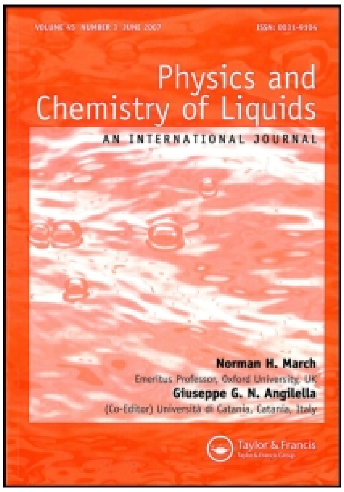

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Relation Between Direct and Total Three-Body Correlations

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Relation Between Direct and Total Three-Body Correlations

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Recent work of Hernando prompts us to give simple derivations of relations between three-body direct and total correlation functions. These relations are then discussed in relation to the decomposition of the Ornstein-Zernike two body function $c(r)$ into 'potential' and 'cooperative' parts. Illustrations are referred to for the two-dimensional plasma and for critical point behaviour.

1 INTRODUCTION

The purpose of the present note is: (i) To give simple derivations of relations between three-body direct and total correlation functions, $c^{(3)}$ and $g^{(3)}$ respectively, prompted by Hernando's recent diagrammatic analysis.[1] (ii) To relate this to our recent discussion[2] of the division of the Ornstein–Zernike two-body correlation function $c(r)$ into the sum of a 'potential' part $c_p(r)$ and a 'cooperative' part $c_c(r)$. (iii) To display the relation of the decoupling scheme of Ichimaru[3] to Hernando's work.

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2 LIQUID STRUCTURE IN AN EXTERNAL POTENTIAL

We begin by studying the statistical mechanics of a liquid in the presence of an external potential V. Introducing the dimensionless quantity

$$v = -V/K_B T \equiv -\beta V, \tag{1}$$

we can write

$$\frac{\delta v(1)}{\delta n(2)} = -\hat{c}(12) = -\left[c(12) - \frac{\delta(12)}{n(1)}\right] \tag{2}$$

with $n(1)$ the single-particle density and $c(12) \equiv c(\mathbf{r}_1, \mathbf{r}_2)$. The three-body direct correlation function $c^{(3)} \equiv c(123)$ is now given in terms of $\hat{c}(12)$ by

$$c(123) = \frac{\delta c(12)}{\delta n(3)} = \frac{\delta \hat{c}(12)}{\delta n(3)} - \frac{\delta(12)\delta(13)}{n(1)^2}. \tag{3}$$

Furthermore we can write

$$\frac{\delta n(1)}{\delta v(2)} = \hat{n}(12) = n(12) - n(1)n(2) + n(1)\delta(12)$$

$$= n(1)n(2)h(12) + n(1)\delta(12) \tag{4}$$

with $n(12)$ the two-point density and $h(12) = g(12) - 1$, where $g(12)$ is the usual liquid pair function. From Eq. (4) we find

$$\frac{\delta \hat{n}(12)}{\delta v(3)} = \hat{n}(123) = n(123) - n(12)n(3) + n(12)[\delta(13) + \delta(23)]$$

$$- n(1)\hat{n}(23) - n(2)\hat{n}(13) + \hat{n}(13)\delta(12)$$

$$= n(1)n(2)n(3)h(123) + \hat{n}(12)\delta(23) + \hat{n}(13)\delta(12)$$

$$+ \hat{n}(23)\delta(13) - n(1)[\delta(13)\delta(12) + \delta(23)\delta(12)]. \tag{5}$$

Next we have the Ornstein-Zernike relation

$$\int d4 \frac{\delta n(1)}{\delta v(4)} \frac{\delta v(4)}{\delta n(2)} = \delta(12) = -\int d4 \hat{n}(14)\hat{c}(42) \tag{6}$$

and taking its functional derivative with respect to $n(3)$ yields:

$$0 = \int d4 \frac{\delta \hat{n}(14)}{\delta n(3)} \hat{c}(42) + \int d4 \hat{n}(14) \frac{\delta \hat{c}(42)}{\delta n(3)}. \tag{7}$$

If we now apply $\int d1\, \hat{c}(1', 1)$ or $\int d2\, \hat{n}(2, 2')$ we obtain

$$\frac{\delta \hat{c}(12)}{\delta n(3)} = \int d4 \int d5\, \hat{c}(15) \frac{\delta \hat{n}(54)}{\delta n(3)} \hat{c}(42) \tag{8}$$

or

$$\frac{\delta \hat{n}(12)}{\delta n(3)} = \int d4 \int d5\, \hat{n}(14) \frac{\delta \hat{c}(45)}{\delta n(3)} \hat{n}(52). \tag{9}$$

