An analytic structure factor for one-component fluid with a screened Coulomb plus power series interaction

2002 J. Phys.: Condens. Matter 14 L165

(http://iopscience.iop.org/0953-8984/14/6/105)

J. Phys.: Condens. Matter **14** (2002) L165–L170 PII: S0953-8984(02)32444-5

LETTER TO THE EDITOR

An analytic structure factor for one-component 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

Received 8 January 2002
Published 1 February 2002
Online at stacks.iop.org/JPhysCM/14/L165

Abstract
From our previous analytic solutions of the Ornstein–Zernike equation in the mean-spherical approximation (Yasutomi M 2001 *J. Phys.: Condens. Matter* **13** L255), we obtain an analytic structure factor for one-component fluid with a screened Coulomb plus power series interaction expressed as

$$c(r) = -\frac{\phi(r)}{k_B T} = \sum_{\tau=-1}^{L} K^{(\tau)} z^{\tau+1} r^{\tau} \mathrm{e}^{-zr} \qquad \sigma < r$$

where $c(r)$ is the direct correlation function, $\phi(r)$ is the interaction potential, k_B is Boltzmann's constant, T is a temperature, r is the interparticle separation, $K^{(\tau)}$ and z are constants, σ is the distance at contact of the particles, and L is an arbitrary integer. The results provide a useful model basis for studying a large variety of one-component fluids because almost all of the interaction potentials between particles can be well approximated by the above closure. As an example, we show a structure factor for a Lennard-Jones fluid.

In previous work (Yasutomi 2001), we have obtained an analytic solution of the Ornstein–Zernike (OZ) equation for systems of hard spheres with a screened Coulomb plus power series interaction expressed as

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

and

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

where L is an arbitrary integer, $c_{ij}(r)$ and $h_{ij}(r)$ are, respectively, 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 the spherical hard core of species i, $K_{ij}^{(n,\tau)}$ and z_n are constants to be adjusted on the basis of physical arguments, $\phi_{ij}(r)$ is the pair-interaction potential in the mean-spherical approximation (MSA), k_B is Boltzmann's constant, and T is a temperature. We note here that the solutions for the Yukawa-type and Sogami–Ise-type closures (Sogami and Ise 1984, Yasutomi and Ginoza 2000) for a multicomponent fluid are given when $L = -1$ and 0, respectively.

The physical properties of the system are obtained from the total correlation function $h_{ij}(r)$ or the distribution function $g_{ij}(r)$. So far, these functions have been obtained for neutral hard-sphere interaction (Henderson *et al* 1976, Waisman *et al* 1976, Thompson *et al* 1980, Henderson *et al* 1980, Plischke and Henderson 1986), sticky hard-sphere interaction (Baxter 1968, Perram and Smith 1975, Barboy and Tenne 1979, Ginoza and Yasutomi 1996), a Yukawa potential (Waisman 1973, Blum and Høye 1978, Blum 1980, Ginoza 1985, 1986), and a sticky hard-sphere Yukawa interaction (Yasutomi and Ginoza 1996). However, these functions have not yet been obtained for Sogami–Ise closure and the closure given by equation (1) for $L \geqslant 1$. In the present letter, we apply the closures (1) and (2) to one-component fluid and obtain the static structure factor. We have closely followed the exposition of our previous work, and the interested reader is referred to it (Yasutomi 2001) for details.

In the present case, the closures are given by

$$c(r) = -\frac{\phi(r)}{k_B T} = \mathrm{e}^{-zr} \sum_{\tau=-1}^{L} K^{(\tau)} z^{\tau+1} r^{\tau} \qquad \sigma < r \tag{3}$$

and

$$g(r) \equiv h(r) + 1 = 0 \qquad r < \sigma. \tag{4}$$

The structure factor is expressed as

$$S(k) = 1 - 4\pi\rho \,\mathrm{Re}\left[\frac{\tilde{g}^{(1)}(s)}{s}\right]_{s=\mathrm{i}k} \tag{5}$$

where $k = (4\pi n/\lambda)\sin(\theta/2)$ (n is the refractive index of the medium, λ is the wavelength of light, and θ is the scattering angle), ρ is the number density of the molecules, and

$$\tilde{g}^{(m)}(s) \equiv \int_{\sigma}^{\infty} \mathrm{d}x\, \mathrm{e}^{-sx} x^m g(x). \tag{6}$$

