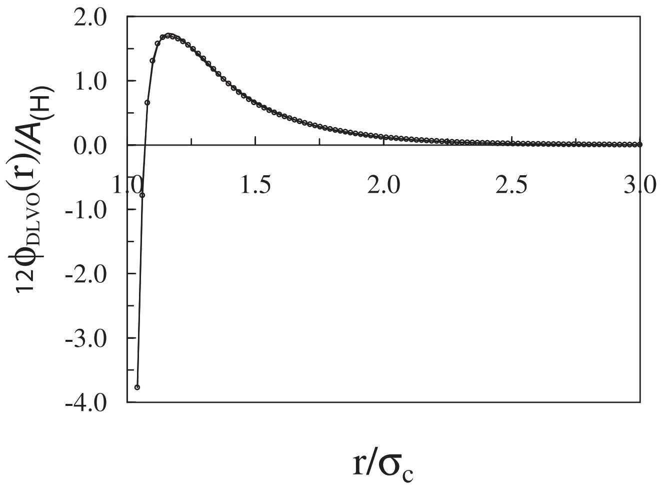

Figure 1. The DLVO interaction potential (the solid line) and its approximate potential given by equation (23) (the circles).

As shown in figure 1, the potential $\phi_{\mathrm{DLVO}}(r)$ (solid line) is well fitted by the right-hand side of equation (23) (circles) where $\kappa\sigma_{\mathrm{c}} = z_1\sigma_{\mathrm{c}} = 3$, $z_2\sigma_{\mathrm{c}} = 26.5526$, $K^{(1,-1)} = -(Z_{\mathrm{c}}^{*}e)^2\mathrm{e}^{\kappa\sigma_{\mathrm{c}}}/\epsilon k_{\mathrm{B}}T = -100A_{\mathrm{H}}\sigma_{\mathrm{c}}/12k_{\mathrm{B}}T$, $L = 27$, and $K^{(2,\tau)}$ for $\tau = -1, 0, 1, 2, 3, \ldots$ and 27 are 3.50304, -5.28592, $-5.23442 \cdot 10^{-2}$, 2.67539, -1.79271, $4.19587 \cdot 10^{-1}$,

$-3.94799 \cdot 10^{-1}$, $-1.10371 \cdot 10^{-1}$, 1.31488, $-5.45468 \cdot 10^{-2}$, $4.11067 \cdot 10^{-1}$, $-5.32089 \cdot 10^{-1}$, $-1.03259 \cdot 10^{-1}$, $-2.34657 \cdot 10^{-1}$, $3.88707 \cdot 10^{-1}$, $6.41650 \cdot 10^{-2}$, $-2.75798 \cdot 10^{-1}$, $-7.17811 \cdot 10^{-2}$, $5.01577 \cdot 10^{-2}$, $-7.39232 \cdot 10^{-2}$, $2.54642 \cdot 10^{-2}$, $-2.62872 \cdot 10^{-3}$, $9.27277 \cdot 10^{-4}$, $3.01694 \cdot 10^{-2}$, $1.30848 \cdot 10^{-2}$, $1.15787 \cdot 10^{-2}$, $1.88114 \cdot 10^{-3}$, $-3.37145 \cdot 10^{-3}$ and $-9.54506 \cdot 10^{-3}$, respectively, in the units of $10^{14} A_{\mathrm{H}}/(12 k_{\mathrm{B}} T z_2^{\tau+1} \sigma_{\mathrm{c}}^{\tau})$.

The good fit of equation (1) would not be restricted to the DLVO potential or the well known potentials mentioned before. We believe that almost all of the pair-interaction potentials including the potentials with soft core can be well approximated. Therefore, the present analytical solution of the OZ equation with the closure given by equations (1) and (2) will be applicable to a large variety of colloidal fluids under the MSA. To obtain the total correlation function from the present solution we will need some lengthy algebra. The author thinks that this is challenging work and will report his work in the near future.

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