Equation (8) derived above by functional differentiation is fully equivalent to Hernando's Eq. (41), which is readily obtained by utilizing the identity

$$\frac{\delta \hat{n}(54)}{\delta n(3)} = \int d6 \frac{\delta \hat{n}(54)}{\delta v(6)} \frac{\delta v(6)}{\delta n(3)} = -\int d6\, \hat{n}(546)\hat{c}(63). \tag{10}$$

By considering $\int d3$ of Eq. (8) or (9) one obtains relations which express $\partial c(12)/\partial n$ in terms of $\partial n(12)/\partial n$ and $c(12)$ or $\partial n(12)/\partial n$ in terms of $\partial c(12)/\partial n$ and $n(12)$, after letting the external potential tend to zero.

Thus one finds

$$\frac{\delta \hat{c}(12)}{\partial n} = \int d4 \int d5\, \hat{c}(14) \frac{\partial \hat{n}(54)}{\partial n} \hat{c}(42) \tag{11}$$

and

$$\frac{\partial \hat{n}(12)}{\partial n} = \int d4 \int d5\, \hat{n}(14) \frac{\partial \hat{c}(45)}{\partial n} \hat{n}(42). \tag{12}$$

By using

$$\frac{\partial \hat{c}(12)}{\partial n} = \frac{\partial c(12)}{\partial n} + \frac{\delta(12)}{n^2} \tag{13}$$

and

$$\frac{\partial \hat{n}(12)}{\partial n} = \frac{\partial n(12)}{\partial n} - 2n + \delta(12) \tag{14}$$

one finds, after a little algebra

$$\frac{\partial c(12)}{\partial n} = -\int d3\, c(13)c(32) + \frac{\partial g(12)}{\partial n} + 2n \int d3\, c(13) \frac{\partial g(32)}{\partial n} + n^2 \int d3 \int d4\, c(13)c(24) \frac{\partial g(34)}{\partial n} \tag{15}$$

and

$$\frac{\partial g(12)}{\partial n} = \int d3\, h(13)h(32) + \frac{\partial c(12)}{\partial n} + \int d3\, h(13) \frac{\partial c(32)}{\partial n} + n^2 \int d3 \int d4\, h(13)h(24) \frac{\partial c(34)}{\partial n}. \tag{16}$$

3 RELATION TO DECOMPOSITION OF $c(r)$

One can insert the decomposition[2]

$$c(r) = c_p(r) + c_c(r) \tag{17}$$

into Eq. (16) and hence obtain an integral equation for $\partial c_c/\partial n$ explicitly in terms of g and of the density derivatives of the quantities determining $c_p(r)$ namely,[2] ϕ, g, $\partial g/\partial r$, $\partial g/\partial n$, $\partial^2 g/\partial n \partial r$. Alternatively, the various derivatives of g may be written in terms of g itself and three, four and five-body Ornstein–Zernike functions.

As in [2], one can make the above quite explicit on the two-dimensional plasma, but though the example is illuminating in the present context it does not yield new results so we shall not give the details.

As a second example, we mention our own critical point work.[4] One can insert into the integral involving $g^{(3)}$, which diverges at the critical point, the above relation between $g^{(3)}$ and $c^{(3)}$. But decoupling still seems to be necessary on $c^{(3)}$ to proceed beyond this point.

4 DECOUPLING OF THREE-BODY DIRECT CORRELATION FUNCTION

Finally, in the context of decoupling, the approximation

$$c(123) = h(12)h(23)h(31) \tag{18}$$

is discussed by Hernando.[1] Since above we have related $g^{(3)}$ and $c^{(3)}$, we can rewrite the so-called force equation

$$-\frac{\partial U(r_{12})}{\partial \mathbf{r}_1} = -\frac{\partial \phi(r_{12})}{\partial \mathbf{r}_1} - \int d\mathbf{r}_3 \frac{n(r_1, r_2, r_3)}{n^2 g(r_{12})} \frac{\partial \phi(r_{13})}{\partial \mathbf{r}_1}, \tag{19}$$

where $g(r) = \exp[-U(r)/K_B T]$ defines the potential of mean-force and $\phi(r)$ is the two-body interparticle pair potential, solely in terms of $c^{(3)}$. Use of the decoupling (18) in the resulting equation does not lead to the Born–Green approximation[5] of liquid structure theory, and presumably transcends it. It turns out,[3] in fact, that Eq. (18) follows from a combination of convolution and Kirkwood superposition approximation.† However, one must not expect Eq. (18) to be sufficiently refined to work near the critical point.

† This corrects a minor inaccuracy in the paper of Hernando [1]; all his major conclusions remain intact.

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