High-order compressibility integrals in classical fluids

Ana Laura Benavides and Fernando del Río

Laboratorio de Termodinámica,
Universidad Autónoma Metropolitana-Iztapalapa,
Apartado postal 55-534, México, D.F., 04390 México.

Abstract. The normalization condition of the 3- and 4-particle distribution functions is used to integrate the closure relations that generalize the well-known Ornstein-Zernike (OZ) integral for the compressibility and the two-particle correlation. In a similar way to the two-body OZ relation, the 3- and 4-particle closure integrals are written in terms of the compressibility and its derivatives, allowing their immediate evaluation. These explicit expressions are useful in the perturbation theory of fluids and in testing approximations for the 3- and 4-particle correlations, such as Kirkwood's superposition approximation. As an illustration, these closure integrals are evaluated for the hard-sphere system.

1. Introduction

The theory of equilibrium classical fluids contains an important theorem relating the isothermal compressibility X to the two-particle total correlation function $h(12)$, namely

$$\frac{\rho X}{\beta} = 1 + \left(\frac{\rho^2}{\langle N \rangle} \right) \int d(12)\, h(12) \tag{1}$$

where $d(12)$ means integration with respect to the positions of particles 1 and 2, $\langle N \rangle$ is the mean number of particles, $\rho = \langle N \rangle / V$ the mean density and $\beta = 1/kT$. Equation (1) was originally obtained by Ornstein and Zernike [1]. In this paper we show how the equivalent closure relations for the 3- and 4-body correlation functions can be written in a form similar to equation (1). Although these relations follow directly by integrating well-known recursion properties of the distribution functions [2,3], they are not currently available in their explicit integrated form [4-6]. The closure relations are useful in several cases, *e.g.*, in liquid-state perturbation theory [7] and in testing Kirkwood's superposition approximation [8].

In order to obtain the closure relations, instead of integrating the recursion relations of the distribution functions [2,3], it is more direct to obtain them from the normalization property of the m-particle distribution function densities $\rho^{(m)}(1,\ldots,m)$.

In the Grand Canonical Ensemble, this property reads [9]

$$\int d(12\ldots m)\rho^{(m)}(1\ldots m) = \left\langle \frac{N!}{(N-m)!} \right\rangle, \tag{2}$$

where the brackets $\langle\ \rangle$ denote the average with respect to the number of particles in the system at constant volume V, temperature T and chemical potential μ. When the fluid is isotropic, the radial distribution functions are defined by [9]

$$g(1\ldots m) = \frac{\rho^{(m)}(1\ldots m)}{\rho^{(m)}}. \tag{3}$$

The case $m = 2$, with $h(r) = h(12) = g(12)-1$, is very well known and equations (2) and (3) lead directly to

$$I_2 = \rho \int d^3r\, h(r) = \frac{\langle(\Delta N)^2\rangle}{\langle N\rangle} - 1, \tag{4}$$

where $\Delta N = N - \langle N\rangle$ is the number deviation. Since the mean square deviation is related to the compressibility by

$$\langle(\Delta N)^2\rangle = \langle N\rangle K, \tag{5}$$

where $K = \rho X/\beta$, one obtains the OZ theorem (1).

2. Three- and four-body compressibility integrals

For three particles, the total correlation function can be appropriately defined by [10]

$$h(123) = g(123) - [h(12) + h(23) + h(13)] - 1, \tag{6}$$

which correctly vanishes when any one particle is far away from the other two. An alternative definition of the total correlation functions, which is equivalent to equation (6), can be given in terms of the Ursell functions [11]. In the absence of long-ranged correlations, this property implies that the integral of $h(123)$ over all relative configurations must be finite. Substituting equations (3) and (6) in (2) for $m = 3$ and using (4) one finds

$$\rho^3 \int d(123)h(123) = \langle(\Delta N)^3\rangle - 3\langle(\Delta N)^2\rangle + 2\langle N\rangle. \tag{7}$$

Similarly, the appropriate definition of the total 4-particle correlation is

$$h(1234) = g(1234)$$

$$- [h(12)h(34) + h(13)h(24) + h(14)h(23)]$$

$$- [h(123) + h(124) + h(134) + h(234)]$$

$$- [h(12) + h(13) + h(14) + h(23) + h(24) + h(34)] - 1, \qquad (8)$$

which vanishes in a fluid when one, two or three particles are far away from the others. Again, the normalization condition (2) gives, using equations (3), (4) (7) and (8),

$$\rho^4 \int d(1234)h(1234) = \langle (\Delta N)^4 \rangle - 3\langle (\Delta N)^2 \rangle^2 - 6\langle (\Delta N)^3 \rangle$$

$$+ 11\langle (\Delta N)^2 \rangle - 6\langle N \rangle. \qquad (9)$$

Equations (7) and (9) are the 3- and 4-body analogues of the equation for the mean square deviation (4). Of course, the averages of powers of the deviations are related to thermodynamic variables [4]

$$\langle (\Delta N)^3 \rangle = \frac{\partial^2 \langle N \rangle}{\partial \alpha^2} \qquad (10)$$

and

$$\langle (\Delta N)^4 \rangle - 3\langle (\Delta N)^2 \rangle^2 = \frac{\partial^3 \langle N \rangle}{\partial \alpha^3} \qquad (11)$$

where $\alpha = \beta\mu$. Equations (5), (10) and (11) allow to write the closure relations for $h(123)$ and $h(1234)$ entirely in terms of thermodynamic properties. Thus, integrating the position of one particle and using relative coordinates $r = r_{12}$ and $r' = r_{13}$, one finally finds for the triple integral

$$I_3 = \rho^2 \int d^3r d^3r' h(123) = 2 + K(K + \rho K_\rho - 3), \qquad (12)$$