The Fourier transform $\tilde{g}^{(1)}(s)$ is given by

$$2\pi\tilde{g}^{(1)}(s) = \frac{A\chi^{(1)}(\sigma, s) + B\chi^{(0)}(\sigma, s) - \sum_{\tau=0}^{L+1} z^{\tau+1} C^{(\tau)} \chi^{(\tau)}(\sigma, z+s)}{[1 - \rho\tilde{Q}^{(0)}(\mathrm{i}s)]}. \tag{7}$$

The coefficients and functions in the right-hand side of (7) are given in the appendix A.

The long-wavelength limit of $S(k)$ is given by

$$S(0) = \rho k_B T K_T = \left(\frac{2\pi}{A}\right)^2 \tag{8}$$

where K_T is the isothermal compressibility.

The radial distribution function is calculated from

$$g(r) = 1 + \frac{1}{2\pi^2\rho r} \int_0^{\infty} \mathrm{d}k\, [S(k) - 1] k \sin kr. \tag{9}$$

The contact value $g(\sigma)$ is given by

$$2\pi\sigma g(\sigma) = A\sigma + B - z\mathrm{e}^{-z\sigma} \sum_{k=0}^{L+1} (z\sigma)^k C^{(k)}. \tag{10}$$

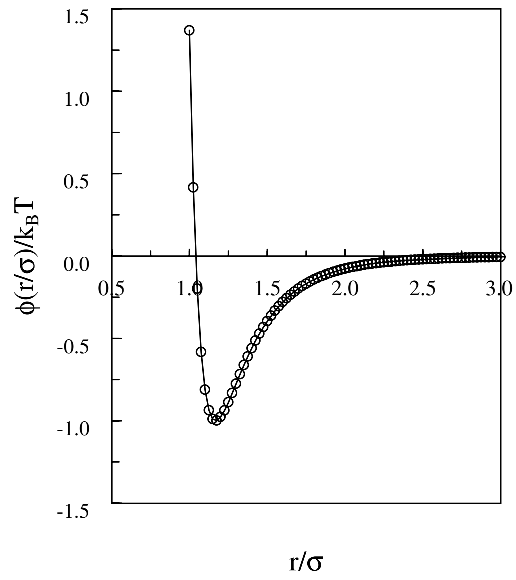

Figure 1. The LJ interaction potential (the circles) and its approximate potential (the solid curve) given by equation (3).

The two sets of parameters $D^{(m)}$ and $\gamma^{(n)}(z)$ are obtained by solving the following two sets of equations:

$$z^{1-m}\gamma^{(m+1)}(z) = \rho\hat{A}_m A + \rho\hat{B}_m B + \sum_{\mu=0}^{L+1}\rho\hat{C}_m^{(\mu)}C^{(\mu)} + \sum_{\mu=-1}^{L}\rho\hat{D}_m^{(\mu)}D^{(\mu)} \qquad (11)$$

and

$$2\pi K^{(m-1)} = zD^{(m-1)}[1-\rho\tilde{Q}^{(0)}(\mathrm{i}z)] - z(m+1)D^{(m)}[1+z\rho\tilde{Q}^{(1)}(\mathrm{i}z)-\rho\tilde{Q}^{(0)}(\mathrm{i}z)]$$
$$+\sum_{\tau=m+1}^{L}D^{(\tau)}z^{\tau+1-m}\rho[(\tau+1)C_{\tau-m}^{\tau}\tilde{Q}^{(\tau-m)}(\mathrm{i}z) - C_{\tau+1-m}^{\tau+1}z\tilde{Q}^{(\tau+1-m)}(\mathrm{i}z)] \qquad (12)$$

where $z^{2-m}\gamma^{(m)}(z) = 2\pi\rho\tilde{g}^{(m)}(z)$, $C_m^n = n!/m!(n-m)!$, and the parameters $\hat{A}_m$, $\hat{B}_m$, $\hat{C}_m^{(k)}$, and $\hat{D}_m^{(\tau)}$ are given in the appendix B. These can be solved by the Newton–Raphson iteration technique. A physical branch of the solution has to be chosen from the manifold of solutions.

