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The δ-function expansion of the modified two-particle Ursell function of a hard-sphere fluid

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Abstract. The expansion of the modified two-particle Ursell function $U(r)$ of a hard-sphere quantal fluid is obtained in terms of a series of derivatives of δ-function. This expansion has been used to expand the second virial co-efficient B_2 of the fluid. The expansion is correct up to the fourth power in thermal wavelength and the terms of the order of λ^3 and λ^4 in the first expa nsion are new.

Keywords. Ursell function; thermal wavelength; second virial co-efficient.

1. Introduction

The expansion of any function in terms of Dirac δ-function and its derivatives is some times convenient if the function is to be used in an integral. In this paper we shall expand $U(r)$ in terms of δ-function and its derivatives correct up to the fourth power in thermal wavelength λ. The coefficients of λ^3 and λ^4 in the expansion are new but those of λ and λ^2 were first suggested by others (Hemmer 1968; Gibson 1975).

To test that the expansion is right we use it to obtain the expansion of B_2 up to the order λ^4. This expansion has also been derived by others (Handelsmann and Keller 1966; Hemmer and Mork 1967) after making lengthy calculations.

In §2, we outline the calculation for the expansion of $U(r)$. An alternative method for obtaining the expansion of B_2 is presented in §3.

2. Expansion of U (r)

The expansion of $U(r)$ is:

$$U(r) = \sum_{i=0}^{3} f_i(q) + \text{higher terms}, \tag{1}$$

where $f_i(q)$'s are given by (Gibson and Byrnes 1975)

$$f_0(q) = -\exp(-q^2), \tag{2}$$

$$f_1(q) = \frac{1}{\sqrt{2}} (\lambda/a)\, q^2 \operatorname{erfc} q, \tag{3}$$

$$f_2(q) = \frac{1}{(3\pi)} (\lambda/a)^2\, q^2\, [(1+q^2) \exp(-q^2) - (3+q^2)\sqrt{\pi}\, q \operatorname{erfc} q] \tag{4}$$

and

$$f_3(q) = \frac{1}{(24\sqrt{2})} \pi^{-3/2} (\lambda/a)^3 q^3 \,[-(16 + 26\, q^2 + 4\, q^4) \exp(-q^2)$$

$$+ (39 + 28\, q^2 + 4\, q^4) \sqrt{\pi}\, q \operatorname{erfc} q] \tag{5}$$

Here $$q \equiv \frac{(2\pi)^{1/2}}{\lambda} (r - a), \tag{6}$$

$$\operatorname{erfc} q = \frac{2}{\sqrt{\pi}} \int_q^{\infty} \exp(-t^2)\, \mathrm{d}t \tag{7}$$

and a is the hard-sphere diameter.

The expansion of any one of the integrable functions $f_i(q)$ in terms of a series of derivatives of δ-function is given by (Messel and Green 1952; Kim 1969)

$$f_i(q) = \sum_{k=0}^{\infty} \frac{(-1)^k f_i(k)\, \delta^{(k)}(q)}{k!} \tag{8}$$

where the moment $f_i(k) = \int_0^{\infty} q^{(k)} f_i(q)\, \mathrm{d}q$ (9)

and the superscript in (8) and in any other equations after (8) represents the number of differentiations with respect to the argument of the function.

We can calculate the moments of any $f_i(q)$ from (9) and its expansion given in one of the equations (2) to (5). The calculations are lengthy but straightforward. We quote here the relevant results:

$$f_0(0) = -\frac{\sqrt{\pi}}{2};\ f_0(1) = f_0(3) = -1/2;\ f_0(2) = -\sqrt{\pi}/4, \tag{10}$$

$$f_1(0) = \lambda/3\sqrt{2\pi}\, a;\ f_1(1) = 3\lambda/16\sqrt{2}\, a;\ f_1(2) = 2\lambda/5\sqrt{2\pi}\, a, \tag{11}$$

$$f_2(0) = -\lambda^2/12\sqrt{\pi}\, a^2;\ f_2(1) = -13\lambda^2/70\pi\, a^2, \tag{12}$$

$$f_3(0) = 8\lambda^3/45\sqrt{2}\, \pi^{3/2} a^3. \tag{13}$$

We can also see from (6) that

$$\delta^{(k)}(q) = \left(\frac{\lambda}{\sqrt{2\pi}}\right)^{k+1} \delta^{(k)}(r-a). \tag{14}$$

The explicit expansion of $f_l(q)$'s can be easily written using (8) and (10) to (14). If we substitute these expansions in (1) we find

$$U(r) = -2^{-3/2}\lambda\,\delta(r-a) + \frac{r^2}{12\pi a}[2\,\delta(r-a) + 3a\,\delta^{(1)}(r-a)]$$

$$-\frac{\lambda^3}{96\sqrt{2}\pi a^2}[8\delta(r-a) + 9a\delta^{(1)}(r-a) + 6a^2\delta^{(2)}(r-a)]$$

$$+\frac{\lambda^4}{5040\pi^2 a^3}[448\delta(r-a) + 468a\delta^{(1)}(r-a) + 252a^2\delta^{(2)}(r-a)$$

$$+ 105a^3\delta^{(3)}(r-a)] + 6(\lambda^5) \tag{15}$$

3. Expansion of B_2

At constant density number ρ and absolute temperature T the quantal pressure P^q of the quantal hard-sphere fluid in terms of its classical pressure P, its classical radial distribution function $g(r)$ and $U(r)$ is given by (Hemmer 1968; Jancovici 1969; Gibson 1975; Sinha and Singh 1977; Kumar and Giri 1980)

$$\beta P^q = \beta P - 2\pi\rho^2 \int g(r)\,U(r)\,r^2\,dr + 6(\rho^3), \tag{16}$$

where $\beta = (KT)^{-1}$, K being the Boltzmann constant.

We also know (Hill 1956) that

$$g(r) = 1 + 6(\rho), \text{ if } r \geqslant a, \tag{17}$$

$$= 0 \qquad , \text{ if } r < a, \tag{18}$$

$$\beta P^q = \rho + \rho^2 B_2 + 6(\rho^3), \tag{19}$$

$$\beta P = \rho + \rho^2 B_2^{(cl)} + 6(\rho^3), \tag{20}$$

and $B_2^{(cl)}$ $(= 2\pi a^3/3)$ is the classical second virial co-efficient of the fluid.

Substitution of (17)–(20) in (16) we find an expression for B_2:

$$B_2 = \frac{2\pi a^3}{3}\left[1 - \frac{3}{a^3}\int_a^\infty U(r)\,r^2\,dr\right]. \tag{21}$$

We have evaluated the quadrature in (21) with the aid of (15) and a formula given below:

$$\int_{-\infty}^{+\infty} F(r)\,\delta^{(k)}(r-a)\,\mathrm{d}r = (-1)^k F^{(k)}(a). \tag{22}$$

Finally we obtain the well known expansion of B_2 correct up to λ^4:

$$B_2 = \frac{2\pi a^3}{3}\left[1 + \frac{3}{2\sqrt{2}}\left(\frac{\lambda}{a}\right) + \frac{1}{\pi}\left(\frac{\lambda}{a}\right)^2 + \frac{1}{16\sqrt{2}\pi}\left(\frac{\lambda}{a}\right)^3 - \frac{1}{105\pi^2}\left(\frac{\lambda}{a}\right)^4 + 6\left(\frac{\lambda}{a}\right)^5\right]. \tag{23}$$

This verifies that (15) is correct.

4. Conclusion

The expansion of $U(r)$ in (15) might be conveniently used for calculating the quantal corrections to the equilibrium thermodynamic quantities of the fluid.

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