and the quadruple integral, with $r'' = r_{14}$, is

$$I_4 = \rho^3 \int d^3r d^3r' d^3r'' h(1234) = K^2(K - 6 + 4\rho K_\rho + \rho^2 K_{\rho\rho})$$

$$+ K(\rho^2 K_\rho{}^2 - 6\rho K_\rho + 11) - 6, \qquad (13)$$

where the subscript ρ means differentiation with respect to the density.
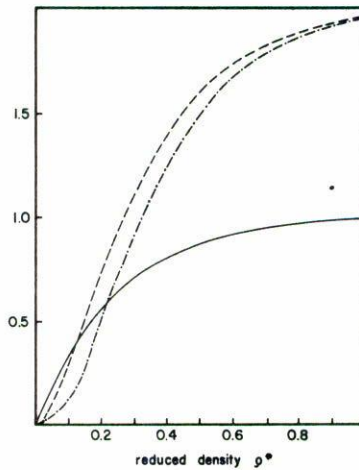
FIGURE 1. High-order compressibility integrals for the hard-sphere system. The continuous line is $-I_2(\rho^*)$; the dashed line represents the triple integral $I_3(\rho^*)$ and the dash-dot line $-I_4(\rho^*)/3$.

3. Discussion and illustration

Since at the critical point $h(r)$ becomes long ranged and the isothermal compressibility diverges, $K \to \infty$, then from equations (12) and (13) the triple and quadruple integrals I_3 and I_4 also diverge. Hence, one notices from these equations that the 3- and 4-body correlations also become long ranged at the critical point. On the other hand, if the interparticle potential has a hard core, the mean deviations in the number of particles must vanish when the system is closed packed, which can happen in the crystalline or the amorphous phase. Therefore, from equations (7) and (9) one finds at any closed-packed state the limiting values $I_3 = 2$ and $I_4 = -6$; of course, the double integral $I_2 = -1$ in the same state.

Equations (12) and (13) allow the exact calculation of I_3 and I_4 from the knowledge of the equation of state of the system of interest. If one uses an approximation for $h(123)$ or $h(1234)$ —or equivalently for $g(123)$ and $g(1234)$— in the LHS of these equations as, *e.g.*, Kirkwood's superposition approximation, the deviations of I_3 and I_4 from their exact values will give an average measure of the error introduced by the approximation.

Second-order terms in the perturbation theory of liquids [7] and in electrolyte theory [10] involve integrals of 3- and 4-body correlations of the type appearing in equations (12) and (13) for the hard-sphere reference system, and the results presented here are useful in those cases [7,12].

As an illustration we present in Fig. 1 the values of I_3 and I_4 as functions of reduced density $\rho^* = \rho\sigma^3$ for a hard-sphere system with diameter σ. The compressibility integral I_2 is also shown as reference. $K(\rho^*)$ was obtained from the

Carnahan-Starling equation of state [13]. In the HS case, I_3 and I_4 vary monotonically with ρ^* between their zero value at $\rho^* = 0$ and their limits at the amorphous closed-packed state, which is at $\rho^* = 6/\pi$ with the CS formula. One also notices from this figure that I_4 is always negative and about thrice I_3.

Nevertheless, one must keep in mind that these theorems are valid for any thermodynamically stable system and thus can have wider applications.

References

1. Ornstein, L.S., and Zernike, F., *Proc. Acad. Sci. (Amsterdam)* **17** (1914) 793.
2. Baxter, R.J., *J. Chem. Phys.* **41** (1964) 553; *Phys. Fluids* **7** (1964) 38.
3. Schofield, P., *Proc. Phys. Soc. Lond.* **88** (1966) 149.
4. Münster, A., *Statistical Thermodynamics*, Academic Press, New York (1969) p. 181.
5. Barker, J.A., and Henderson, D.H., *Rev. Mod. Phys.* **48** (1976) 587.
6. Gray, C.G., and Gubbins, K.E., *Theory of molecular fluids*, Vol. 1, *Fundamentals*, Oxford Science Publications, Clarendon Press, Oxford (1984).
7. Benavides, A.L., and Del Río, F. *Mol. Phys.* **68** No. 5, (1989) 983.
8. Kirkwood, J.G., *J. Chem. Phys.* **3** (1935) 300.
9. Hansen, J.P., and Mc Donald, I.R., *Theory of simple liquids*, Academic Press, London (1976).
10. Stell, G., and Lebowitz, J.L., *J. Chem. Phys.* **49** (1968) 3706.
11. Percus, J.K., in *The equilibrium theory of classical fluids*, H.L. Frisch and J.L. Lebowitz eds., Benjamin, New York (1964).
12. Larsen, B., Rasaiah, J.C., and Stell, G., *Mol. Phys.* **33** (1977) 987.
13. Carnahan, N.F., and Starling, K.E., *J. Chem. Phys.* **51** (1969) 635.

Resumen. La condición de normalización de las funciones de distribución de 3 y 4 partículas se utiliza para integrar las relaciones de cerradura que generalizan la bien conocida integral de Ornstein-Zernike (OZ) para la compresibilidad y la función de correlación de dos partículas. De manera similar que para la correlación de dos cuerpos de OZ, las integrales de cerradura de 3 y 4 partículas se expresan en términos de la compresibilidad y sus derivadas, permitiendo así su cálculo inmediato. Estas expresiones explícitas son útiles en la teoría de perturbaciones de fluidos y pueden servir para probar las aproximaciones de correlaciones de 3 y 4 partículas tales como la aproximación de superposición de Kirkwood. A manera de ilustración, estas integrales se evalúan para el sistema de esferas duras.