To solve (11) and (12) for the parameters $D^{(m)}$ and $\gamma^{(n)}(z)$ we first multiply $K^{(\tau)}$ by a factor f. We next change f from 0 to 1 in steps. When we can get solutions for f for a certain step, we can use them as approximate solutions to the next step. Then we obtain exact solutions by the Newton–Raphson method. In this way we can finally obtain exact solutions for $f = 1$ after some steps. Thus, our problems are reduced to obtaining the solutions for $f = 0$. In this case, from (11) and (A.3) we obtain

$$D^{(m-1)} = C^{(m)} = 0 \qquad (m = 0, 1, 2, \ldots, L+1). \qquad (13)$$

Substitutions of (13) into (A.1) and (A.2) lead to

$$A = \frac{\pi}{\Delta}\left(2+\frac{\pi\zeta_3}{\Delta}\right) \qquad B = -\frac{\zeta_4}{2}\left(\frac{\pi}{\Delta}\right)^2. \qquad (14)$$

From (11) with (B.1) and (B.2) we get

$$z\gamma^{(1)}(z) = \frac{\rho[A\chi^{(1)}(\sigma,z)+B\chi^{(0)}(\sigma,z)]}{1-\rho[(A/2)\Phi^{(2,0)}(z,0)+B\Phi^{(1,0)}(z,0)]} \qquad (15)$$

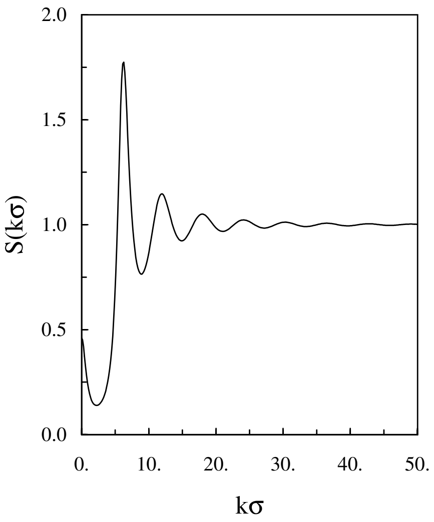

Figure 2. The structure factor $S(k\sigma)$ for a LJ fluid.

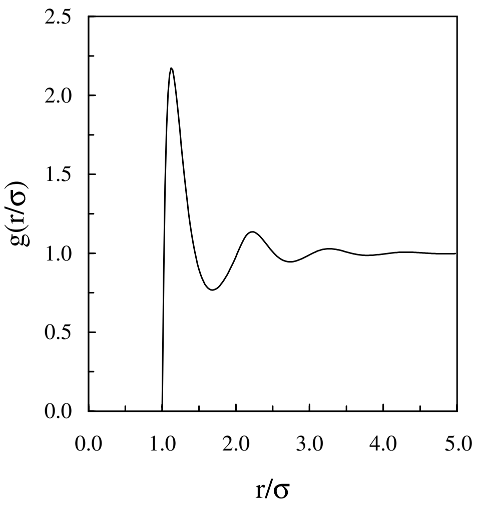

Figure 3. The distribution function $g(r/\sigma)$ for a LJ fluid.

and

$$z^{1-m}\gamma^{(m+1)} = \left\{1 - \rho\left[\frac{A}{2}\Phi^{(2,0)}(z,0) + B\Phi^{(1,0)}(z,0)\right]\right\}^{-1} \times \left\{\rho[A\chi^{(m+1)}(\sigma,z) + B\chi^{(m)}(\sigma,z)] + \sum_{\xi=0}^{m-1} C_\xi^m \rho\left[\frac{A}{2}\Phi^{(m-\xi+2,m-\xi)}(z,0) + B\Phi^{(m-\xi+1,m-\xi)}(z,0)\right] z^{1-\xi}\gamma^{(\xi+1)}\right\} \qquad (m \geqslant 1). \tag{16}$$

We believe that the present results can be applied to almost all one-component fluids, because the interaction potentials between particles can be well approximated by the present closure. As a demonstration, we consider here a fluid of Lennard-Jones (LJ) particles at temperature $T = 100$ K and packing fraction $\pi\rho\sigma^3/6 = 0.3$. The LJ potential between two LJ particles is written as

$$\phi_{LJ}(r) = 4\epsilon\left[\left(\frac{\sigma_0}{r}\right)^{12} - \left(\frac{\sigma_0}{r}\right)^{6}\right] \tag{17}$$

where the potential parameters $\sigma_0 = 0.3405$ nm and $\epsilon/k_B = 119.8$ K are adopted. These are the LJ parameters for argon.

As shown in figure 1, the LJ potential (the circles) is well approximated by equation (3) (the solid line) with parameters $\sigma = 0.961\sigma_0$, $z\sigma = 13.7687$, $L = 20$, and $K^{(\tau)}/\sigma = -5.122\,46 \times 10^{10}$, $1.301\,37 \times 10^{10}$, $-7.872\,17 \times 10^{8}$, $-5.181\,58 \times 10^{7}$, $6.575\,96 \times 10^{5}$, $-2.473\,53 \times 10^{4}$, $-2.058\,32 \times 10^{4}$, $1.243\,63 \times 10^{3}$, $-2.815\,70 \times 10$, $-1.952\,11$, $2.688\,24 \times 10^{-2}$, $9.040\,13 \times 10^{-3}$, $1.791\,85 \times 10^{-4}$, $-1.512\,96 \times 10^{-5}$, $-2.253\,08 \times 10^{-6}$, $-3.624\,83 \times 10^{-8}$, $1.712\,31 \times 10^{-8}$, $-3.949\,57 \times 10^{-10}$, $-3.329\,26 \times 10^{-11}$, 2.065×10^{-12}, $-4.389\,95 \times 10^{-14}$ and $3.388\,66 \times 10^{-16}$ for $\tau = -1, 0, 1, 2, 3, \ldots$, and 20, respectively. The structure factor $S(k\sigma)$ and the distribution function $g(r/\sigma)$ are shown in figures 2 and 3, respectively.

The present results would provide a useful model basis for studying a large variety of one-component fluids.

Appendix A

The coefficients and functions in (7) are

$$A = \frac{\pi}{\Delta}\left(2+\frac{\pi\zeta_3}{\Delta}\right) + \frac{2\pi}{\Delta}\sum_{\mu=-1}^{L}\rho D^{(\mu)}\left[\frac{\pi\zeta_2}{\Delta}H^{(\mu,1)} - \left(1+\frac{1}{2}\frac{\pi\zeta_3}{\Delta}\right)H^{(\mu,0)}\right] \quad \text{(A.1)}$$

$$B = -\frac{\zeta_4}{2}\left(\frac{\pi}{\Delta}\right)^2 + \frac{\pi}{\Delta}\sum_{\mu=-1}^{L}\rho D^{(\mu)}\left[\left(2-\frac{\pi\zeta_3}{\Delta}\right)H^{(\mu,1)} + \frac{\pi\zeta_4}{2\Delta}H^{(\mu,0)}\right] \quad \text{(A.2)}$$

$$C^{(k)} = -D^{(k-1)} + (k+1)D^{(k)} + \sum_{\tau=1}^{(L+2)-k} C_{\tau-1}^{\tau+k-1} D^{(\tau+k-2)}\gamma^{(\tau)}(z) \quad \text{(A.3)}$$

$$\tilde{Q}^{(m)}(\mathrm{i}s) = \frac{1}{2}A\Phi^{(m+2,m)}(s,0) + B\Phi^{(m+1,m)}(s,0) + \sum_{k=0}^{L+1}C^{(k)}k!\sum_{\xi=0}^{k}\frac{z^{k-\xi}}{(k-\xi)!}\Phi^{(m+k-\xi,m)}(s,z)$$
$$+ \sum_{\tau=-1}^{L} D^{(\tau)} z^{\tau+1}\chi^{(m+\tau+1)}(0,z+s) \quad \text{(A.4)}$$

$$\chi^{(k)}(b,a) = k!\mathrm{e}^{-ab}\sum_{\xi=0}^{k}\frac{b^{k-\xi}}{a^{\xi+1}(k-\xi)!} \qquad (b \neq 0) \quad \text{(A.5)}$$

$$\chi^{(k)}(0,x+\mathrm{i}y) = \frac{k!}{(x^2+y^2)^{(k+1)/2}}\left\{\cos\left[(k+1)\tan^{-1}\frac{y}{x}\right] - \mathrm{i}\sin\left[(k+1)\tan^{-1}\frac{y}{x}\right]\right\} \quad \text{(A.6)}$$

$$\Phi^{(n,m)}(s,z) = \chi^{(n)}(0,z+s) - \chi^{(n)}(\sigma,z+s) - \sigma^{n-m}\mathrm{e}^{-z\sigma}[\chi^{(m)}(0,s) - \chi^{(m)}(\sigma,s)] \quad \text{(A.7)}$$

$$\zeta_k = \rho\sigma^k \qquad \Delta = 1 - \pi\zeta_3/6 \quad \text{(A.8)}$$

and

$$H^{(\mu,m)} = z^{\mu+1}[\chi^{(m+\mu+1)}(0,z) - \Phi^{(m+\mu+1,m)}(0,z)]$$
$$+ \sum_{k=0}^{\mu+1}k!C_{\mu+1-k}^{\mu+1}\gamma^{(\mu+2-k)}(z)\sum_{\xi=0}^{k}\frac{z^{k-\xi}}{(k-\xi)!}\Phi^{(m+k-\xi,m)}(0,z). \quad \text{(A.9)}$$

Appendix B

The coefficients in (11) and (12) are

$$\hat{A}_m = \chi^{(m+1)}(\sigma,z) + \tfrac{1}{2}\sum_{\xi=0}^{m}z^{1-\xi}\gamma^{(\xi+1)}(z)C_\xi^m\Phi^{(m-\xi+2,m-\xi)}(z,0) \quad \text{(B.1)}$$

$$\hat{B}_m = \chi^{(m)}(\sigma,z) + \sum_{\xi=0}^{m}z^{1-\xi}\gamma^{(\xi+1)}(z)C_\xi^m\Phi^{(m-\xi+1,m-\xi)}(z,0) \quad \text{(B.2)}$$

$$\hat{C}_m^{(k)} = \sum_{\xi=0}^{m}z^{1-\xi}\gamma^{(\xi+1)}(z)C_\xi^m\sum_{\tau=0}^{k}\frac{z^{k-\tau}k!}{(k-\tau)!}\Phi^{(m-\xi+k-\tau,m-\xi)}(z,z) - z^{k+1}\chi^{(m+k)}(\sigma,2z) \quad \text{(B.3)}$$

and

$$\hat{D}_m^{(\tau)} = z^{\tau+1}\sum_{\xi=0}^{m}z^{1-\xi}\gamma^{(\xi+1)}(z)C_\xi^m\chi^{(m-\xi+\tau+1)}(0,2z). \quad \text{(B.4)}$$

References

Barboy B and Tenne R 1979 *Chem. Phys.* **38** 369
Baxter R J 1968 *J. Chem. Phys.* **49** 2770
Blum L 1980 *J. Stat. Phys.* **22** 661
Blum L and Høye J S 1978 *J. Stat. Phys.* **19** 317
Ginoza M 1985 *J. Phys. Soc. Japan* **54** 2783
Ginoza M 1986 *J. Phys. Soc. Japan* **55** 95
Ginoza M and Yasutomi M 1996 *Mol. Phys.* **87** 593
Henderson D, Abraham F F and Barker J A 1976 *Mol. Phys.* **31** 1291
Henderson D, Lebowitz J L, Blum L and Waisman E 1980 *Mol. Phys.* **39** 47
Perram J W and Smith E R 1975 *Chem. Phys. Lett.* **35** 138
Plischke M and Henderson D 1986 *Proc. R. Soc.* A **404** 323
Sogami I and Ise N 1984 *J. Phys. Chem.* **81** 6320
Thompson N E, Isbister D J, Bearman R J and Freasier B C 1980 *Mol. Phys.* **39** 27
Waisman E 1973 *Mol. Phys.* **25** 45
Waisman E, Henderson D and Lebowitz J L 1976 *Mol. Phys.* **32** 1373
Yasutomi M 2001 *J. Phys.: Condens. Matter* **13** L255
Yasutomi M and Ginoza M 1996 *Mol. Phys.* **89** 1755
Yasutomi M and Ginoza M 2000 *J. Phys.: Condens. Matter* **12** L605